Photoinduced Free Radical Chemistry of the Acyl Tellurides: Generation, Inter- and Intramolecular Trapping, and ESR Spectroscopic Identification of Acyl Radicals

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Abstract: Acyl tellurides are prepared in good to excellent yield by the reaction of sodium aryl tellurides with acyl chlorides, or mixed anhydrides, and are found to be moderately air-stable substances. In contrast to previous literature reports, acyl tellurides of aryl and vinyl carboxylic acids are found to be excellent sources of acyl radicals on photolysis with a simple white light source. The acyl radicals so generated may be trapped intermolecularly by dichalcogenides, or by TEMPO in excellent yield. Trapping by *N*-*tert*-butyl-α-phenyl nitrone produces a stable nitroxide radical which has been characterized by ESR spectroscopy. The very efficient trapping of acyl radicals by acyl tellurides themselves is demonstrated by a crossover experiment. Acyl tellurides are shown to participate in very efficient radical cyclization reactions onto alkenes with the formation of five-, six-, and eight-membered rings. The immediate products of the cyclizations onto alkenes are α-[(aryltelluro)methyl] ketones and the chemistry of these relatively unstable species is briefly described. Treatment with hydrogen peroxide affords α-methylene ketones in high yield. When elimination of the aryl telluro group is not possible the α-[(aryltelluro)methyl] ketones are stable species that may subsequently be employed in further radical chain reactions, for example with tributyltin hydride and methyl acrylate. Cyclization onto alkynes yields α-[(aryltelluro)methylene] ketones which are stable species and which take part in substitution reactions with higher order cuprates or with diphenyl diselenide.

Introduction

Acyl radicals are highly reactive species with considerable potential for use in organic synthesis, particularly when generated in a controlled fashion in one of the propagation steps of a free radical chain reaction. A number of synthetic methods have been developed on this basis, each of which is characterized by its own set of advantages and disadvantages.[2] The direct addition of aldehydes to alkenes, initiated by either photochemical or thermal decomposition of peroxides, as reported by Kharasch and exploited by numerous workers, is one such radical chain process involving acyl radicals. It is limited by a relatively poor chain transfer step which in turn requires the use of high concentrations of the aldehyde and even its use as solvent.[3,4] Nevertheless, this method was adequate for Cadogan and Hey to demonstrate the nucleophilic character of acyl radicals.[5] More recently acyl radicals generated in this manner have been shown to react efficiently with the central bond of [1.1.1]propelane,[6] and aldehydes have been transformed into acyl bromides by reaction with *N*-bromosuccinimide with the evident intermediacy of acyl radicals.[7] Acyl radical cyclizations onto both alkenes and aromatic rings using aldehydes as precursors have also been reported, although typically in meager yield.[8] A modified sequence relying on electrophilic thiyl radicals to abstract aldehydic hydrogen atoms can lead to efficient chain processes.[9] Acyl radicals may be generated by carbonylation of alkyl radicals, themselves accessed from the reaction of alkyl halides with stannanes, resulting in preparatively useful C–C bond-forming reactions, but the pressures required (~75 atm) diminish the utility of this process.[10] The reaction of stannyl radicals with acyl chlorides and bromides yields acyl radicals which may either be reduced directly to aldehydes or trapped by cyclization onto alkenes.[11] Ingold has however demonstrated that the reaction of stannanes with acyl halides is complicated by parallel nonradical mechanisms, as might reasonably be expected for such highly electrophilic species.[12] The most practical system to date involves the acyl aryl selenides, which were first revealed to be excellent precursors for acyl radicals when used in conjuction with stannanes

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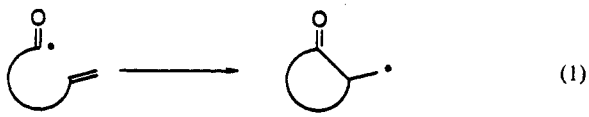
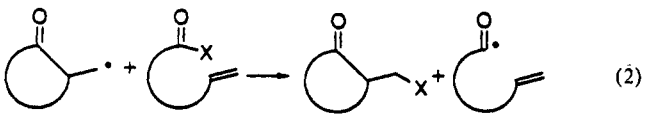
by Graf and co-workers, who studied decarbonylation as a function of temperature and substitution.[13] More recently Boger and Mathvink,[14] Curran and Liu,[15] and ourselves[16] have applied the acyl selenide/stannane reaction as a means of generating acyl radicals for use in inter- and intramolecular additions to alkenes. Although purification is rarely a problem, the stannane may be replaced if necessary by tris(trimethylsilyl)silane.[17] The closely analogous aryl selenocarbonates have been studied extensively by Bachi and collaborators.[18] The generation of acyl radicals by photolysis of *S*-2-naphthyl thiol esters has been recently described.[19] The acyl selenides have three principal advantages over the acyl chlorides and bromides as sources of acyl radicals when used in conjunction with stannanes: they are not significantly electrophilic and can therefore be used in the presence of numerous functional groups; they react cleanly and efficiently, on AIBN initiation, with stannyl radicals at a convenient rate in either benzene at reflux or at or below room temperature on mercury photolysis and do not appear to suffer appreciably from competing polar reaction pathways. Despite these advantages the acyl selenide/stannane reaction suffers the major limitation of all stannane-mediated radical chain processes, namely the obligatory reductive chain transfer step involving hydrogen atom transfer from the stannane. This limitation could in principle be readily overcome through the implementation of a simple chain sequence consisting of the two propagation steps in eqs 1 and 2 in which X is a suitable heteroatom-based group. Atom transfer cyclization



(1)

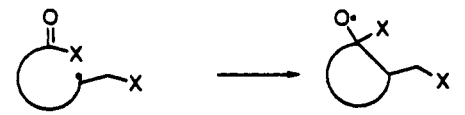


(2)

reactions of simple alkyl iodides have been demonstrated to be very powerful synthetic tools mainly by the Curran group,[20] and the related phenylseleno group transfer has been studied by Byers and others.[21]

One solution to this problem has been provided by Pattenden in the form of the acyl cobaltoximes and acyl cobalt salophens (eqs 1 and 2, X = Co^{III}).[22] A further solution is provided by the *S*-acyl xanthates [eqs 1 and 2, X = SC(=S)OEt].[23] A conceptually different approach involves the phosphite deoxygenation of acyloxy radicals, generated by the *O*-acyl thiohydroxamate method,[24] to acyl radicals with chain transfer by attack at thiocarbonyl sulfur.[25] The acyltriphenylgermanes, initially reported as convenient photolytic sources of acyl radicals,[26] have been shown to undergo cyclization by an alternative mechanism involving attack of carbon-centered radicals at carbonyl carbon (eqs 3–5, X = $GePh_3$).[27] The free radical chemistry of the acyl silanes parallels that of the acylgermanes in so far as the carbonyl carbon is readily attacked by nucleophilic alkyl radicals.[28]

(3)



(4)

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On the basis of a number of reports of S_H2 reactions at alkyl aryl tellurides and dialkyl tellurides,[29,30] we elected to explore the free radical chemistry of the acyl tellurides with the aim of establishing a simple chain reaction (eqs 1 and 2, X = TeAr).

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Scheme 1

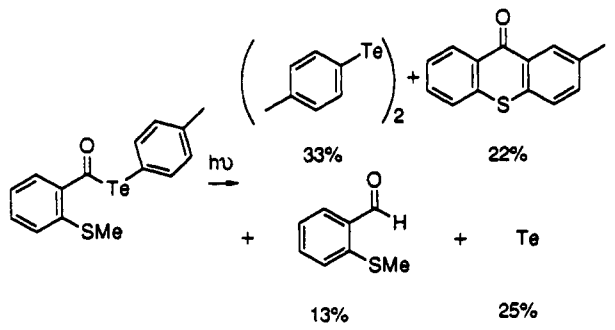


Table 1. Preparation of Acyl Tellurides from Carboxylic Acids

acyl telluride	% yield
1	100
2	92
3	91
4	86
5	89
12	89
13	85
14	97
15	76
16	81
17	94
18	88
19	100
20	63
33	57
36	70
40[a]	99
46	65
49	100

[a] Prepared by the mixed anhydride route.

Previous studies of the photochemistry of acyl aryl tellurides were not terribly encouraging. Not only was UV photolysis apparently required, despite the red brown color of the substrates, but complex reaction mixtures usually resulted after prolonged irradiation.[31,32] Nevertheless, the spectrum of products observed, which typically included the aldehyde and diaryl ditelluride as for example in Scheme 1, provided circumstantial evidence for the generation of acyl radicals.

We report here that photolysis of simple acyl aryl tellurides does indeed provide a clean source of acyl radicals for use in conjunction with efficient radical traps. The synthetic scope and limitations of the desired process are described and evidence in support of the initial mechanistic hypothesis is provided.[33]

Results and Discussion

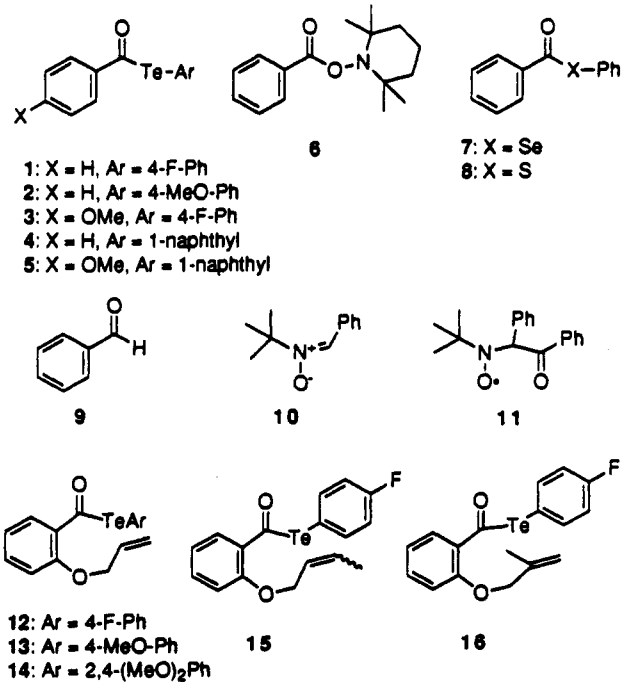
Intermolecular Trapping and Mechanism. We began our investigation with the preparation of a number of simple acyl aryl tellurides (**1–5**) (Table 1, entries 1–5) by reduction of the appropriate diaryl ditelluride with sodium borohydride in 10/1 THF/MeOH, followed by reaction with the requisite acyl chloride.[34] For the most part these acyl aryl tellurides were obtained as red brown crystalline solids that could be handled in air without significant decomposition and which most often provided satisfactory microanalytical data. These aroyl tellurides typically exhibited a ^{13}C chemical shift of δ 190 ± 1 ppm in $CDCl_3$ for the carbonyl carbon and an IR carbonyl stretch of ~1640 cm^{-1}.

Table 2. Intermolecular Trapping Experiments

entry	acyl telluride	trap (equivs)	method[a]	time (h)	products (% yield)
1	**1**	TEMPO (1)	A	2	**6** (86)
2	**1**	PhSeSePh (1)	A	1.5	**7** (100)
3	**1**	PhSSPh (1)	A	6	**8** (85)
4	**2**	TEMPO (1.5)	A	1.5	**6** (100)
5	**2**	PhSeSePh (1)	A	1	**7** (93)
6	**2**	PhSSPh (5.0)	A	1	**8** (71)
7	**2**	NapTeTeNap (1)	A	1.3	**2** (50) + **4** (50)
8	**4**	PhSH (3.7)	A	2	**9** (80)
9	**1**	TEMPO (1.2)	B	5	**6** (100)
10	**1**	PhSeSePh (1.1)	B	2	**7** (80)
11	**1**	PhSSPh (1.1)	B	16	**8** (16)

[a] A, tungsten photolysis at 8 °C; B, thermolysis in benzene at reflux in the dark.

Photolysis of **1** with white light, through Pyrex, in the presence of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) resulted in the formation and isolation of the *O*-acyl hydroxylamine **6** in 86% yield after 2 h at 8 °C (Table 2, entry 1). Photolysis of **1** in the presence of diphenyl diselenide led to the formation of the selenoester **7** in essentially quantitative yield after 1.5 h, whereas with diphenyl disulfide the thioester **8** was formed in 85% yield but only after 6 h (Table 2, entries 2 and 3). Grossly analogous results were obtained on photolysis of **2** with dichalcogenides and with TEMPO as trap (Table 2, entries 4–6). Photolysis of **2** with 1,1′-dinaphthyl ditelluride led, within 1.3 h, to complete equilibration and formation of an essentially 1:1 mixture of **2** and **4** (Table 2, entry 7). Photolysis of the acyl telluride **4** with thiophenol cleanly provided benzaldehyde (Table 2, entry 8). The various trapping experiments could also be conducted thermally in benzene at reflux in the dark (Table 2, entries 9–11).



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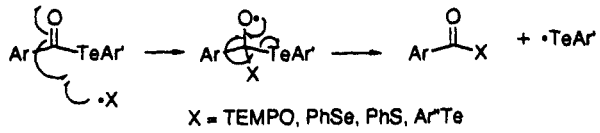
Scheme 2



Each of the above experiments may be interpreted in terms of homolysis of the acyl–TeAr bond with quenching of the acyl radical by the trap in question. However, with the exception of trapping by thiophenol, each result may also potentially be explained by an alternative mechanism, paralleling that established for the acyl germanes, in which either TEMPO or a chalogenide radical (PhSe•, PhS•, or 1-naphthylTe•) attacks at the carbonyl of the acyl telluride to give a tetrahedral intermediate, followed by expulsion of an aryl telluroyl radical (Scheme 2).

We considered this latter mechanism to be unlikely because the first step, generation of an alkoxyl radical from a chalcogenide radical and especially from a stable nitroxyl radical, appears to be somewhat unfavorable. Moreover, this type of mechanism is unable to account for the reduction of acyl tellurides to aldehydes on photolysis with thiophenol. However, in light of the proposed mechanism for the cyclization of unsaturated acyltriphenylgermanes[27] and the considerable number of radical rearrangements described in recent years involving attack of radicals at the carbonyl carbon of aldehydes[35] and ketones,[36] it deserves consideration. Direct observation of acyl radicals by ESR spectroscopy would provide evidence for their intermediacy in such reactions. Unfortunately, direct observation by ESR spectroscopy of radical intermediates in these trapping experiments can fail due to their low steady state concentrations, among other reasons; thus negative results are inconclusive. Trapping experiments with nitrones which could lead to the formation of stable nitroxide radicals, which accumulate in the reaction medium, was deemed more promising. *N-tert*-butyl-α-phenylnitrone (**10**) was chosen as trap since the benzoyl radical adduct (**11**) had been previously observed and characterized at 300 K (a_N = 14.23; a_H = 4.52 G) in benzene solution using benzoyl radicals generated by photolysis of benzaldehyde in the presence of di-*tert*-butyl peroxalate (concentrations not reported).[37] In the event, photolysis of **1** (6.7×10^{-2} M) in the presence of **10** (1.1×10^{-1} M) in deuteriobenzene in a standard 5 mm NMR tube at 8 °C for 2 h with the usual 250 W tungsten lamp followed by insertion of the tube into the microwave cavity of the ESR spectrometer resulted in a clean spectrum consisting of the anticipated six line spectrum (doublet of triplets) with a_N = 13.25 and a_H = 4.23 G (Figure 1). These values are quantitatively rather far from the published[37] ones, but they have been shown to be quite solvent dependent.[37] Even though both experiments were done in benzene solution, the relatively high concentrations of the different diamagnetic radical precursors would contribute differently to the solvent effects on the two sets of reported ESR data. In order to confirm that our spectrum was due to the addition of the benzoyl radical to **10**, a sample of **1** labeled with ^{13}C at the carbonyl carbon was prepared from the corresponding commercial 99% mono-^{13}C-labeled benzoic acid.[38] Photolysis of this labeled acyl telluride with **10** gave a solution of the trapped radical (**11**) with a twelve line ESR spectrum interpreted as a doublet of doublet of triplets with a_N = 13.17, a_H = 4.05, and $a_{^{13}C}$ = 5.36 G (Figure 2). This large ^{13}C coupling requires that the labeled carbon atom be close to the radical center, or bound

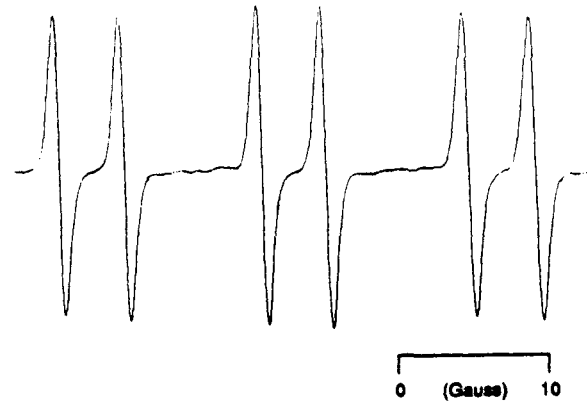


Figure 1.

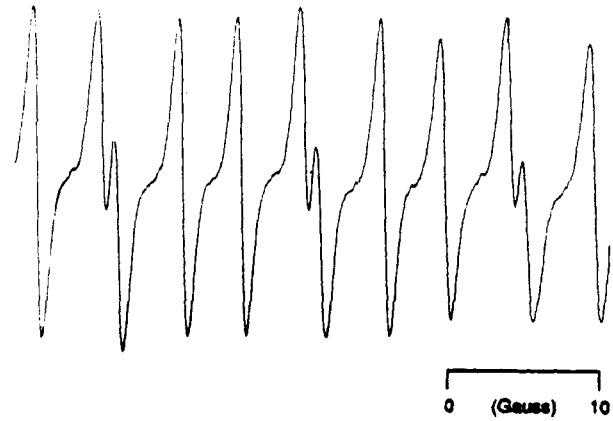
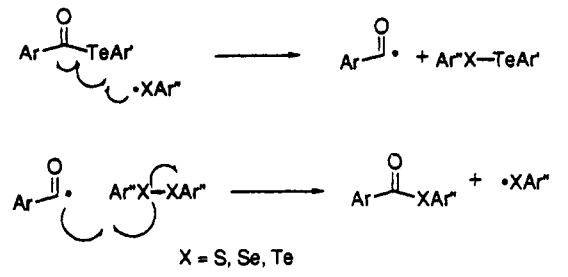


Figure 2.

Scheme 3



to the β-carbon, in the product nitroxide. The trapped radical is thus the labeled benzoyl radical [$Ph^{13}C(=O)$•].

The evidence therefore points to scission of the ArC(O)–TeAr' bond, with generation of acyl radicals, as the principal homolytic reaction pathway for the acyl aryl tellurides. Further unequivocal evidence that this is indeed the case was subsequently provided in the course of application of this chemistry to cyclization reactions (*vide infra*). Nevertheless, several puzzling features remained unexplained. Firstly, why was the previously published photochemistry of acyl aryl tellurides so inefficient when compared to that described here? Secondly, how are the obviously very different rates of reaction with diphenyl diselenide and diphenyl disulfide to be reconciled with a mechanism in which the primary event is homolytic scission of the acyl–TeAr bond? This latter observation may be readily accounted for by assuming a chain reaction (Scheme 3) with the rate-determining step being the attack of the acyl radical on the dichalcogenide. Indeed it is known that diselenides are far better traps for alkyl radicals than are disulfides.[39] This then poses the question as to why the evidently nonchain reactions of the various acyl tellurides with TEMPO are so rapid? A final question was uncovered when TLC inspection of the reaction mixtures used to generate the

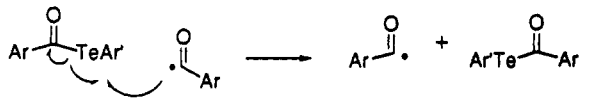
(35) (a) Tsang, R.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1986**, *108*, 2116. (b) Tsang, R.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1986**, *108*, 8102. (c) Tsang, R.; Dickson, J. K.; Pak, H.; Walton, R.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1987**, *109*, 3484. (d) Beckwith, A. L. J.; Hay, B. P. *J. Am. Chem. Soc.* **1988**, *110*, 4415.

(36) Dowd, P.; Zhang, W. *Chem. Rev.* **1993**, *93*, 2091.

(37) Janzen, E. G.; Coulter, G. A.; Oehler, U. M.; Bergsma, J. P. *Can. J. Chem.* **1982**, *60*, 2725.

(38) Obtained from Cambridge Isotope Laboratories, Woburn, MA 01801.

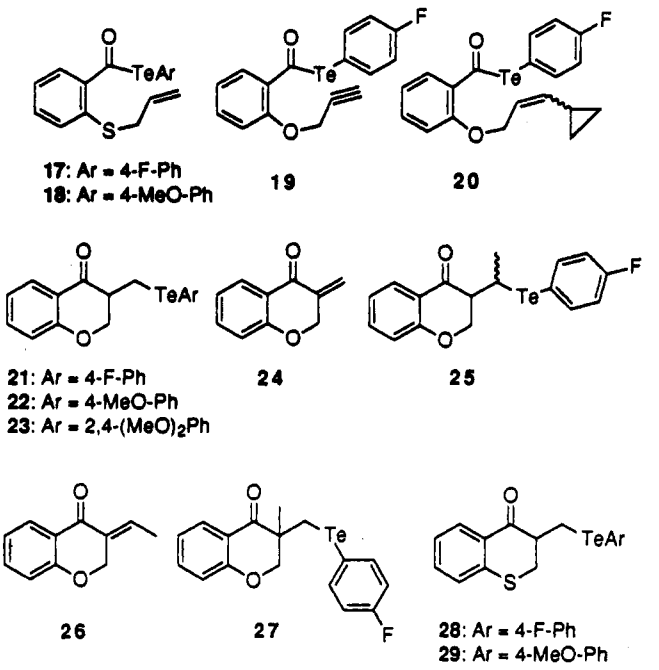
Scheme 4



ESR spectra of Figures 1 and 2 revealed very low conversion, even after prolonged photolysis.

The existence of a degenerate background reaction in which acyl radicals react very rapidly with acyl tellurides (Scheme 4) would reconcile all of the above disparate facts. To probe this hypothesis an equimolar mixture of **3** and **4** was photolyzed in deuteriochloroform at 8 °C and the photolysate examined by ^1H and ^{19}F NMR spectroscopy. Within 1 h complete scrambling had occurred, resulting in an almost equimolar mixture of the four acyl tellurides **1**, **3**, **4**, and **5**. This experiment, which was very clean and produced only trace quantities of the various possible diaryl ditellurides, provides very strong support for the degenerate background rearrangement (Scheme 4). Thiophenol, diaryl diselenides, diaryl ditellurides, and TEMPO[40] are excellent and very rapid traps for alkyl radicals and evidently also for acyl radicals.[41] They evidently compete effectively with the acyl tellurides themselves to trap the acyl radicals in the reaction mixture and so lead to rapid consumption of the starting materials and high yielding clean reactions. On the other hand diaryl disulfides, relatively sterically hindered nitrones, and the various systems previously described in the literature are relatively poor traps for acyl radicals when compared with acyl tellurides. The degenerate background reaction therefore predominates, and acyl radicals are only slowly leached off in product-forming reactions, resulting in prolonged reaction times and ultimately the formation of byproducts through heterolytic processes.

Intra- and Intermolecular C–C Bond-Forming Reactions. Having established the value of the acyl tellurides as acyl radical sources we next directed our attention to acyl radical cyclizations with transfer of the aryltelluro group as depicted in eqs 1 and 2 (X = TeAr). The acyl tellurides **12–20** were prepared, in good to excellent yield, in the standard manner by the reaction of the sodium borohydride/diaryl ditelluride couple with the appropriate salicyloyl chloride. White light photolysis of **12–14** in either deuteriobenzene or deuteriochloroform (Table 3, entries 1–3) resulted in clean and rapid rearrangement with the crude reaction mixtures consisting mainly of the expected cyclization/telluride transfer products (**21–23**) and minor amounts of the α-methylene ketone **24**. The β-aryltelluro ketones **21–23** were generally unstable with respect to elimination, as illustrated by the quantitative decomposition of a solution of **21** in $CDCl_3$ to **24** on standing at room temperature in the ambient laboratory light. Furthermore, attempts at the isolation of pure samples of **21–23** through chromatography were largely unsuccessful, owing to their decomposition, to **24**, on silica gel. We therefore developed a protocol in which, after photolysis, the crude reaction mixture was briefly treated with aqueous hydrogen peroxide, resulting in clean conversion directly to **24** (Table 3, entry 4). Next we investigated rearrangement of **15** with its internal alkene. As with **12–14**, photoinitiated cyclization was rapid and efficient giving the anticipated product **25**, contaminated with a small amount of its elimination product **26**, in excellent yield (Table 3, entry 5). Again an excellent yield of the pure elimination product was readily obtained by brief treatment of the crude photolysate with hydrogen peroxide (Table 3, entry 6). Most intriguingly, photolysis of **16** (Table 3, entry 7) also resulted in very clean cyclization, in the 6-exo mode, to **27**; this proved to be a stable crystalline solid owing to its inability to undergo elimination. This last cyclization was slow relative to the previous ones, requiring around 4 h to reach completion, but it was clean and quantitative indicating (i) that δ-hydrogen abstraction by acyl radicals is not a problem in such relatively slow 6-exo trig cyclizations and (ii) that 7-endo mode cyclization does not compete effectively in this case. The thiosalicylic acid derivatives **17** and **18** behaved analogously to the salicylic acid derivatives in so far as ready exo-mode cyclization was observed (Table 3, entries 8 and 9) with the products **28** and **29** being susceptible to elimination, even on rapid passage over silica gel (Table 3, entry 10). 6-Exo-dig cyclization of the acyl radical derived from **19** is also evidently the favored process, resulting in the isolation of the stable vinyl telluride **31** in essentially quantitative yield (Table 3, entry 11).[42] This cyclization was especially interesting as previous attempts, in this laboratory, to conduct 6-exo-dig cyclizations of acyl radicals by the tin hydride/acyl selenide method had failed.[43] Subsequently Bachi has reported one such 6-exo-dig cyclization of an alkoxycarbonyl radical in high yield.[18d] It would appear that our previous speculations[43] about the transition state for cyclization of σ-radicals onto alkynes were premature. The cyclization/elimination sequence (eg **12** → **24**) is analogous to the direct cyclization of an acyl radical onto a *terminal* alkyne with quenching of the cyclized radical by a hydrogen atom donor. This is especially noteworthy as attempts to conduct such cyclizations (for acyl, alkoxycarbonyl, and vinyl radicals) under the usual stannane mediated conditions are marred by rapid competing hydrostannylation of the cyclization product.[18,43,44]



A further example involved the photolysis of the acyl telluride **20**. This substance was prepared by the method outlined in Scheme 5 from ethyl *O*-allylsalicylate. As indicated in Table 3 (entry 12) cyclization was very clean and was followed by cleavage of the intermediate cyclopropylmethyl radical to give **32** essentially quantitatively, as demonstrated by ^1H NMR spectroscopy.

(39) (a) Russell, G. A.; Tashtoush, H. *J. Am. Chem. Soc.* **1983**, *105*, 1398. (b) Perkins, M. J.; Turner, E. S. *J. Chem. Soc., Chem. Commun.* **1981**, 139. (c) Curran, D. P.; Martin-Esker, A. A.; Ko, S.-B.; Newcomb, M. *J. Org. Chem.* **1993**, *58*, 4691.

(40) (a) Beckwith, A. L. J.; Bowry, V. W.; Ingold, K. U. *J. Am. Chem. Soc.* **1992**, *114*, 4983. (b) Bowry, V. W.; Ingold, K. U. *J. Am. Chem. Soc.* **1992**, *114*, 4992.

(41) The rate of trapping of the benzoyl radical by TEMPO has recently been determined to be 1.0×10^9 M^{-1} s^{-1} and very close to that for the trapping of a primary alkyl radical: Mendenhall, G. D.; Protasiewicz, J. D.; Brown, C. E.; Ingold, K. U.; Lusztyk, J. *J. Am. Chem. Soc.* **1994**, *114*, 1718.

(42) Intermolecular free radical carbotelluration of alkynes and addition of diaryl ditelluides across alkynes has been reported: (a) Han, L-B.; Ishihara, K.-I.; Kambe, N.; Ogawa, A.; Ryu, I.; Sonoda, N. *J. Am. Chem. Soc.* **1992**, *114*, 7591. (b) Ogawa, A.; Yokoyama, K.; Obayashi, R.; Han, L.-B.; Kambe, N. *Tetrahedron*, **1993**, *49*, 1177.

(43) Crich, D.; Fortt, S. M. *Tetrahedron Lett.* **1987**, *28*, 2895.

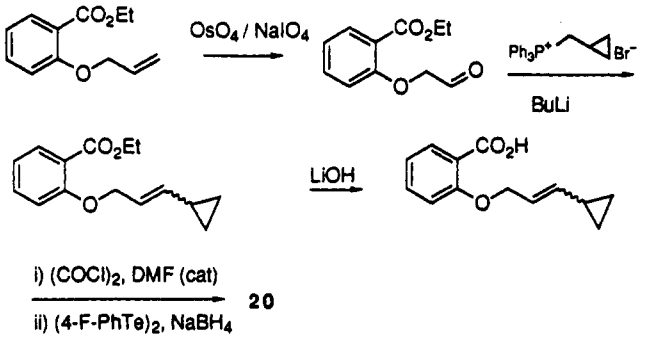
(44) Parsons, P. J.; Stefanovic, M.; Willis, P.; Meyer, F. *Synlett* **1992**, 864.

Table 3. Cyclization Reactions

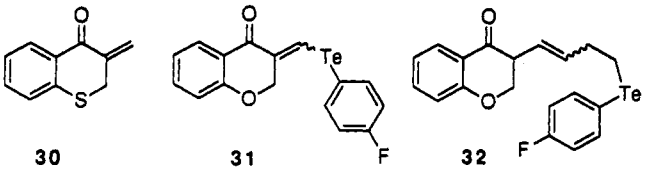
entry	acyl telluride	method[a]	time (h)	products (% yield)
1	**12**	A	0.5	**21** (96), **24** (4)
2	**13**	A	0.3	**22** (80), **24** (20)
3	**14**	A	0.25	**23** (86), **24** (14)
4	**14**	C	0.25	**24** (89)
5	**15**	B	1.5	**25** (93), **26** (7)
6	**15**	C	0.5	**26** (94)
7	**16**	B	4.0	**27** (100)
8	**17**	B	9.5	**28** (69), **30** (10)
9	**18**	B	1.5	**29** (90), **30** (10)
10	**18**	D	0.3	**30** (41)
11	**19**	B	4.0	**31** (100)
12	**20**	B	2.0	**32** (100)
13	**33**	B	1.0	**34** (100) → **35** (88)
14	**36**	B	48	degradation
15	**40**	C	5.5	**43**:**44** (63% [3.7:1])
16	**46**	C	0.5	**47** (100) → **48** (74)
17	**49**	A	3.5	degradation

[a] A, *hν*, room temperature → reflux (NMR yields); B, *hν*, 8 °C (NMR yields); C, *hν*, room temperature → reflux, and then H_2O_2, THF, H_2O; D, *hν*, room temperature, and then SiO_2 chromatography.

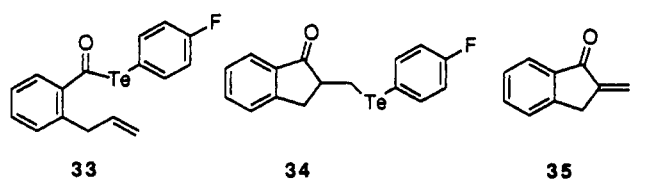
Scheme 5



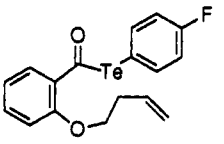
Unfortunately **32** was somewhat unstable, especially toward silica gel chromatography which prevented its isolation. This experiment nevertheless provides very strong support for the acyl radical mechanism and nicely confirms the conclusions drawn from the intermolecular trapping experiments and the ESR spectroscopy.



The nature of past and present target molecules under study in our laboratory has concentrated our efforts on the formation of six-membered rings by radical cyclizations, as opposed to the more common five-membered rings. The *o*-allylbenzoyl telluride **33** was constructed by standard methods in order to demonstrate the applicability of this chemistry to 5-exo-trig cyclizations. The anticipated cyclization occurred smoothly to give **34** (Table 3, entry 13), and after treatment with hydrogen peroxide the α-methyleneindanone **35** was isolated in good yield.

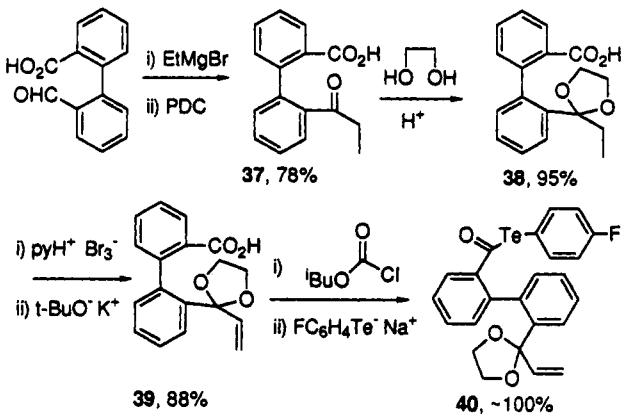


While the formation of five- and six-membered rings[2] and, since the pioneering work of Porter,[45] even of macrocycles[46] by means of radical cyclizations is relatively common, medium ring formation is still somewhat unusual.[47] We reasoned that in the absence of effective competing reactions the acyl tellurides might provide a useful means of preparing medium-sized rings by radical cyclization methodology. The acyl telluride **36** was prepared by alkylation of ethyl salicylate with 4-bromobutene followed by saponification and conversion of the acid to the acyl telluride in the usual manner. It was felt that **36** was a good candidate for 8-endo-trig cyclization and formation of a benzo-fused cyclooctanone, given the propensity of the 7-octen-1-yl radical to cyclize, albeit at a minimal rate, in the endo mode.[48] In the event, extended photolysis of **36** for periods of up to 2 days did not result in cyclization but eventually in degradation of the substrate (Table 3, entry 14).



36

Scheme 6



A more conformationally restrained substrate (**39**) for an eventual 8-endo-trig cyclization was synthesized uneventfully as outlined in Scheme 6 from diphenaldehydic acid. Conversion of this acid to the acyl telluride **40** by the standard route proved problematic owing to the instability of the intermediate acid chloride. Hence an alternative preparation was developed involving reaction of the acid with isobutyl chloroformate to give a mixed carboxylic–carbonic anhydride, followed by treatment

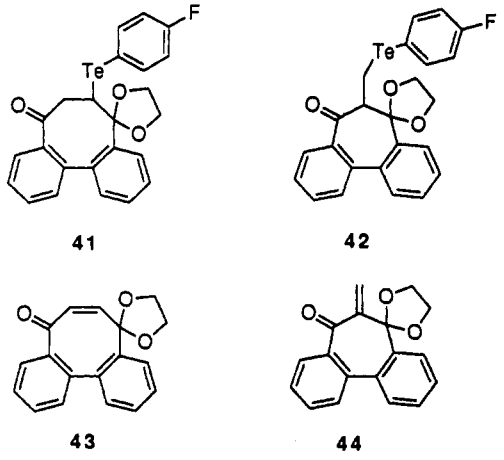
(45) (a) Porter, N. A.; Magnin, D. R.; Wright, B. T. *J. Am. Chem. Soc.* **1986**, *108*, 2787. (b) Porter, N. A.; Chang, V. H. T. *J. Am. Chem. Soc.* **1987**, *109*, 4976. (c) Porter, N. A.; Chang, V. H. T.; Magnin, D. R.; Wright, B. T. *J. Am. Chem. Soc.* **1988**, *110*, 3554.

(46) (a) Scott, D. M.; McPhail, A. T.; Porter, N. A. *J. Org. Chem.* **1993**, *58*, 1178. (b) Yamaoto, T.; Ishibuchi, S.; Ishizuka, T.; Haratake, M.; Kunieda, T. *J. Org. Chem.* **1993**, *58*, 1997. (c) Feldman, K. S.; Berven, H. M.; Romanelli, A. L.; Parvez, M. *J. Org. Chem.* **1993**, *58*, 6851. (d) Astley, M. P.; Pattenden, G. *Synlett* **1992**, 101. (e) Baldwin, J. E.; Adlington, R. M.; Ramcharitar, S. H. *Tetrahedron* **1992**, *48*, 3413. (f) Cox, N. J. G.; Mills, S. D.; Pattenden, G. *J. Chem. Soc. Perkin Trans. 1*, **1992**, 1313. (g) Hitchcock, S. A; Pattenden, G. *J. Chem. Soc., Perkin Trans. 1* **1992**, 1323. (h) O'Shea, K. J.; O'Dell, R.; Sasaki, D. Y. *Tetrahedron Lett.* **1992**, *33*, 4699. (i) Hitchcock, S. A.; Pattenden, G. *Tetrahedron Lett.* **1992**, *33*, 4843, 7448. (j) Mirade, G. S.; Cannizzaro, S. M.; Porter, N. A. *J. Am. Chem. Soc.* **1992**, *114*, 9683.

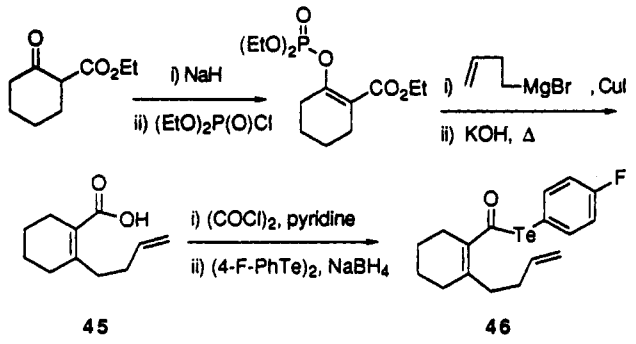
(47) (a) Lee, E.; Yoon, C. H.; Lee, T. H. *J. Am. Chem. Soc.* **1992**, *114*, 10981. (b) Feldman, K. S.; Ensel, S. M. *J. Am. Chem. Soc.* **1993**, *115*, 1162. (c) Vauzeilles, B.; Cravo, D.; Mallet, J.-M.; Sinaÿ, P. *Synlett* **1993**, 522. (d) Finch, H.; Pegg, N. A.; Evans, B. *Tetrahedron Lett.* **1993**, *34*, 8353. (e) Pirrung, F. O. H.; Steeman, W. J. M.; Hiemstra, H.; Speckamp, W. N.; Kaptein, B.; Boesten, W. H. J.; Schoemaker, H. E.; Kamphuis, J. *Tetrahedron Lett.* **1992**, *33*, 5141. (f) Lamas, C.; San, C.; Castedo, L.; Dominguez, D. *Tetrahedron Lett.* **1992**, *33*, 5653. (g) Snider, B. B.; Merritt, J. E. *Tetrahedron*, **1991**, *47*, 8663. (h) Sundberg, R. J.; Cherney, R. J. *J. Org. Chem.* **1990**, *55*, 6028. (k) Ghosh, K.; Ghosh, A. K.; Ghatak, U. R. *J. Chem. Soc., Chem. Commun.* **1994**, 629. (l) Molander, G. A.; McKie, J. A. *J. Org. Chem.* **1994**, *59*, 3186.

(48) Beckwith, A. L. J.; Schiesser, C. H. *Tetrahedron* **1985**, *41*, 3925.

with the sodium aryl telluride in the usual manner to give **40**, isolated in essentially quantitative yield. White light photolysis of this acyl telluride resulted in complete consumption within 5.5 h. ^{1}H NMR analysis of the crude photolysate revealed the absence of olefinic protons, and so the probable formation of **41** and/or **42**. Following brief treatment with hydrogen peroxide, a 3.7/1 mixture of the dibenzocyclooctenone **43** and the somewhat sensitive methylenecycloheptanone **44**[49] was isolated in 63% overall yield (Table 3, entry 15). The possibility that the formal 8-endo product arises by 7-exo cyclization followed by a radical ring expansion[36] cannot be rigorously excluded at this time. However, this appears unlikely in view of the probable very rapid trapping of the cyclized radical by the acyl telluride and the absence of formal endo mode products in any of the other cyclizations described above. Evidently, as illustrated by the failure of **36** to undergo cyclization, the absence of effective competing reactions is not sufficient by itself to enable 8-endo mode cyclizations of 7-octenoyl radicals, but the addition of conformational restraint enables such cyclizations to proceed.

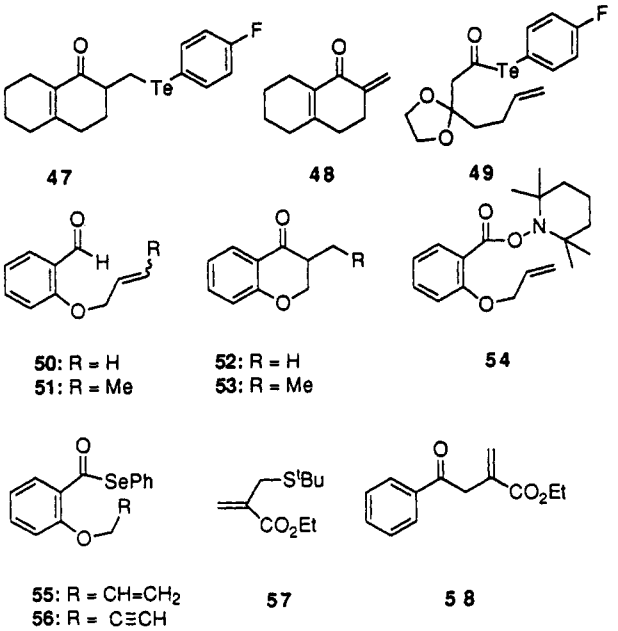


Scheme 7



Scheme 7 describes the straightforward preparation of an α,β-unsaturated carboxylic acid (**45**) and its conversion to the acyl telluride **46**. This substance (δ_C 198.4 ppm; ν 1685 cm^{-1}) underwent clean cyclization to **47** under the standard conditions (Table 3, entry 16); treatment with hydrogen peroxide led to the isolation of the cross-conjugated dienone **48**. Interestingly, **48** showed no tendency, either under the reaction conditions or on silica gel chromatography, to suffer tautomerization to the corresponding tetralin.

Each of the above cyclizations involves an acyl telluride directly conjugated with an aromatic ring or, as in the case of **46**, with an alkene. We therefore prepared the nonconjugated aliphatic acyl telluride **49** (δ_C 198.6 ppm; ν 1699 cm^{-1}) from the corresponding, known,[16b] acyl chloride. No cyclization was observed on prolonged photolysis of this substance with either white light or with Pyrex-filtered light from a medium pressure mercury lamp (Table 3, entry 17). This result was unexpected, in light of the known propensity of the acyl radical in question to undergo efficient cyclization,[16b] and seems to indicate that the nonconjugated acyl radical is not a sufficiently good leaving group in an S_H2 reaction at tellurium (II) for chain propagation to occur.



A series of trapping experiments (Table 4), in which the 6-exo-trig cyclization was pitted against reaction of the acyl radical with thiophenol, diaryl dichalcogenides or TEMPO, was conducted. Photolysis of **12** in the presence of thiophenol led to the formation of the salicyl aldehyde **50** together with the methyl chromanone **52** and the typical tellurium transfer product **21** (Table 4, entry 1). Grossly similar results were obtained on photolysis of **15** with thiophenol (Table 4, entry 2). Evidently thiophenol is able to compete with cyclization for trapping of the acyl radical; it is also able to compete with the acyl telluride for trapping of the cyclized radical. TEMPO and diphenyl diselenide are very effective traps for the acyl radical and effectively prevent cyclization (Table 4, entries 3 and 4) while diphenyl disulfide is a poor trap both for the acyl radical and the cyclized radical (Table 4, entry 5) and is simply a spectator to the usual cyclization with tellurium transfer. Similar results were obtained with the acetylenic acyl telluride **19**, with the diselenide effectively capturing the acyl radical and the disulfide playing no apparent part in the reaction (Table 4, entries 6 and 7). These reactions reinforce the conclusions drawn above regarding the effectiveness of the various traps employed for acyl radicals. More importantly they serve to further dispel the notion of an alternative mechanism for cyclization in which a chalcogenide radical (eqs 3–5, X = ArTe$^\bullet$, ArSe$^\bullet$, ArS$^\bullet$) adds to the alkene followed by cyclization of the adduct onto the carbonyl carbon of the acyl telluride with eventual expulsion of an aryltelluro radical and formation of arylchalcogenomethyl chromanones. No such products were observed in the reactions with thiophenol, diphenyl diselenide, and diphenyl disulfide where, were such a mechanism operating, they might reasonably have been expected.

Our attempts at intermolecular C–C bond formation by photolysis of the acyl tellurides in the presence of electron-deficient terminal alkenes were for the most part disappointing. Thus photolysis of **1** with up to 3.5 equiv of methyl acrylate at 8 °C for 2 h resulted only in the recovery of unchanged **1**. Heating **1** to reflux, with the heat generated by the lamp, with increased quantities of methyl acrylate resulted only in degradation.

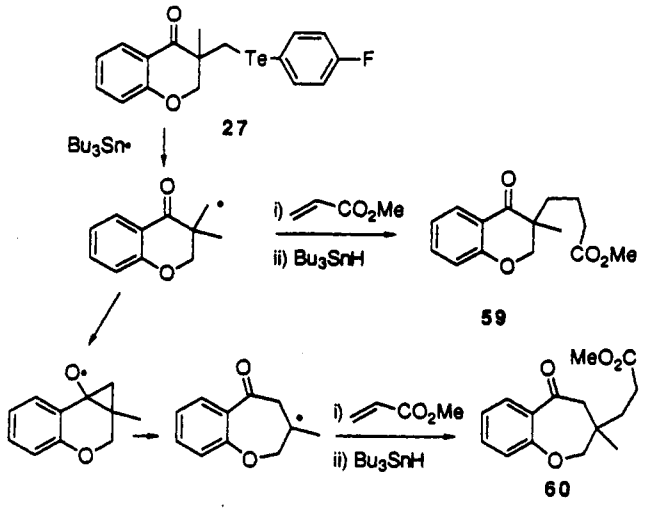
(49) The instability of the methylenecycloheptanone **44** is very reminiscent of that observed earlier in this laboratory for the closely analogous 3,3-(ethylenedioxy)-2-methylenecyclohexanone.[16i]

Table 4. Competition Experiments

entry	acyl telluride	trap (equiv)	method[a]	time (h)	products (% yield)
1	**12**	PhSH (1.5)	A	0.5	**50** (17),[b] **52** (24),[b] **21** (59)[b]
2	**15**	PhSH (2.7)	A	2.0	**51** (8),[b] **53** (73)[b] **25** (19)[b]
3	**13**	TEMPO (1.2)	A	2.0	**54** (78)
4	**13**	PhSeSePh (1.5)	A	2.5	**55** (87)
5	**13**	PhSSPh (1.0)	A	1.0	**22** (90)[b]
6	**19**	PhSeSePh (1.5)	A	2	**56** (73), **31** (trace)
7	**19**	PhSSPh (1.8)	A	7	**31** (100)[b]

[a] A, *hν*, 8 °C. [b] NMR yield.

Scheme 8



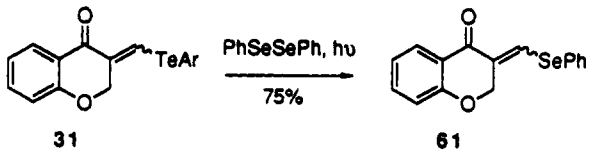
Similarly photolysis of **14** with 2 equiv of methyl acrylate also resulted only in the isolation of **23** in 95% yield. These results are best explained by the inability of methyl acrylate to compete with the very efficient background reaction of acyl radicals with the acyl telluride and likewise the efficient trapping of cyclized radicals by the acyl telluride function. Eventually success was obtained when **2** was subjected to photolysis with 3.9 molar equiv of the nonpolymerizable alkene **57**[50] for 26 h, after which the adduct **58** was isolated in 52% yield.

The utility of the acyl radical cyclizations with tellurium group transfer is evidently a function of the further transformations which may be applied to the cyclization products.[51] Above we have demonstrated how the products of cyclization onto alkenes may be readily eliminated, on treatment with hydrogen peroxide, to give α-alkylidene ketones in high yield. The reduction of simple alkyl aryl tellurides to alkanes with stannanes has previously been reported by Clive[29] and their use in conjunction with the *O*-acyl thiohydroxamates as sources of alkyl radicals by Barton.[30]

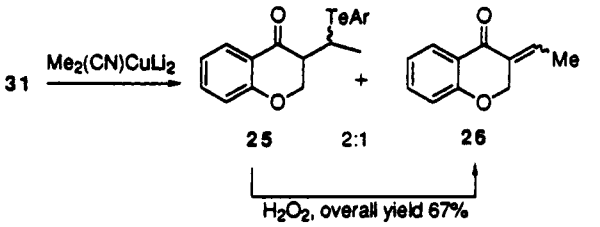
Treatment of the stable β-aryltelluro ketone **27** with tributyltin hydride and methyl acrylate in benzene at reflux resulted in the formation of **59** and **60** in 53 and 18% yields respectively. While **59** is the product of a simple radical chain reaction, **60** is formed by a ring expansion process[36] involving attack of the first formed alkyl radical on the ketone to give a cyclopropyloxy radical followed by cleavage of the endo cyclic bond and then trapping by methyl acrylate (Scheme 8).

White light photolysis of **31** with 10 molar equiv diphenyl diselenide at 8 °C for 6 h resulted in the isolation of the vinyl selenide **61** in 75% yield (Scheme 9). This simple reaction may be adequately rationalized in terms of conjugate addition of the phenylseleno radical followed by elimination of the aryltelluro radical.

Scheme 9



Scheme 10



Treatment of **31** with the Lipshutz higher order cuprate derived from methyllithium and cuprous cyanide[52] in THF at −78 °C followed by warming to room temperature gave an approximately 2:1 mixture of the adduct **25** (as a 1:1 mixture of diastereomers) and the addition elimination product **26** (as a 44:56 mixture of geometric isomers). This mixture was treated in the usual way with hydrogen peroxide at room temperature resulting in the eventual isolation of **26** in 67% overall yield in the form of 3:1 *E*:*Z* mixture (Scheme 10). This 1,4-addition reaction was particularly interesting in the light of recent reports by Comassetto on the transmetalation of vinyl tellurides with higher order cuprates.[53] This difference in behavior can probably be explained by the polarized nature of the vinyl telluride **31**.

Experimental Section

General. All solvents were dried and distilled by standard procedures. Unless otherwise stated all reactions were run under a dry nitrogen atmosphere. THF was distilled, under N_2, immediately prior to use from sodium benzophenone ketyl. ^1H, ^{13}C, and ^{19}F NMR spectra were run in $CDCl_3$ at 300, 75, and 282 MHz respectively unless otherwise stated. ^1H and ^{13}C chemical shifts (δ_H and δ_C) are downfield from Me_4Si and ^{19}F chemical shifts (δ_F) upfield from $CFCl_3$. Unless otherwise stated IR spectra (υ) and specific rotations were recorded as $CHCl_3$ or CH_2Cl_2 solutions. ESR spectra were obtained at room temperature with a Varian E-4 spectrometer.

Toxicity. Relatively little is known about the toxicity of organotellurium derivatives. Accordingly, all such derivatives should be handled with care in a well ventilated hood.[54]

Bis(4-fluorophenyl) Ditelluride. To a solution of (4-fluorophenyl)-magnesium bromide in THF prepared from 4-bromofluorobenzene (13.8 g, 80 mmol) and magnesium turnings (2.4 g, 100 mmol) in THF (50 mL) was added tellurium powder (10.0 g, 80 mmol). The reaction mixture

(50) Barton, D. H. R.; Crich, D. *J. Chem. Soc., Perkin Trans. 1* **1986**, 1613.

(51) Reviews on organotellurium chemistry: (a) Petragnani, N.; Comasseto, J. V. *Synthesis* **1986**, 1. (b) Petragnani, N.; Comasseto, J. V. *Synthesis*, **1991**, 897.

(52) Lipshutz, B. H.; Sengupta, S. *Org. Reacts.* **1992**, *41*, 135.

(53) (a) Tucci, F.; Chieffi, A.; Comasseto, J. V. *Tetrahedron Lett.* **1992**, *33*, 5721. (b) Marino, J. P.; Tucci, F.; Comasseto, J. V. *Synlett* **1993**, 761. (c) Comasseto, J. V.; Berriel, J. N. *Syn. Commun.* **1990**, *20*, 1681. (c) Also see: Ogawa, A.; Tsuboi, Y.; Obayashi, R.; Yokoyama, K.; Ryu, I.; Sonoda, N. *J. Org. Chem.* **1994**, *59*, 1600.

(54) See: Sadeh, T. In *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Ed., Wiley Interscience: New York, 1987; Vol. 2, p 367 and references therein.

was heated to reflux with stirring for 3 h and then cooled to room temperature and quenched with saturated NH_4Cl solution and then filtered on a pad of celite. The filtrate was extracted with ether, and the extracts were washed with brine, dried ($MgSO_4$), and concentrated to give a dark red crystalline mass which was recrystallized from ethanol to give the title ditelluride as dark red crystals (11.5 g, 67%) with mp 66–67 °C: δ_H 6.86 (4H, dd, J = 8.7 and 8.8 Hz), and 7.69 (4H, dd, J = 5.6 and 8.7 Hz); δ_C 101.74 (d, J = 4.2 Hz), 116.40 (d, J = 21.8 Hz), 140.10 (d, J = 7.5 Hz), and 163.22 (d, J = 247.5 Hz); δ_F −114.19 (tt, J = 5.6 and 8.8 Hz). Anal. Calcd for $C_{12}H_8F_2Te_2$: C, 32.36; H, 1.81. Found: C, 32.29; H, 1.76.

Di-1-naphthyl Ditelluride. Tellurium powder (16.5 g, 0.125 mmol) was added in one portion to a solution of the Grignard reagent prepared from 1-bromonaphthalene (17.5 mL, 0.125 mmol) and magnesium turnings (3.0 g, 0.125 mmol) in THF (50 mL). After 3 h of stirring at room temperature the reaction mixture was exposed to the air and stirred overnight at room temperature. Water was then added and the reaction mixture extracted with ether. The extracts were dried ($MgSO_4$), evaporated, and crystallized from THF/hexanes to yield di-1-naphthyl ditelluride as a brown solid (9.0 g, 29%) with mp 112 °C: δ_H 7.16 (2H, dd, J = 7.3 and 8.0 Hz), 7.29 (2H, ddd, J = 1.0, 6.9, and 8.3 Hz), 7.41 (2H, dt, J = 1.0 and 7.8 Hz), 7.74 (4H, t, J = 8.5 Hz), 7.98 (2H, d, J = 8.4 Hz), and 8.11 (2H, dd, J = 1.0 and 7.1 Hz); δ_C 114.46, 126.32, 126.37, 126.80, 126.86, 130.21, 131.41, 132.96, 136.17, and 140.72. Anal. Calcd for $C_{20}H_{14}Te_2$: C, 47.15; H, 2.77. Found: C, 47.09; H, 2.75.

2-(2-Butenyloxy)benzoic Acid. Ethyl salicylate (3.3 g, 20 mmol) and potassium hydroxide (1.2 g, 22 mmol) were stirred in EtOH (20 mL) until a clear solution was obtained (~5 min), after which crotyl bromide (2.9 mL of 85%, 24 mmol) was added, resulting in the rapid formation of a white precipitate. After 2 h at room temperature the reaction mixture was filtered on a short silica plug, eluting with ethyl acetate, to give an essentially quantitative yield (4.4 g, 100%) of ethyl 2-(2-butenyloxy)-benzoate as a colorless oil. Without further purification, this oil (2.2 g, 10 mmol) was heated to reflux in EtOH (10 mL) with a 10% solution of sodium hydroxide in water (10 mL) for 1 h. After cooling to room temperature the reaction mixture was diluted with water (10 mL), washed with CH_2Cl_2 (2 × 15 mL), acidified to pH 2 with concentrated HCl and finally extracted into ethyl acetate (3 × 30 mL). The dried ($MgSO_4$) extracts were concentrated to dryness to give the title acid[55] as a colorless oil (1.80 g, 94%): δ_H 1.77 (3H, dd, J = 1.2 and 6.5 Hz), 4.78 (2H, d, J = 6.8 Hz), 5.75 (1H, m), 5.95 (1H, m), 7.07 (1H, d, J = 8.3 Hz), 7.09 (1H, ddd, J = 1.0, 7.6, and 7.8 Hz), 7.53 (1H, ddd, J = 1.8, 7.6, and 8.3 Hz), 8.13 (1H, dd, J = 1.8 and 7.8 Hz), and 10.60 (1H, br s); δ_C 17.70, 70.59, 113.04, 121.77, 123.89, 131.63, 133.28, 133.43, 134.62, 157.29, and 165.78; ν (film) 3257, 3027, 2944, 1733, 1603, and 1582 cm^{-1}.

2-[2-(Ethoxycarbonyl)phenoxy]acetaldehyde. Ethyl *O*-allylsalicylate[56] (7.21 g, 35 mmol) dissolved in 75% aqueous dioxane (180 mL) was treated with OsO_4 (1 small crystal) and then with $NaIO_4$ (15.72 g, 70 mmol) portionwise over 45 min with stirring. After 1.5 h of additional stirring the white slurry was extracted with ether (5 × 50 mL), and the combined organic layers were dried ($MgSO_4$), concentrated, and purified by chromatography on silica gel (eluent, ethyl acetate/ hexane 1.5:1) and finally distillation (bulb to bulb) to give 2-[2-(ethoxycarbonyl)phenoxy]-acetaldehyde (4.38 g, 60%) with bp 114–120 °C (0.95 mm): δ_H 1.40 (3H, t, J = 7.1 Hz), 4.37 (2H, q, J = 7.1 Hz), 4.62 (2H, s), 6.85 (1H, d, J = 7.7 Hz), 7.07 (1H, t, J = 7.1 Hz), 7.43 (1H, m), 7.83 (1H, d, J = 7.7 Hz), and 9.90 (1H, t, J = 1.1Hz); δ_C 14.13, 60.86, 73.76, 114.07, 121.69, 131.80, 133.31, 157.04, 165.68, and 198.95. For analytical purposes this aldehyde was converted to its crystalline 2,4-dinitrophenylhydrazone: mp 144–147 °C (85% EtOH). Anal. Calcd for $C_{17}H_{16}N_4O_7$: C, 52.58; H, 4.15; N, 14.43. Found: C, 52.51; H, 4.24; N, 14.30.

Ethyl 2-[(3-Cyclopropylallyl)oxy]benzoate. 2-[2-(Ethoxycarbonyl)-phenoxy]acetaldehyde (1.358 g, 6.53 mmol) was added at −78 °C to a THF solution of (cyclopropylmethylidene)triphenylphosphorane formed by treating (cyclopropylmethyl)triphenylphosphonium bromide (2.85 g, 7.18 mmol) in THF (50 mL) at −78 °C with nBuLi (3.265 mL of 2.0M in pentane, 6.53 mmol) followed by stirring at room temperature for 1 h. After 2 h of further stirring at room temperature the reaction mixture was poured into a mixture of ether (50 mL) and water (50 mL) and finally acidified with dilute HCl. The ether layer was decanted off and the aqueous phase further ether extracted (2 × 25 mL). The combined organic layers were washed with water and brine, dried ($MgSO_4$), concentrated, and chromatographed on silica gel (eluent: ethyl acetate/ hexane 6/1) to give ethyl 2-[(3-cyclopropylallyl)oxy]benzoate (1.2563 g, 78%) as an approximately 3.5:1 cis/trans mixture: the cis isomer, δ_H 0.40 (2H, m), 0.75 (2H, m), 1.35 (3H, t, J = 7.0 Hz), 1.60 (1H, m), 4.35 (2H, q, J = 7.0 Hz), 4.80 (2H, d, J = 6.8 Hz), 4.95 (1H, t, J = 10.5 Hz), 5.58 (1H, dt, J = 10.5 and 6.7 Hz), 6.95 (2H, m), 7.40 (1H, m), and 7.75 (1H, d, J = 7.7 Hz); δ_C 7.15, 10.12, 14.26, 60.70, 65.57, 113.78, 120.18, 121.17, 122.62, 131.42, 133.05, 138.17, 158.40, and 166.70; the minor, trans isomer, δ_H 0.40 (2H, m), 0.75 (2H, m), 1.35 (3H, t, J = 7.0 Hz), 1.45 (1H, m), 4.35 (2H, q, J = 7.0 Hz), 4.50 (2H, d, J = 6.7 Hz), 5.38 (1H, dd, J = 15 and 9.0 Hz), 5.78 (1H, dt, J = 15.0 and 6.8 Hz), 6.95 (2H, m), 7.40 (1H, m), and 7.75 (1H, d, J = 7.7 Hz); δ_C 6.75, 13.60, 14.26, 60.70, 69.59, 113.78, 120.18, 121.17, 121.95, 131.42, 133.05, 139.00, 158.40, and 166.70. Anal. Calcd for $C_{15}H_{18}O_3$: C, 73.14; H, 7.36. Found: C, 73.11; H, 7.33.

2-[(3-Cyclopropylallyl)oxy]benzoic Acid. Saponification of ethyl 2-[(3-cyclopropylallyl)oxy]benzoate (100 mg, 0.4 mmol) with LiOH (57 mg, 2.4 mmol) in water (1.0 mL) and THF (4.0 mL) for 3 days at room temperature followed by acidifcation and ether extraction gave 2-[(3-cyclopropylallyl)oxy]benzoic acid as a colorless oil (78 mg, 90%) in the form of a 3.3:1 cis/trans mixture: ν (film) 1731 cm^{-1}; the major cis isomer, δ_H 0.40 (2H, m), 0.80 (2H, m), 1.60 (1H, m), 4.93 (2H, d, J = 6.9 Hz), 5.14 (1H, t, J = 10.5 Hz), 5.61 (1H, m), 7.09 (2H, m), 7.51 (1H, m), 8.15 (1H, m), and 11.0 (1H, broad); δ_C 7.46, 10.25, 66.30, 113.07, 119.50, 119.61, 122.14, 133.65, 134.90, 142.10, 157.30, and 165.51; the minor trans isomer, δ_H 0.40 (2H, m), 0.80 (2H, m), 1.45 (1H, m), 4.68 (2H, d, J = 6.5 Hz), 5.41 (1H, dd, J = 15.0 and 9.0 Hz), 5.73 (1H, m), 7.10 (2H, m), 7.51 (1H, m), 8.15 (1H, m), and 11.0 (1H, broad); δ_C 7.15, 13.64, 70.96, 113.07, 117.96, 119.50, 122.14, 133.65, 134.90, 143.20, 157.30, and 165.51. Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.52; H, 6.39.

2-(3-Butenyloxy)benzoic Acid. To a solution of sodium (0.39 g, 17 mmol) in absolute EtOH (25 mL) was added ethyl salicylate (2.35 mL, 16.0 mmol) at 0 °C resulting in formation of a white precipitate. Further EtOH (25 mL) was added, resulting after warming to room temperature in a homogeneous solution. 4-Bromobutene (1.62 mL, 16.0 mmol) and NaI (0.24 g) were added, and the reaction mixture was heated to reflux with stirring for 7 days before it was poured into 5% NaOH solution (100 mL) and ether extracted (4 × 30 mL). The combined ether layers were washed with brine, dried ($MgSO_4$), and concentrated to yield ethyl 2-(3-butenyloxy)benzoate as a yellow oil (1.27 g, 36%) of sufficient purity for use in the next step. The ester (0.73 g, 3.3 mmol) was heated to reflux in water (15 mL) with KOH (0.245 g, 3.7 mmol) for 3 h, before cooling to room temperature and washing with ether. Acidification to pH 2 with dilute HCl, ether extraction (3 × 10 mL), drying ($MgSO_4$), and concentration gave 2-(3-butenyloxy)benzoic acid as a colorless oil (0.56 g, 88%): δ_H 2.66 (2H, m), 4.30 (2H, t, J = 6.2 Hz), 5.23 (2H, m), 5.86 (1H, m), 7.03 (1H, d, J = 8.4 Hz), 7.11 (1H, t, J = 7.6 Hz), 7.54 (1H, m), 8.16 (1H, dd, J = 1.8, and 7.8 Hz) and 10.85 (1H, broad); δ_C 33.37, 68.71, 112.42, 117.58, 118.94, 122.16, 132.93, 133.76, 134.96, 157.35, and 165.42; ν (CH_2Cl_2) 3299, 2893, 1736, 1694, 1644, and 1604 cm^{-1}. HRMS calcd for $C_{11}H_{12}O_3$ 192.07864, found 192.07827. For analytical purposes the acid was converted to its crystalline dicyclohexylammonium salt: mp 107–108 °C (Et_2O). Anal. Calcd for $C_{23}H_{35}NO_3$: C, 73.96; H, 9.44; N, 3.75. Found: C, 73.64; H, 9.42; N, 3.83.

2′-Propanoylbiphenyl-2-carboxylic Acid (37). A solution of diphenaldehydic acid[57] (0.859 g, 3.80 mmol) in THF (5 mL) was cooled to 0 °C and treated with ethylmagnesium bromide in THF (8.4 mL of 1M, 8.4 mmol). The ice bath was removed and the reaction mixture stirred at room temperature for 4 h before it was poured into ice cold dilute HCl (25 mL) and extracted with ether (30 mL). The extracts were washed repeatedly with brine, dried ($MgSO_4$), and concentrated to yield 2′-(1-hydroxypropyl)-2-biphenylcarboxylic acid as a yellow oil (1.01 g). This hydroxy acid underwent lactonization on standing, even at 0°C; consequently, it was immediately converted to the corresponding ketone by stirring with pyridinium dichromate (5.00 g, 13.3 mmol) in DMF (10 mL) at 0 °C for 15 h followed by dilution with water (100 mL) and ether extraction (4 × 30 mL). The combined ethereal layers were stirred with $MgSO_4$, then filtered, and concentrated to ca. 15 mL before stirring with saturated aqueous Na_2SO_3 (4 mL) for 1 h. The ether phase was then extracted into 5% NaOH (4 × 25 mL), followed by acidification to pH 2 with HCl , reextraction into ether (4 × 25 mL), washing with brine,

(55) Kondo, H.; Takai, Y.; Shintani, S. Jap. Patent. 1988, JP 63,186,728 (*Chem. Abstr.* **1989**, *110*, 96554x).

(56) Claisen, L. *Ber. Deut. Chem. Ges.* **1912**, *45*, 3165.

(57) Bailey, P. S.; Erickson, R. E. *Organic Syntheses;* Wiley: New York, 1973; Collect. Vol. 5, p 493.

drying ($MgSO_4$), and concentration to give the keto acid as a pale yellow oil (0.702 g, 73%) which solidified on standing. The keto acid **37** so obtained was sufficiently pure for the next step; however, an analytical sample was obtained by chromatography on silica gel eluting with hexane/ether 1:1. It was a white crystalline solid: mp 107–108 °C; δ_H 0.98 (3H, t, J = 7.3 Hz), 2.66 (2H, q, J = 7.3 Hz), 7.13 (1H, d, J = 6.4 Hz), 7.15 (1H, dd, J = 1.8 and 7.3 Hz), 7.41–7.52 (4H, m), 7.66 (1H, dd, J = 2.1 and 6.2 Hz), 7.96 (1H, dd, J = 1.2 and 7.8 Hz), 11.0 (1H, broad); δ_C 8.20, 34.50, 127.47, 127.52, 127.55, 129.24, 130.46, 130.50, 130.66 (2C), 132.01, 138.47, 140.16, 142.55, 171.56, and 205.95; ν 3489, 3080–2880 (broad), 1740, 1695, 1596, and 1574 cm^{-1}. Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.58; H, 5.55. Found: C, 75.70; H, 5.63.

2′-[1,1-(Ethylenedioxy)propyl]biphenyl-2-carboxylic Acid (38). The acid **37** (0.815 g, 3.20 mmol) was heated to reflux under a Dean-Stark water separator with ethylene glycol (0.72 mL, 12 mmol) and a catalytic quantity of tosic acid in benzene (15 mL) overnight. After cooling to room temperature the reaction mixture was diluted with ether (40 mL) and extracted into 5% NaOH (4 × 20 mL). The alkaline solution was acidified to pH 2 with HCl and reextracted into ether (4 × 20 mL). The extracts were washed with brine, dried ($MgSO_4$), and concentrated to dryness giving the acetal **38** as a white crystalline solid (0.906 g, 95%): mp 141–142 °C (ether/hexane); δ_H 0.69 (3H, t, J = 7.4 Hz), 1.60 (2H, m), 3.63 (1H, m), 3.74 (2H, m), 3.85 (1H, m), 7.04 (1H, dd, J = 1.4 and 6.3 Hz), 7.20 (1H, dd, J = 1.1 and 7.0 Hz) 7.27-7.33 (2H, m), 7.42 (1H, m), 7.48 (1H, m), 7.59 (1H, dd, J = 1.7 and 6.8 Hz), 7.98 (1H, dd, J = 1.2 and 7.7 Hz), and 11.0 (1H, broad); δ_C 7.95, 32.65, 64.32, 64.68, 111.34, 126.64, 126.69, 127.11, 127.29, 129.99, 130.78, 131.05, 131.19, 138.41, 139.66, 143.74, and 172.18; ν 3490, 3080–2886 (broad), and 1696 cm^{-1}. Anal. Calcd for $C_{18}H_{18}O_4$: C, 72.47; H, 6.08. Found: C, 72.59; H, 6.07.

2′-[1,1-(Ethylenedioxy)-2-propen-1-yl]biphenyl-2-carboxylic Acid (39). To a solution of the acid **38** (0.445 g, 1.49 mmol) in THF (5 mL) at 0 °C was added pyridinium perbromide [0.479 g, 1.5 mmol (freshly recrystallized from AcOH)], and the reaction mixture was stirred for 2 h at 0 °C and then 5 h at room temperature. The precipated pyridinium bromide was removed by filtration and the filtrate diluted with ether (20 mL), washed with 5% Na_2SO_3 (2 × 10 mL), and extracted with 5% NaOH (4 × 10 mL). The alkaline solution was acidified to pH 2 with HCl and extracted into ether (4 × 10 mL). The ether layers were washed with brine, dried ($MgSO_4$), and concentrated to yield slightly impure 2′-[(2-bromo-1,1-(ethylenedioxy)propyl]biphenyl-2-carboxylic acid, a mixture of two diastereomers, as a light yellow solid (0.542 g, 96%): δ_H 1.41 (3H, d, J = 6.9 Hz), 3.61–4.09 (5H, m), 7.01–7.15 (2H, m), 7.29–7.35 (2H, m), 7.42–7.46 (1H, m), 7.50–7.54 (1H, m), 7.64–7.67 (1H, m), 8.00–8.03 (1H, m), 11.0 (1H, broad). The bromo acid (0.561 g, 1.49 mmol) was stirred with potassium *tert*-butoxide (0.51 g, 4.5 mmol) in DMSO (5 mL) at room temperature for 20 h. The reaction mixture was then diluted with ether (30 mL) and extracted into water (3 × 20 mL). The aqueous phases were acidified with HCl to pH 2 and reextracted into ether (3 × 20 mL). After washing with brine the extracts were dried ($MgSO_4$) and concentrated to dryness affording **39** as a white solid (0.405 g, 92%): mp 159–160 °C; δ_H 3.47–3.57 (2H, m), 3.66–3.80 (2H, m), 5.13 (1H, dd, J = 10.5 and 1.5 Hz), 5.15 (1H, dd, J = 1.5 and 17.2 Hz), 5.83 (1H, dd, J = 10.6 and 17.2 Hz), 7.10 (1H, m), 7.20 (1H, m), 7.30–7.48 (4H, m), 7.63 (1H, m), 7.68 (1H, m), and 10.63 (1H, broad); δ_C 64.10, 64.55, 108.80, 116.58, 126.98, 127.15, 127.20, 128.29, 129.27, 130.32, 130.61, 131.10, 131.80, 136.59, 137.06, 140.05, 142.36, and 171.29; ν 3496, 3142–2902 (broad), 1700, 1599, and 1575 cm^{-1}; HRMS calcd for $C_{18}H_{16}O_4$ 296.104859, found 296.104821 ($M^{\bullet+}$).

2-But-3-enylcyclohexene-1-carboxylic Acid (45). 4-Bromo-1-butene (2.0 mL, 19.7 mmol) in THF (3 mL) was added dropwise to a suspension of magnesium turnings (0.627 g, 25.8 mmol) in THF (10 mL) and the mixture brought to gentle reflux with stirring. After the addition was complete, reflux was maintained for 0.5 h before the reaction mixture was cooled to room temperature and transferred via a cannula to a vigorously stirred suspension of CuI (1.43 g, 7.5 mmol) in THF (5 mL) at −78 °C. 2-(Ethoxycarbonyl)cyclohexanone was converted to diethyl 2-(ethoxycarbonyl)cyclohexenyl phosphate according to the literature procedure[58] and a solution of this enol phosphate (1.05 g, 3.4 mmol) in THF (5 mL) added dropwise to the above cuprate at −78 °C. Stirring was continued at −78 °C for 4 h before the reaction was quenched by pouring into ice cold saturated aqueous NH_4Cl (10 mL) and ether extracted (3 × 10 mL). The extracts were washed with 15% NH_4OH saturated with NaCl until the washings were no longer blue and then with brine, dried ($MgSO_4$), and concentrated to yield a light yellow oil (0.68 g) which contained ethyl 2-but-3-enylcyclohexenecarboxylate and ethyl cyclohexenecarboxylate in the ratio 3.7:1 as determined by ^1H NMR spectroscopy. Reaction of this oil with KOH (0.11 g) in water (5 mL) at reflux for 3 h followed by cooling to room temperature and ether extraction (3 × 10 mL) gave ethyl 2-but-3-enylcyclohexenecarboxylate as a colorless oil (0.49 g) devoid of ethyl cyclohexenecarboxylate which had been preferentially saponified. This oil and KOH (1.2 g) were then dissolved in EtOH (10 mL) and water (2 mL) and stirred at room temperature for 48 h before pouring into water and washing with ether (3 × 5 mL). The aqueous phase was acidified to pH 2 with concentrated HCl and extracted with ether (3 × 10 mL), and the extracts were dried ($MgSO_4$), concentrated, and filtered on silica gel (eluent hexane:ether 1:1) to yield 2-but-3-enylcyclohexene-1-carboxylic acid (**45**) as a colorless oil (0.38 g, 62%) which solidified on standing in the freezer: mp 35–37 °C; δ_H 1.55–1.66 (4H, m), 2.17–2.33 (6H, m), 2.54 (2H, t, J = 7.7 Hz), 4.95 (1H, dd, J = 2.6 and 10.1 Hz), 5.02 (1H, dd, J = 3.5 and 17.1 Hz), 5.85 (1H, m), and 11.0 (1H, broad); δ_C 22.19, 22.29, 26.33, 32.25, 32.85, 35.02, 114.59, 123.88, 138.41, 153.31, and 174.20; ν 3502, 3119, 2938, 2863, 1720, 1684, and 1640 cm^{-1}. Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.94. Found: C, 73.27; H, 9.00.

***Te*-4-Fluorophenyl Tellurobenzoate (1): Standard Protocol for the Formation of Telluroesters.** Bis(4-fluorophenyl) ditelluride (450 mg, 1.0 mmol) was dissolved in THF (8 mL) with stirring at room temperature and treated with $NaBH_4$ (150 mg, 4.0 mmol). MeOH (~1 mL) was added dropwise to this suspension which was then stirred vigorously until a light yellow solution formed. Benzoyl chloride (300 mg, 2.2 mmol) was then added dropwise and the resulting mixture stirred for a further 30 min. The reaction was quenched by addition of degassed water (5 mL) and extracted into benzene (3 × 30 mL), and the combined extracts were dried (Na_2SO_4) and concentrated to give a pale yellow oil which solidifed on standing in the freezer (660 mg, 100%) and which was sufficiently pure for use in subsequent experiments. An analytical sample was obtained by recrystallization from hexanes: mp 60–61 °C; δ_H 7.07 (2H, dd, J = 8.7 and 8.8 Hz), 7.48 (2H, dd, J = 7.6 and 7.8 Hz), 7.63 (1H, t, J = 7.6 Hz), 7.74 (2H, d, J = 7.8 Hz), and 7.76 (2H, dd, J = 8.7 and 6.2 Hz); δ_C 107.65, 117.14 (2C, d, J = 19.9 Hz), 127.06 (2C), 129.22 (2C), 134.18, 142.54 (2C, d, J = 10.5 Hz), 142.61, 164.10 (d, J = 248.6 Hz), and 196.02; δ_F −112.75; ν (melt) 1672 cm^{-1}; HRMS Calcd for $C_{13}H_9FOTe$ 329.9704, found 329.9701. Anal. Calcd for $C_{13}H_9FOTe$: C, 47.62; H, 2.75. Found: C, 47.49; H, 2.74.

***Te*-4-Methoxyphenyl Tellurobenzoate (2).** This substance was prepared according to the standard protocol using bis(4-methoxyphenyl) ditelluride.[59] Recrystallization from ether/hexane gave yellow needles (92%): mp 89–92 °C; δ_H 3.84 (3H, s), 6.91 (2H, d, J = 8.7 Hz), 7.46 (2H, dd, J = 7.7 and 7.3 Hz), 7.61 (1H, dt, J = 7.3 and 1.0 Hz), 7.70 (2H, d, J = 8.7 Hz), and 7.74 (2H, dd, J = 7.7 and 1.0 Hz); δ_C 55.24, 103.17, 115.68, 127.01, 129.13, 133.98, 142.16, 142.67, 160.49, and 197.01; ν 1663 cm^{-1}; HRMS calcd for $C_{14}H_{12}O_2Te$ 341.9904, found 341.9905.

***Te*-4-Fluorophenyl 4-Methoxytellurobenzoate (3).** This substance was prepared according to the standard protocol from bis(4-fluorophenyl) ditelluride and 4-methoxybenzoyl chloride. Obtained in 91% yield after crystallization from ether/hexanes, it was a yellow solid: mp 74–76 °C; δ_H 3.87 (3H, s), 6.94 (2H, dt, J = 2.2 and 6.9 Hz), 7.04 (2H, tt, J = 2.1 and 8.9 Hz), and 7.69–7.85 (4H, m); δ_C 55.63, 113.95, 114.24, 116.97 (d, J = 22.4 Hz), 129.49, 142.56 (d, J = 7.2 Hz), 163.10 (d, J = 251.0 Hz), 164.38, and 192.90; ν (film) 1675 cm^{-1}. Anal. Calcd for $C_{14}H_{11}FO_2Te$: C,46.99; H, 3.10. Found; C, 47.06; H, 3.14.

***Te*-1-Naphthyl Tellurobenzoate (4).** This substance was prepared according to the standard protocol from di-1-naphthyl ditelluride and benzoyl chloride. Obtained in 86% yield after crystallization from ether/hexanes, it was a yellow solid: mp 125–126 °C; δ_H 7.43–7.58 (5H, m), 7.64 (1H, tt, J = 1.2 and 7.4 Hz), 7.60–7.66 (3H, m), 7.90 (1H, d, J = 8.2 Hz), 8.19 (1H, dd, J = 1.1 and 7.0 Hz), and 8.24 (1H, dd, J = 3.4 and 4.6 Hz); δ_C 117.24, 126.43, 126.56, 127.19, 128.95, 129.19, 130.93, 131.32, 132.52, 133.83, 134.07, 136.47, 141.99, 142.73, and 195.45; ν (film) 1674 cm^{-1}. Anal. Calcd for $C_{17}H_{12}OTe$: C, 56.74; H, 3.36. Found: C, 56.82; H, 3.41.

***Te*-1-Naphthyl 4-Methoxytellurobenzoate (5).** This substance was prepared according to the standard protocol from di-1-naphthyl ditelluride and 4-methoxybenzoyl chloride. Obtained in 89% yield after crystallization from ether/hexanes, it was a yellow solid: mp 86–88 °C; δ_H 3.85

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(3H, s), 6.94 (2H, dt, J = 1.2 and 6.9 Hz), 7.44 (1H, dd, J = 7.2 and 8.1 Hz), 7.54 (2H, m), 7.79 (2H, dt, J = 1.2 and 6.9 Hz), 7.85 (1H, ddd, J = 1.5, 4.0, and 5.1 Hz), 7.98 (1H, d, J = 8.2 Hz), 8.20 (1H, dd, J = 1.0 and 7.0 Hz), and 8.25 (1H, J = 4.3 and 5.4 Hz); δ_C 55.68, 114.27, 117.33, 126.37, 126.53, 127.12, 128.68, 128.92, 129.67, 130.78, 131.65, 132.64, 135.63, 142.04, 164.36, and 192.63; υ (film) 1675 cm^{-1}. Anal. Calcd for $C_{18}H_{14}O_2Te$: C, 55.45; H, 3.62. Found: C, 55.45; H, 3.64.

***Te*-4-Fluorophenyl 2-(Allyloxy)tellurobenzoate (12).** This compound was prepared according to the standard protocol from 2-(allyloxy)benzoyl chloride[56] and bis(4-fluorophenyl) ditelluride. It was obtained, after crystallization from ether/hexane, as yellow green crystals (mp 50–51 °C) in 89% yield: δ_H 4.74 (2H, ddd, J = 5.8, 1.3, and 1.1 Hz), 5.39 (1H, ddt, J = 10.4, 1.3, and 1.1 Hz), 5.48 (1H, ddt, J = 17.2, 1.3, and 1.3 Hz), 6.22 (1H, ddt, J = 17.2, 10.4, and 5.8 Hz), 6.94 (1H, dd, J = 8.0 and 7.4 Hz), 6.95 (1H, d, J = 8.7 Hz), 7.00 (2H, ddd, J = 8.7, 7.0, and 2.5 Hz), 7.45 (1H, ddd, J = 8.7, 7.4, and 1.8 Hz), 7.67 (1H, dd, J = 8.0 and 1.8 Hz), and 7.73 (2H, ddd, J = 8.7, 5.9, and 2.5 Hz); δ_C 69.99, 113.20, 113.30, 116.56, 119.85, 121.14, 127.21, 128.26, 132.04, 134.52, 142.23 (d, J = 10.9 Hz), 158.60, 163.10 (d, J = 247.5 Hz), and 189.97; δ_F −113.41 (tt, J = 7.0 and 5.9 Hz); υ 1641 cm^{-1}; HRMS calcd for $C_{16}H_{13}FO_2Te$ 385.9966, found 385.9961. Anal. Calcd for $C_{16}H_{13}FO_2Te$: C, 50.06; H, 3.41. Found: C, 49.89; H, 3.46.

***Te*-4-Methoxyphenyl 2-(Allyloxy)tellurobenzoate (13).** This compound was prepared according to the standard from 2-(allyloxy)benzoyl chloride[56] and bis(4-methoxyphenyl)ditelluride.[59] It was obtained, after crystallization from ether/hexane, as yellow crystals (mp 79–80 °C) in 85% yield: δ_H 3.83 (3H, s), 4.62 (2H, ddd, J = 5.8, 1.3, and 1.2 Hz), 5.41 (1H, ddt, 10.2, 1.3, and 1.2 Hz), 5.53 (1H, ddt, J = 17.1, 1.3, and 1.3), 6.28 (1H, ddt, J = 17.1, 10.2, and 5.8 Hz), 6.90 (2H, d, J = 8.5 Hz), 7.00 (1H, dd, J = 8.0 and 7.8 Hz), 7.01 (1H, d, J = 8.0 Hz), 7.50 (1H, ddd, J = 8.0, 8.0, and 2.0), 7.69 (1H, dd, J = 7.8 and 2.0 Hz), and 7.71 (2H, d, J = 8.5 Hz); δ_C 55.05, 69.94, 108.82, 113.17, 115.20, 119.64, 121.07, 127.21, 128.56, 132.16, 134.28, 141.63, 158.57, 160.01, and 190.81; υ 1638 cm^{-1}. Anal. Calcd for $C_{17}H_{16}O_3Te$: C, 51.57; H, 4.04. Found: C, 51.49; H, 4.03.

***Te*-2,4-Dimethoxyphenyl 2-(Allyloxy)tellurobenzoate (14).** This compound was prepared according to the standard from 2-(allyloxy)benzoyl chloride[56] and bis(2,4-dimethoxyphenyl) ditelluride.[60] It was obtained as a yellow oil in 97% yield: δ_H 3.78 (3H, s), 3.61 (3H, s), 4.79 (2H, ddd, J = 5.8, 1.3, and 1.1 Hz), 5.40 (1H, ddt, J = 10.3, 1.3, and 1.1 Hz), 5.50 (1H, ddt, J = 17.2, 1.3, and 1.3 Hz), 6.28 (1H, ddt, J = 17.2, 10.3, and 5.8 Hz), 6.52 (1H, d, J = 8.1 Hz), 6.53 (1H, s), 6.96 (1H, dd, J = 8.0 and 7.8 Hz), 6.97 (1H, d, J = 7.8 Hz), 7.45 (1H, ddd, J = 8.0, 7.8, and 1.5 Hz), 7.68 (1H, dd, J = 7.8 and 1.5 Hz), and 7.72 (1H, d, J = 8.1 Hz); δ_C 55.32, 55.99, 69.97, 98.31, 100.32, 106.25, 113.08, 119.60, 121.01, 127.21, 128.26, 132.31, 134.04, 142.82, 158.55, 161.70, 162.53, and 190.29; υ (film) 1640 cm^{-1}; HRMS calcd for $C_{18}H_{18}O_4Te$ 428.0272, found 428.0264.

***Te*-4-Fluorophenyl 2-(2-Butenyloxy)tellurobenzoate (15).** 2-(2-Butenyloxy)benzoyl chloride was prepared from the corresponding acid by reaction with oxalyl chloride and was then subjected to the standard protocol for acyl telluride formation using bis(4-fluorophenyl) ditelluride. The acyl telluride **15** was isolated, after chromatography on silica gel eluting with ethyl acetate/hexanes 9:1, as a yellow crystalline solid in 76% yield: mp 60–62 °C; δ_H 1.81 (3H, d, J = 8.2 Hz), 4.70 (2H, dd, J = 1.1 and 4.2 Hz), 5.90–6.00 (2H, m), 6.93–7.04 (4H, m), 7.46 (1H, ddd, J = 1.7, 7.2, and 8.4 Hz), 7.68 (1H, dd, J = 1.7 and 8.4 Hz), and 7.75 (2H, ddt, J = 2.0, 5.9, and 8.7 Hz); δ_C 17.87, 69.68, 113.02, 113.19, 116.56 (d, J = 20.0 Hz), 120.95, 124.93, 127.18, 130.06, 132.63, 134.49, 142.26 (d, J = 7.0 Hz), 158.88, 163.13 (d, J = 247.1 Hz), and 190.09; δ_F −117.02; υ (melt) 1645 cm^{-1}. Anal. Calcd for $C_{17}H_{15}FO_2Te$: C, 51.32; H, 3.80. Found: C, 51.53; H, 3.90.

***Te*-4-Fluorophenyl 2-(Methallyloxy)tellurobenzoate (16).** 2-(Methallyloxy)benzoic acid[61] was converted to the corresponding chloride by reaction with oxalyl chloride and then to the telluride **16** in the normal manner. It was isolated in 81% yield as a yellow crystalline solid: mp 70–71 °C; δ_H 1.95 (3H, s), 4.73 (2H, s), 5.13 (1H, s), 5.19 (1H, s), 6.96–7.06 (4H, m), 7.48 (1H, ddd, J = 1.8, 7.3, and 8.6 Hz), 7.69 (1H, dd, J = 1.8 and 8.0 Hz), and 7.75 (2H, ddt, J = 2.0, 5.0, and 8.7 Hz); δ_C 19.93, 72.62, 113.11, 113.26, 115.16, 116.65 (d, J = 20.4 Hz), 121.15, 127.30, 130.04, 134.49, 139.63, 142.58 (d, J = 7.3 Hz), 158.85, 163.21, (d, J = 247.1 Hz), and 190.30; δ_F −116.90; υ(film) 1645 cm^{-1}; HRMS calcd for $C_{17}H_{15}FO_2Te$ 400.0123, found 400.0120.

***Te*-4-Fluorophenyl 2(Allylthio)tellurobenzoate (17).** The compound was prepared by the standard method from 2-(allylthio)benzoyl chloride[62] and bis(4-fluorophenyl) ditelluride and isolated, after chromatography on silica gel eluting with ethyl acetate/hexanes (1:1), as a yellow oil (94%): δ_H 3.59 (2H, ddd, J = 1.1, 1.3, and 6.8 Hz), 5.14 (1H, ddt, J = 1.1, 1.3, and 10.0 Hz), 5.21 (1H, ddt, J = 1.3, 1.3, and 16.9 Hz), 5.89 (1H, ddt, J = 6.7, 10.0, and 16.9 Hz), 7.03 (2H, ddd, J = 2.7, 8.3, and 8.8 Hz), 7.27 (1H, ddd, J = 1.3, 7.8, and 7.9 Hz), 7.38 (1H, dd, J = 1.3 and 8.0 Hz), 7.46 (1H, ddd, J = 1.4, 7.8, and 8.0 Hz), 7.68 (1H, ddd, J = 1.4, 7.8, and 8.0 Hz), 7.68 (1H, dd, J = 1.4 and 7.9 Hz), and 7.75 (2H, ddd, J = 2.7, 5.8, and 8.8 Hz); δ_C 37.20, 110.83, 116.95 (d, J = 20.2 Hz), 118.95, 125.80, 129.34, 130.36, 131.23, 132.34, 136.02, 142.31 (d, J = 9.0 Hz), 163.35 (d, J = 248.9 Hz), and 194.99; δ_F −113.11 (tt, J = 5.8, and 8.3 Hz); υ (film) 1668 cm^{-1}.

***Te*-4-Methoxyphenyl 2-(Allylthio)tellurobenzoate (18).** This compound was prepared according to the standard from 2-(allylthio)benzoyl chloride[62] and bis(4-methoxyphenyl)ditelluride.[59] It was obtained, after crystallization from ether/hexane, as yellow crystals (mp 60–63 °C) in 88% yield: δ_H 3.56 (2H, d, J = 6.7 Hz), 3.80 (3H, s), 5.12 (1H, dd, J = 10.2 and 1.2 Hz), 5.21 (1H, dd, J = 17.0 and 1.2 Hz), 5.87 (1H, ddt, J = 17.2, 10.2, and 6.7 Hz), 6.87 (2H, d, J = 8.7 Hz), 7.24 (1H, ddd, J = 7.7, 6.9, and 1.1 Hz), 7.33 (1H, dd, J = 6.8 and 1.1 Hz), 7.42 (1H, ddd, J = 6.9, 6.8, and 1.3 Hz), 7.68 (1H, dd, J = 7.7 and 1.3 Hz), and 7.69 (2H, d, J = 8.7 Hz); δ_C 36.84, 55.11, 105.98, 115.50, 118.77, 125.51, 128.29, 128.86, 130.39, 132.31, 132.43, 139.68, 141.89, 160.28, and 195.95; υ (melt) 1667 cm^{-1}; HRMS calcd for $C_{17}H_{16}O_2STe$ 413.9938, found 413.9937. Anal. Calcd for $C_{17}H_{16}O_2STe$: 49.56; H, 3.91. Found: C, 49.27; H, 3.91.

***Te*-4-Fluorophenyl 2-(Propargyloxy)tellurobenzoate (19).** 2-(Propargyloxy)benzoic acid[63] was converted to the corresponding acid chloride by reaction with oxalyl chloride and then to the telluride **19** in the usual manner. It was isolated in quantitative yield as a yellow crystalline solid: mp 63–65 °C (ether/hexane); δ_H 2.66 (1H, t, J = 2.4 Hz), 4.91 (2H, d, J = 2.4 Hz), 7.00–7.07 (3H, m), 7.13 (1H, d, J = 8.2 Hz), 7.52 (1H, ddd, J = 1.8, 7.3, and 8.2 Hz), 7.69 (1H, dd, J = 1.8 and 7.9 Hz), 7.75 (2H, ddt, J = 2.1, 5.9, and 8.7 Hz); δ_C 56.18, 77.07, 77.39, 112.85, 112.90, 116.67 (d, J = 20.9 Hz), 121.93, 127.41, 130.51, 134.42, 142.35 (d, J = 7.8 Hz), 157.43, 163.15 (d, J = 218.3 Hz), and 190.02; δ_F −116.62; υ (film) 1635 cm^{-1}; HRMS calcd for $C_{16}H_{11}FO_2Te$ 383.9810, found 383.9810.

***Te*-4-Fluorophenyl 2-[(3-Cyclopropylallyl)oxy]tellurobenzoate (20).** 2-[(3-Cyclopropylallyl)oxy]benzoic acid (40 mg, 0.18 mmol) was dissolved in benzene (5 mL) and treated with oxalyl chloride (0.02 mL, 0.54 mmol) and DMF (1 small drop). After 1 h of stirring at room temperature the solvent was removed under vacuum and the acid chloride purified by bulb to bulb distillation, yielding 31 mg of a colorless oil. This oil in THF (5 mL) was added to a THF solution of sodium 4-fluorophenyl telluride preformed by treatment of bis(4-fluorophenyl) ditelluride (25.5 mg, 0.06 mmol) and $NaBH_4$ (10.3 mg) in THF (5 mL) and MeOH (0.6 mL). After 15 min at room temperature water (5 mL) was added and the reaction mixture extracted with benzene (3 × 10 mL), dried ($MgSO_4$), concentrated, and chromatographed on silica gel (eluent hexane/ethyl acetate 9/1) to give the telluroester **20**, in the form of a 10:1 cis/trans mixture, as a yellow oil (34.5 mg, 63%): the cis-isomer, δ_H 0.51 (2H, m), 0.91 (2H, m), 1.71 (1H, m), 4.99 (2H, dd, J = 6.8 and 1.20 Hz), 5.17 (1H, t, J = 10.5 Hz), 5.82 (1H, m), 7.07 (4H, m), 7.53 (1H, t, J = 7.23 Hz), 7.70 (1H, d, J = 8.0 Hz), and 7.78 (2H, m); δ_C 7.43, 10.35, 65.43, 113.17, 116.48, 116.76, 121.04, 121.19, 127.29, 134.49, 140.46, 142.27, 142.37, 158.97, 163.20 (d, J = 246.0 Hz) and 190.28; υ (film) 1648 cm^{-1}; the minor trans isomer was characterized by δ_H 4.73 (2H, d, J = 5.7 Hz), 5.50 (1H, dd, J = 13.8 and 9.0 Hz), and 6.00 (1H, m). Anal. Calcd for $C_{19}H_{17}FO_2Te$: C, 53.83; H, 4.04. Found: C, 53.55; H, 4.02.

***Te*-4-Fluorophenyl 2-Allyltellurobenzoate (33).** 2-Allylbenzoyl chloride[64] (0.18 g, 1 mmol) in THF (5 mL) was added at 0 °C to a solution of sodium 4-fluorophenyl telluride prepared in the usual way from bis(4-fluorophenyl) ditelluride (190 mg, 0.43 mmol) and $NaBH_4$ (71 mg) in THF (10 mL) and methanol (1.0 mL). After 15 min of stirring at room temperature water (15 mL) was added and the reaction mixture extracted with benzene (3 × 15 mL), dried ($MgSO_4$), concentrated, and purified by chromatography on silica gel (eluent hexane/ethyl acetate 9/1) to give the acyl telluride **33** as a yellow oil (210 mg, 57%): δ_H 3.59 (2H, d, J = 6.5 Hz), 5.05 (2H, m), 5.96 (1H, m), 7.08 (2H, m), 7.29

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(1H, d, J = 7.5 Hz), 7.38 (1H, t, J = 7.5 Hz), 7.48 (1H, t, J = 7.5 Hz), 7.70 (1H, d, J = 7.7 Hz), and 7.77 (2H, m); δ_C 37.43, 109.63 (d, J = 3.6 Hz), 116.27, 117.11 (d, J = 20.55 Hz), 126.81, 128.97, 131.18, 132.37, 138.28, 138.41, 142.22, 142.23 (d, J = 7.8 Hz), 163.41 (d, J = 248.02), and 198.66; ν (film) 1689 cm^{-1}. Anal. Calcd for $C_{16}H_{13}FOTe$: C, 52.23; H, 3.56. Found: C, 51.90; H, 3.54.

***Te*-4-Fluorophenyl 2-(3-Butenyloxy)tellurobenzoate (36).** 2-(3-Butenyloxy)benzoic acid (0.458 g, 2.38 mmol) was mixed with thionyl chloride (10 mL) and heated to reflux for 3 h before the excess thionyl chloride was removed under vacuum. Dry benzene was twice added and removed under vacuum before the resulting acid chloride was subjected to the standard procedure for the formation of acyl tellurides. The acyl telluride **36** was isolated, after extraction, by filtration on silica gel (eluent hexane/ether 9:1) in 70% yield. It was a yellow crystalline solid: mp 58–59 °C (hexane); δ_H 2.67 (2H, m), 4.31 (2H, t, J = 7.0 Hz), 5.21 (1H, dd, J = 2.7 and 10.2 Hz), 5.28 (1H, dd, J = 3.1 and 17.9 Hz), 6.02 (1H, m), 7.07 (4H, m), 7.53 (1H, m), 7.70 (1H, m), and 7.77 (2H, m); δ_C 33.63, 68.90, 112.71, 113.10, 116.64 (d, J = 20.5 Hz), 118.10, 121.05, 127.42, 130.04, 133.52, 134.56, 142.30 (d, J = 7.8 Hz), 158.93, 163.20 (d, J = 248.4 Hz), and 189.98; ν 1643, 1594 cm^{-1}. Anal. Calcd for $C_{17}H_{15}FO_2Te$: C, 51.32; H, 3.80. Found: C, 51.29; H, 3.79.

***Te*-4-Fluorophenyl 2′-[1,1-(Ethylenedioxy)-2-propen-1-yl]biphenyl-2-tellurocarboxylate (40).** The acid **39** (0.1552 g, 0.524 mmol) and triethylamine (95 μL, 0.681 mmol) were stirred in THF (5 mL) at 0 °C and treated with isobutyl chloroformate (82 μL, 0.63 mmol), resulting in the immediate formation of a white precipitate. After 1 h of further stirring at 0 °C a solution of sodium 4-fluorophenyl telluride, prepared in the standard manner from the ditelluride (0.140 g, 0.314 mmol) and $NaBH_4$ (47.5 mg, 1.26 mmol) in THF (4 mL) and MeOH (0.3 mL), was added via a cannula and stirring maintained for 45 min before addition of degassed water (5 mL). The reaction mixture was then extracted with benzene (3 × 10 mL), and the combined organic phases were dried ($MgSO_4$) and concentrated to dryness to give the telluroester **40** as a yellow oil (0.216 g, 99%). No further purification of this oil was attempted: δ_H 3.66–3.86 (4H, m), 5.06 (1H, dd, J = 1.5 and 10.9 Hz), 5.07 (1H, dd, J = 1.5 and 16.9 Hz), 5.82 (1H, virtual multiplet), 6.96 (2H, t, J = 8.9 Hz), 7.20 (2H, m), 7.33–7.50 (4H, m), 7.59 (2H, m), and 7.70 (2H, td, J = 1.9 and 7.1 Hz); δ_C 64.29, 65.14, 108.29, 110.47 (d, J = 3.4 Hz), 115.99, 116.79 (d, J = 21.2 Hz), 127.13, 127.31, 127.95, 128.01, 130.63, 131.30, 131.41, 132.00, 132.24, 137.88, 138.04, 139.10, 140.07, 142.00, 142.10, 163.17 (d, J = 248.8 Hz), and 195.52; ν 2892, 1687, and 1579 cm^{-1}.

***Te*-4-Fluorophenyl 2-But-3-enyl-1-cyclohexene-1-tellurocarboxylate (46).** 2-But-3-enylcyclohexenecarboxylic acid (**45**) (0.302 g, 1.68 mmol) was dissolved in 95% EtOH (4 mL) and stirred with anhydrous $NaHCO_3$ (0.141 g, 1.68 mmol) for 1 h at room temperature before the EtOH was removed under reduced pressure and the solid residue dried overnight on the oil pump at 60 °C. This salt was suspended in benzene at room temperature and treated with pyridine (1 drop) and then oxalyl chloride (0.44 mL, 5.0 mmol). After 2 h of stirring the precipitated NaCl was removed by filtration on a sinter and the volatiles were removed under vacuum. Benzene (5 mL) was added and removed under vacuum. The so-obtained acid chloride was then subjected immediately to the standard protocol for formation of telluroesters resulting in the isolation, after chromatography on silica gel (eluent first hexane then hexane/benzene 4:1), of the telluroester **46** as a light yellow oil (0.420 g, 65%): δ_H 1.52–1.72 (4H, m), 2.02–2.19 (4H, m), 2.21–2.56 (4H, m), 4.98 (2H, m), 5.79 (1H, m), 7.04 (2H, m), and 7.67 (2H, m); δ_C 21.71, 22.22, 26.28, 31.31, 32.51, 34.63, 108.92, 114.84, 116.88 (d, J = 21.1 Hz), 136.07, 138.02, 142.44 (d, J = 7.8 Hz), 144.73, 163.25 (d, J = 248 Hz), and 198.45; ν 1685 and 1581 cm^{-1}. Anal. Calcd for $C_{17}H_{19}OFTe$: C, 52.91; H, 4.96. Found: C, 52.14; H, 4.84.

***Te*-4-Fluorophenyl 3,3-(Ethylenedioxy)telluro-6-heptenoate (49).** 3,3-(Ethylidenedioxy)-6-heptenoic acid[16b] (186 mg, 1.0 mmol) was dissolved in benzene (10 mL) and treated with oxalyl chloride (0.24 mL) followed by DMF (1 drop). After 1 h of stirring at room temperature the solvent was removed under vacuum to give a yellow oil which was taken up in THF (3 mL) and added at 0 °C to a solution of sodium 4-fluorophenyl telluride prepared from the ditelluride (250 mg, 0.56 mmol) and $NaBH_4$ (120 mg, 3.1 mmol) in THF (10 mL) and MeOH (1.0 mL) as described in the general protocol. After 10 min of stirring at 0 °C water (8 mL) was added and the reaction mixture extracted with CH_2Cl_2 (2 × 40 mL). After the mixture was dried (Na_2SO_4) and concentrated, purification by chromatography on silica gel eluting with ethyl acetate/petroleum ether 1:9 gave the telluroester **49** as an oil (330 mg, 100%): δ_H 1.82 (2H, m), 2.23 (2H, m), 3.00 (2H, s), 4.00 (4H, m), 4.95 (1H, d, J = 10.2 Hz), 5.01 (1H, d, J = 17.2 Hz), 5.79 (1H, ddt, J = 6.4, 10.2, and 17.2 Hz), 6.99 (2H, t, J = 7.2 Hz), 7.66 (2H, dd, J = 5.9 and 8.7 Hz); δ_C 27.59, 30.28, 36.96, 60.21, 65.15, 108.49, 109.78, 114.75, 116.87 (d, J = 21.7 Hz), 137.67, 142.05 (d, J = 7.8 Hz), 163.21 (d, J = 250.7 Hz), and 198.64; δ_F −113.13 (tt, J = 5.9, and 8.7 Hz); ν (film) 1699 and 1641 cm^{-1}.

1-(Benzoyloxy)-2,2,6,6-tetramethylpiperidine (6). Typical Procedure for Photolysis in the Presence of TEMPO. Photolysis of **1** (34 mg, 0.1 mmol) and TEMPO (16 mg, 0.1 mmol) in benzene (5 mL), under argon in a cold water bath (8 °C) with a 250 W GE sunlamp from a distance of 15 cm, gave, after 2.5 h and subsequent chromatography on silica gel (eluent hexane/ethyl acetate 9:1), the *O*-acylhydroxylamine **6** in 86% yield as a white crystalline solid: mp 87–88 °C; δ_H 1.12 (6H, s), 1.28 (6H, s), 1.35–1.38 (6H, m), 7.46 (2H, t, J = 7.4 Hz), 7.58 (1H, tt, J = 7.4 and 2.0 Hz), and 8.08 (2H, dd, J = 7.4 and 2.0 Hz); δ_C 17.07, 20.19, 32.04, 39.11, 60.48, 128.52, 129.64, 129.79, 132.90, and 166.45; ν 1744 cm^{-1}. Anal. Calcd for $C_{16}H_{23}NO_2$: C, 73.53; H, 8.87. Found: C, 73.68; H, 8.84.

1-[[(2-(Allyloxy)benzoyl]oxy]-2,2,6,6-tetramethylpiperidine (54). Photolysis of **13** in the presence of TEMPO according to the general protocol gave 87% of **54** as a white crystalline solid: 64–65 °C; δ_H 1.18 (6H, s), 1.21 (6H, s), 1.40–1.75 (6H, m), 4.63 (2H, ddd, J = 5.2, 1.5, and 1.5 Hz), 5.26 (1H, ddt, J = 10.4, 1.5, and 1.5 Hz), 5.45 (1H, ddt, J = 17.1, 1.5, and 1.5 Hz), 6.05 (1H, ddt, J = 17.1, 10.4, and 1.5 Hz), 6.95 (1H, d, J = 8.0 Hz), 6.99 (1H, ddd, J = 7.6, 7.6, and 0.9), 7.42 (1H, ddd, J = 8.0, 7.6, and 1.8 Hz), and 7.71 (1H, dd, J = 7.6 and 1.8 Hz); δ_C 17.04, 20.84, 31.96, 39.12, 60.28, 69.37, 113.07, 117.64, 120.36, 121.16, 131.04, 132.81, 157.29, and 167.29; ν 1757 cm^{-1}. Anal. Calcd for $C_{19}H_{27}NO_3$: C, 71.89; H, 8.57. Found: C, 71.80; H, 8.66.

***Se*-Phenyl Selenobenzoate (7). Typical Procedure for Photolysis in the Presence of Diphenyl Diselenide.** A solution of telluroester **1** (64 mg, 0.2 mmol) and diphenyl diselenide (63 mg, 0.2 mmol) in benzene (5mL) under nitrogen in a circulating cold water bath (8 °C) was irradiated with a 250 W GE sunlamp from a distance of ca. 15 cm until TLC monitoring indicated loss of **1**. The solvent was removed and the residue chromatographed on silica gel (eluant hexane/ethyl acetate 9:1) to give the selenoester (52 mg, 93%) whose spectral characteristics were identical to those recorded in the literature.[62]

***Se*-Phenyl 2-(Allyloxy)selenobenzoate (55).** Photolysis of **13** in the presence of diphenyl diselenide according to the standard protocol gave 78% of **55** which was identical with an authentic sample.[16d]

***S*-Phenyl Thiobenzoate (8).** Photolysis of **1** in the presence of 6 equiv of diphenyl disulfide according to the standard for the formation of selenoesters gave 71% of **7** after chromatography on silica gel (eluent hexane/ethyl acetate 9:1). The product had a melting point and spectral characteristics in accordance with those described in the literature.[65]

***Se*-Phenyl 2-(Propargyloxyl)selenobenzoate (56).** A solution of the telluroester **12** (15 mg, 39 μmmol) and diphenyl diselenide (15 mg, 48 μmol) in $CDCl_3$ (0.5 mL) was photolyzed according to the standard protocol for 2 h at 8 °C. Preparative TLC on silica gel of the reaction mixture, eluting with ethyl acetate/hexanes 1:4, gave the selenoester **56** as an oil (9.5 mg, 73%): δ_H 2.54 (1H, t, J = 2.4 Hz), 4.85 (2H, d, J = 2.4 Hz), 7.02 (1H, dd, J = 7.2 and 7.9 Hz), 7.11 (1H, d, J = 8.4 Hz), 7.35 (3H, m), 7.47 (1H, ddd, J = 1.7, 7.2, and 8.4 Hz), 7.53 (2H, m), 7.76 (1H, dd, J = 1.7 and 7.9 Hz); δ_C 56.47, 76.62, 77.60, 113.68, 121.79, 127.78, 128.88, 129.19, 134.25, 136.35, 148.18, 156.65, and 190.72; ν (film) 3288, 2122, and 1658 cm^{-1}. HRMS calcd for $C_{16}H_{12}O_2Se$ 316.0002, found 315.9998.

Photolysis of 4 in the Presence of Thiophenol. Isolation of Benzaldehyde. A solution of the telluroester **4** (15 mg, 41.7 μmol) and thiphenol (17 mg, 154 μmol) in $CDCl_3$ (0.6 mL) was photolyzed with the 250 W white light source at 8 °C for 2 h. Preparative TLC on silica gel of the reaction mixture, eluting with ethyl acetate/hexanes 1:9, gave benzaldehyde (3.5 mg, 80%).

Photolysis of 12 in the Presence of Thiophenol. Formation of 2-(Allyloxy)benzaldehyde (50), 3-Methylchroman-4-one (52), and the Telluride 21. A solution of the telluroester **12** (12 mg, 31 μmol) and thiophenol (5 mg, 45 μmol) were photolyzed in $CDCl_3$ (0.5 mL) at 8 °C for 0.5 h. Examination of the reaction mixture by ^{1}H NMR revealed complete consumption of the starting material. 2-(Allyloxy)benzaldehyde (**50**) [δ_H 4.64 (2H, d), 5.36 (1H, d), 5.46 (1H, d), 6.10 (1H, m), 7.0–7.8 (4H, m), and 10.76 (1H, s)],[66] 3-methylchroman-4-one (**52**) [δ_H 1.23 (3H, d), 2.87 (1H, m), 4.16 (1H, dd), 4.50 (1H, dd), and 7.0–7.8 (4H,

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m)],[67] and the telluride **21** (data below) were identified in the ratio 17:24:59 on the basis of their respective spectral data.

Photolysis of 15 in the Presence of Thiophenol. Formation of 2-(2-Butenyloxy)benzaldehyde (51), 3-Ethylchroman-4-one (53), and the Telluride 25. A solution of the telluroester **15** (12 mg, 30 μmol) and thiophenol (9 mg, 82 μmol) were photolyzed in $CDCl_3$ (0.5 mL) at 8 °C for 0.5 h. Examination of the reaction mixture by ^1H NMR revealed complete consumption of the starting material. 2-(2-Butenyloxy)-benzaldehyde (**51**) [δ_H 1.78 (3H, d), 4.60 (2H, d), 5.75 (1H, m), 5.91 (1H, m), 6.90–7.95 (4H, m), and 10.52 (1H, s)],[66] 3-ethylchroman-4-one (**53**) [δ_H 1.04 (3H, t, J = 7.5 Hz), 1.59 (1H, ddq, J = 7.5, 7.5, and 15.0), 1.93 (1H, ddq, J = 7.5, 7.5, and 15.0 Hz), 2.58 (1H, dddd, J = 7.5, 7.5, 4.4, and 8.5 Hz), 4.30 (1H, dd, J = 8.5 and 11.4 Hz), 4.53 (1H, dd, J = 4.4 and 11.4 Hz), 6.96 (1H, d, J = 8.4 Hz), 7.01 (1H, dd, J = 7.1 and 7.7 Hz), 7.46 (1H, dd, J = 7.1 and 8.4 Hz), 7.89 (1H, d, J = 7.7 Hz)],[18e] and the telluride **25** (data below) were identified in the ratio 8:73:19 on the basis of their respective spectral data.

Photolysis of 3 and Di-1-naphthyl Ditelluride. The telluroester **3** (9 mg, 25 μmmol) and di-1-naphthyl ditelluride (13 mg, 25 μmmol) in $CDCl_3$ (0.5 mL) were photolyzed with a 250 W white light source for 1.3 h, after which a combination of ^1H and ^{19}F NMR spectroscopy revealed the presence of an almost 1:1 mixture of the ditellurides **3** and **5**.

Irradiation of 1 and of $^{13}C\alpha$-1 in the Presence of *tert*-Butyl-α-phenylnitrone. Observation of 11 by ESR Spectroscopy. The acyl telluride **1** (30 mg, 0.10 mmol) and *N*-*tert*-butyl-α-phenylnitrone (30 mg, 0.17 mmol) were dissolved in C_6D_6 (1.5 mL) and sealed under Ar in a standard 5 mm NMR tube. The tube was photolyzed, in a cold water bath (8 °C), for 2 h with a 250 W sun lamp and then transferred to the microwave cavity of the ESR spectrometer when the spectrum illustrated in Figure 1 was recorded. A parallel experiment was conducted with a sample of **1** prepared from mono-^{13}C-labeled benzoic acid leading to the spectrum of Figure 2.

Crossover of Acyl Tellurides 3 and 4. The telluroesters **3** (8 mg, 30 μmmol) and **4** (9 mg, 25 μmol) were photolyzed at 8 °C in $CDCl_3$ with a 250 W white light source. After 1 h examination by ^1H and ^{19}F NMR revealed an essentially 1:1:1:1 mixture of the acyl tellurides **1**, **3**, **4**, and **5**. The formation of the various diaryl ditellurides was not observed in any more than trace quantities.

Typical Procedure for Rearrangement with Aryl Tellurium Group Transfer: Formation of 3-[(Aryltelluro)methyl]chromanones. In a 5mL flask fitted with a reflux condenser the telluroester (0.1 mmol) was photolyzed under argon in benzene (3 mL) with 250 W GE sunlamp from a distance of 15 cm. Either no cooling bath was used and the heat from the lamp caused the solution to reflux or the reaction was maintained at 8 °C by means of a circulating cold water bath (See Table 2). After completion (TLC control) the solvent was removed in vacuo and the residue analyzed by ^1H NMR spectroscopy. In every case the product mixture was composed of the expected 2-[(aryltelluro)methyl]chromanone as the very major product together with the corresponding elimination product and the diaryl ditelluride. Spectral analysis was facilitated by the possesion of authentic samples of the ditellurides and, eventually, of the elimination products. The product ratios, and hence yields, were determined by integration of the ^1H NMR spectra. Attempted purification by chromatography on silica gel led only to less pure samples contaminated with increased amounts of ditelluride and elimination products, consequently the spectral characteristics given below were taken from the crude reaction mixtures.

3-[[(4-Fluorophenyl)telluro]methyl]chromanone (21): Yield 96%; δ_H 2.77 (1H, dd, J = 12.2 and 8 Hz), 3.09 (1H, dddd, J = 10.0, 8.0, 5.9, and 4.0 Hz), 3.27 (1H, dd, J = 12.2 and 5.9 Hz), 4.37 (1H, dd, J = 11.3 and 10.1 Hz), 4.56 (1H, dd, J = 11.3 and 4.8 Hz), 6.93 (2H, dddd, J = 8.8, 8.7, 2.8, and 2.1 Hz), 6.95 (1H, dd, J = 8.6 and 1.0 Hz), 7.02 (1H, ddd, J = 7.5, 7.4, and 1.0), 7.48 (1H, ddd, J = 8.6, 7.4, and 1.7 Hz), 7.75 (2H, ddd, J = 8.7, 5.8, and 2.7 Hz), and 7.88 (1H, dd, J = 7.5 and 1.7 Hz); δ_C 2.99, 47.37, 71.53, 106.45, 116.74 (d, J = 20.5 Hz), 117.75, 121.58, 127.44, 128.29, 136.10, 140.98 (d, J = 8.6 Hz), 161.54, 162.98 (d, J = 248.8 Hz), and 193.35; δ_F –114.13 (tt, J = 8.7 and 5.8 Hz); ν 1686 cm^{-1}.

3-[[(4-Methoxyphenyl)telluro]methyl]chromanone (22): Yield 80%; δ_H 2.73 (1H, dd, J = 12.3 and 8.6 Hz), 3.02 (1H, dddd, J = 10.2, 8.6, 5.4, and 4.6 Hz), 3.24 (1H, dd, J = 12.3 and 5.4 Hz), 3.79 (3H, s), 4.37 (1H, dd, J = 11.1 and 10.2 Hz), 4.55 (1H, dd, J = 11.1 and 4.6 Hz), 6.76 (2H, d, J = 8.4 Hz), 6.93 (1H, d, J = 7.4 Hz), 7.00 (1H, dd, J = 8.0 and 7.00 Hz), 7.46 (1H, ddd, J = 7.4, 7.0, and 1.0 Hz), 7.68 (2H, d, J = 8.4 Hz), and 7.86 (1H, dd, J = 8.0 and 1.0 Hz); δ_C 2.87, 47.34, 71.59, 101.40, 115.38, 117.78, 121.94, 127.45, 128.32, 136.02, 140.31, 159.95, 160.28, and 193.50; ν (film) 1686 cm^{-1}.

3-[[(2,4-Dimethoxyphenyl)telluro]methyl]chromanone (23): Yield 86%; δ_H 2.70 (1H, dd, J = 12.4 and 9.3 Hz), 3.01 (1H, dddd, J = 9.5, 9.3, 5.1, and 4.7 Hz), 3.28 (1H, dd, J = 12.4 and 5.1 Hz), 3.80 (3H, s), 3.84 (3H, s), 4.40 (1H, dd, J = 11.4 and 9.5 Hz), 4.57 (1H, dd, J = 11.4 and 4.7 Hz), 6.43 (1H, s), 6.44 (1H, d, J = 9.0 Hz), 6.95 (1H, dd, J = 8.4 and 1.0 Hz), 7.01 (1H, ddd, J = 7.9, 7.5, and 1.0 Hz), 7.46 (1H, ddd, J = 8.4, 7.5, and 1.7 Hz), 7.53 (1H, d, J = 9.0 Hz), and 7.88 (1H, dd, J = 7.9 and 1.7 Hz); δ_C 0.39, 47.48, 55.42, 55.93, 71.62, 92.50, 98.34, 106.31, 117.75, 121.91, 127.45, 128.10, 135.96, 136.89, 158.10, 161.18, 161.60, and 193.68; ν (film) 1686 cm^{-1}.

3-[1-[(4-Fluorophenyl)telluro]ethyl]chromanone (25): Yield 93%; δ_H 1.65 (0.3 × 3H, d, J = 7.4 Hz, isomer 1), 1.71 (0.7 × 3H, d, J = 7.4 Hz, isomer 2), 2.96 (0.3 × 1H, ddd, J = 4.5, 5.3, and 11.1 Hz, isomer 1), 3.04 (0.7 × 1H, J = 6.3, 4.7, and 8.8 Hz, isomer 2), 3.62 (0.7 × 1H, dq, J = 6.3 and 7.4 Hz, isomer 2), 3.83 (0.3 × 1H, dq, J = 4.5 and 7.4 Hz, isomer 1), 4.53 (0.3 × 1H, dd, J = 11.1 and 11.3 Hz, isomer 1), 4.54 (0.7 × 1H, dd, J = 4.7 and 11.4 Hz, isomer 2), 4.63 (0.7 × 1H, dd, J = 8.8 and 11.4 Hz, isomer 2), 4.67 (0.3 × 1H, dd, J = 5.3 and 13.3 Hz, isomer 1), 6.90–7.10 (4H, m), 7.50 (1H, m), and 7.75–7.90 (3H, m); δ_C 17.5 + 17.65, 21.81 + 22.40, 52.36 + 53.11, 69.88 + 71.20, 113.19, 116.64 (d, J = 19.7 Hz), 117.76, 121.67, 126.40, 127.54, 136.11, 142.76 (d, J = 8.8 Hz), 161.70, 163.08 (d, J = 256.5 Hz), and 192.60; δ_F –117.04 (0.3F, isomer 1), –117.13 (0.7F, isomer 2); ν 1683 cm^{-1}.

3-[[(4-Fluorophenyl)telluro]methyl]-3-methylchromanone (27): Yield 100%; mp 88–89 °C; δ_H 1.25 (3H, s), 3.04 (1H, d, J = 12.2 Hz), 3.08 (1H, d, J = 12.2 Hz), 4.12 (1H, d, J = 11.5 Hz), 4.41 (1H, d, J = 11.5 Hz), 6.88 (2H, ddd, J = 2.0, 8.8, and 8.8 Hz), 6.95 (1H, m), 7.01 (1H, ddd, J = 1.0, 7.3, and 7.7 Hz), 7.46 (1H, ddd, J = 1.7, 7.3, and 8.5 Hz), 7.72 (2H, ddd, J = 2.0, 5.6, and 8.8 Hz), 7.86 (1H, dd, J = 1.7 and 7.7 Hz); δ_C 15.25, 19.95, 45.49, 75.48, 106.42, 116.61 (d, J = 22.3 Hz), 117.63, 121.67, 127.80, 129.87, 135.93, 141.06 (d, J = 5.9 Hz), 160.89, 162.93 (d, J = 246.08 Hz), and 195.37; δ_F –117.64; ν (film) 1682 and 1606 cm^{-1}; HRMS calcd for $C_{17}H_{15}FO_2Te$ 400.0123, found 400.0116.

3-[[(4-Fluorophenyl)telluro]methyl]thiochromanone (28): Yield 69%; δ_H 2.97 (1H, dd, J = 7.0 and 11.6 Hz), 3.19 (1H, dddd, J = 3.5, 5.8, 7.0, and 10.2 Hz), 3.21 (1H, dd, J = 3.5 and 13.4 Hz), 3.27 (1H, dd, J = 5.8 and 11.6 Hz), 3.36 (1H, dd, J = 10.2 and 13.4 Hz), 6.93 (2H, ddd, J = 2.8, 8.7, and 8.8 Hz), 7.16 (1H, dd, J = 7.6 and 8.2 Hz), 7.25 (1H, d, J = 6.9 Hz), 7.37 (1H, ddd, J = 1.6, 6.8, and 8.2 Hz), 7.75 (2H, ddd, J = 2.8, 5.8, and 8.7 Hz), and 8.07 (1H, dd, J = 1.4 and 7.6 Hz); δ_C 7.79, 32.65, 48.88, 107.20, 116.99 (d, J = 20.0 Hz), 125.06, 127.36, 129.79, 130.39, 133.44, 141.05 (d, J = 7.5 Hz), 141.74, 163.43 (d, J = 248.7 Hz), and 195.36; δ_F –114.42 (tt, J = 5.8, 8.7 Hz).

3-[[(4-Methoxyphenyl)telluro]methyl]thiochromanone (29): Yield 90%; δ_H 2.96 (1H, dd, J = 7.8 and 11.8 Hz), 3.13 (1H, dddd, J = 3.7, 6.0, 7.8, and 10.2 Hz), 3.25 (1H, dd, J = 3.7 and 13.2 Hz), 3.27 (1H, dd, J = 6.0 and 11.8 Hz), 3.38 (1H, dd, J = 10.2 and 13.2 Hz), 3.80 (3H, s), 6.77 (2H, d, J = 8.6 Hz), 7.16 (1H, dd, J = 7.6 and 8.2 Hz), 7.25 (1H, d, J = 6.9 Hz), 7.37 (1H, ddd, J = 1.6, 6.8, and 8.2 Hz), 7.72 (2H, d, J = 8.6 Hz), and 8.07 (1H, dd, J = 1.4 and 7.6 Hz); δ_C 7.52, 32.59, 48.68, 55.18, 101.67, 115.33, 124.97, 127.33, 129.76, 130.30, 133.32, 141.17, 141.77, 159.92, and 195.38; ν (film) 1670 cm^{-1}.

3-[[(4-Fluorophenyl)telluro]methylene]chromanone (31): Yield 100%; photolysis of the telluro ester **19** (140 mg) in benzene (3 mL) in the usual way for 4 h at 8 °C followed by evaporation to dryness gave a yellow gum which consisted of a 62:38 mixture of *E*/*Z* isomers of **31** in quantitative yield; recrystallization from diethyl ether/hexanes gave the pure major isomer as a yellow crystalline solid; mp 92–94 °C; δ_H 5.05 (2H, d, J = 1.3 Hz), 6.96 (1H, d, J = 8.7 Hz), 7.00 (2H, tt, J = 2.0 and 8.7 Hz), 7.08 (1H, dd, J = 6.9 and 7.9 Hz), 7.50 (1H, ddd, J = 1.7, 6.9, and 8.7 Hz), 7.80 (2H, ddt, J = 2.0, 5.8, and 8.5 Hz), 7.99 (1H, dd, J = 1.7 and 7.9 Hz), and 8.53 (1H, t, J = 1.3 Hz); δ_C 72.10, 112.50, 116.73 (d, J = 20.3 Hz), 116.82, 118.08, 122.20, 127.69, 132.13, 135.84, 136.97, 140.06 (d, J = 9.1 Hz), 161.15, 163.24 (d, J = 222.0 Hz), and 185.78; δ_F –117.19; ν (film) 1631 cm^{-1}; HRMS calcd for $C_{16}H_{11}FO_2Te$ 383.9810, found 383.9810. The minor isomer was characterized by δ_H 4.90 (2H, d, J = 1.4 Hz), 6.96–7.08 (4H, m), 7.48 (1H, ddd, J = 1.7, 7.3, and 8.5 Hz), 7.75–7.80 (2H, m), 7.98 (1H, dd, J = 1.7 and 7.8 Hz), and 8.70 (1H, t, J = 1.9 Hz); δ_F –115.65; ν 1659 cm^{-1}.

3-[4-[(4-Fluorophenyl)telluro]-1-butenyl]chromanone (32). Photolysis of telluroester **20** (20 mg, 0.047 mmol) in C_6D_6 (1 mL) according to the standard protocol for 2 h at 8 °C resulted in complete transformation to the chromanone **32** which was formed as a 4:1 trans/cis mixture.

(67) Barloco, D.; Cignarella, G. *Synthesis* **1985**, 876.

Attempted isolation of this material resulted in decomposition: the major trans isomer, δ_H 2.18 (2H, dt, J = 7.2 and 7.2 Hz), 2.40 (2H, t, J = 7.2 Hz), 2.88 (1H, m), 3.80 (1H, dd, J = 8.3 and 11.3 Hz), 3.92 (1H, dd, J = 11.3 and 4.8 Hz), 5.34 (2H, m), 6.58 (2H, m), 6.64 (1H, m), 6.82 (1H, d, J = 8.4 Hz), 6.98 (1H, m), 7.38 (2H, m), and 8.12 (1H, d, J = 7.9 Hz); the minor cis isomer δ_H 2.28 (2H, m), 2.58 (2H, m), 3.20 (1H, m), 3.70 (1H, dd, J = 9.4 and 11.2 Hz), 3.90 (1H, dd, J = 4.4 and 11.4 Hz), 5.34 (2H, m), 6.58 (2H, m), 6.64 (1H, m), 6.82 (1H, d, J = 8.4 Hz), 6.98 (1H, m), 7.38 (2H, m), and 8.05 (1H, d, J = 7.9 Hz).

2-[[(4-Fluorophenyl)telluro]methyl]-2,3-dihydroindan-1-one (34): Yield 100%; δ_H (C_6D_6) 2.37 (1H, dd, J = 4.2 and 18 Hz), 2.60 (2H, m), 2.78 (1H, dd, J = 7.7 and 18 Hz), 3.20 (1H, dd, J = 4.0 and 10.0 Hz), 6.58 (2H, t, J = 8.0 Hz), 6.95 (2H, m), 7.15 (1H, t, J = 7.0 Hz), 7.42 (2H, t, J = 7.7 Hz), and 7.67 (1H, d, J = 7.7 Hz); δ_C (C_6D_6) 9.35, 34.97, 48.43, 116.74 (d, J = 15.7 Hz), 124.20, 126.54, 127.58, 134.62, 138.91, 141.10 (d, J = 7.8 Hz), 152.68, 163.07 (d, J = 231 Hz), and 205.64; ν (film) 1713 cm^{-1}.

2-[[(4-Fluorophenyl)telluro]methyl)]-1,2,3,4,5,6,7,8-octahydronaphthalen-1-one (47). Photolysis of the telluroester **46** (0.134 g, 0.35 mmol) in benzene (10 mL) for 30 min resulted in quantitative conversion to the octahydronaphthalenone **47**: δ_H 1.40–2.00 (6H, m), 2.00–2.50 (6H, m), 2.60–2.80 (2H, m), 3.23 (1H, m), 6.88 (2H, m), and 7.72 (2H, m); δ_C (C_6D_6) 10.05, 22.15, 22.24, 22.61, 30.41, 30.80, 31.42, 48.67, 105.63, 116.48 (d, J = 20.45 Hz), 131.79, 140.63 (d, J = 7.2 Hz), 155.12, 163.05 (d, J = 247.6 Hz), and 198.86.

3-Methylenechroman-4-one (24) by Cyclization of 14 Followed by Oxidative Elimination. A solution of **14** (86 mg, 0.2 mmol) in benzene (5 mL) was rearranged photolytically to **23** as described in the general protocol. After completion (TLC control) the cooled solution was diluted with THF (10 mL) and 30% hydrogen peroxide (70 μL, 3.4 equiv) added dropwise. The resulting mixture was stirred at room temperature for 30 min, then diluted with water (10 mL), and treated with Na_2SO_3 (1 g). After a further 30 min the solution was extracted with CH_2Cl_2 (3 × 20 mL). The extracts were dried (Na_2SO_4), filtered, and evaporated to give a colorless oil which on chromatography on silica gel (eluent hexane/ethyl acetate 4:1) gave **24**[23b] as a colorless oil (28.5 mg, 89%): δ_H 5.01 (2H, dd, J = 1.5 and 1.3 Hz), 5.58 (1H, dt, J = 1.5 and 1.1 Hz), 6.32 (1H, dt, J = 1.3 and 1.1 Hz), 6.98 (1H, dd, J = 8.4 and 0.9 Hz), 7.06 (1H, ddd, J = 8.0, 7.8, and 0.9 Hz), 7.49 (1H, ddd, J = 8.4, 7.8, and 1.8 Hz), and 7.99 (1H, dd, J = 8.0 and 1.8 Hz); δ_C 71.17, 118.08, 121.91, 122.45, 127.93, 128.00, 136.02, 138.64, 161.90, and 182.03; ν (film) 1687 cm^{-1}; HRMS calcd for $C_{10}H_8O_2$ 160.0524, found 160.0520.

3-Ethylidenechroman-4-one (26) by Cyclization of 15 Followed by Oxidative Elimination. The telluroester **15** (100 mg, 0.25 mmol) in toluene (8 mL) was photolyzed with a white light source (250 W) without cooling for 0.5 h. After cooling to room temperature the reaction mixture was stirred with 30% hydrogen peroxide (0.2 mL) for 15 min, after which it was concentrated under vacuum and the residues taken up in hexane and dried ($MgSO_4$) and then filtered through silica gel (eluent ethyl acetate/hexane 1:9) to give the ethylidenechromanone **26** as a white solid (40 mg, 94%): mp 62–65 °C; δ_H 1.90 (3H, d, J = 7.2 Hz), 5.05 (2H, d, J = 1.2 Hz), 6.96 (1H, d, J = 8.3 Hz), 7.01 (1H, tq, J = 1.2 and 7.2 Hz), 7.04 (1H, ddd, J = 1.0, 7.4, and 7.6 Hz), 7.46 (1H, ddd, J = 1.8, 7.4, and 8.3 Hz), and 7.98 (1H, dd, J = 1.8 and 7.8 Hz); δ_C 13.78, 66.58, 117.90, 121.79, 126.40, 127.99, 134.94, 135.66, 135.90, 161.60, and 181.91; ν (film) 1683, 1633, and 1603 cm^{-1}. Anal. Calcd for $C_{11}H_{10}O_2$: C, 75.84; H, 5.79. Found: C, 75.72; H, 5.84.

3-Methylenethiochroman-4-one (30) by Cyclization of 18 Followed by Elimination on Silica Gel. The telluroester **18** (82 mg, 0.2 mmol) in benzene (5 mL) was photolyzed according to the standard protocol. After rearrangement was complete (TLC control), the solvent was evaporated and the residue chromatographed on silica gel (eluent hexane/ethyl acetate 9:1) to give **30** as a pale yellow oil (14 mg, 41%): δ_H 3.86 (2H, d, J = 0.8 Hz), 5.58 (1H, dd, J = 0.8 and 0.8 Hz), 6.23 (1H, d, J = 0.8 Hz), 7.23 (1H, ddd, J = 7.9, 7.7, and 1.5 Hz), 7.29 (1H, dd, J = 8.6 and 1.5 Hz), 7.39 (1H, ddd, J = 8.6, 7.9, and 1.4 Hz), and 8.16 (1H, dd, J = 7.7 and 1.4 Hz); δ_C 33.73, 123.35, 125.78, 126.76, 127.93, 130.30, 133.18, 133.42, 140.46, and 185.12; ν (film) 1693 cm^{-1}; HRMS calcd for $C_{10}H_8OS$ 176.0296, found 176.0297.

2-Methylene-2,3-dihydroindan-1-one (35). The indanone **34** (144 mg, 0.39 mmol) in THF (1 mL) was treated with 30% hydrogen peroxide (0.15 mL) for 30 min at room temperature. Dilution with water, ether extraction, and preparative TLC on silica gel eluting with ethyl acetate/hexane 1:2 gave 2-methylene-2,3-dihydroindanone (**35**)[68] as a pale yellow oil (49.6 mg, 88%): δ_H 3.75 (2H, s), 5.65 (1H, m), 6.37 (1H, m), 7.38 (1H, t, J = 7.7 Hz), 7.48 (1H, d, J = 5.0 Hz), 7.60 (1H, t, J = 5.0 Hz), and 7.85 (1H, d, J = 7.7 Hz); δ_C 31.77, 118.30, 124.61, 126.35, 127.58, 134.88, 138.21, 143.27, 149.88, and 183.46; ν (film) 1707 cm^{-1}; HRMS calcd for $C_{10}H_8O$ 144.0575; found 144.0580.

2-Methylene-2,3,4,5,6,7,8-octahydronaphthalene-1-one (48). The ketone **47** (0.134 g, 0.35 mmol) was dissolved in THF (3 mL) and treated with 30% H_2O_2 (2 mL). After stirring overnight at room temperature the reaction mixture was extracted with ether. The extracts were dried ($MgSO_4$), concentrated, and purified by filtration on silica gel (eluent hexane/ether 3:1) to give the enone **48** as a pale yellow oil (0.042 g, 74%): δ_H 1.58–1.68 (4H, m), 2.19–2.34 (6H, m), 2.64–2.70 (2H, m), 5.20 (1H, d, J = 3.4 Hz), and 5.93 (1H, d, J = 3.4 Hz); δ_C 21.98 (2C), 22.43, 30.71, 31.49, 31.96, 118.56, 133.08, 143.14, 157.23, and 188.40; ν 1660 and 1611 cm^{-1}; λ_{max} 198 and 260 nm; HRMS calcd for $C_{11}H_{14}O$ 162.1044, found 162.1045.

8,8-(Ethylenedioxy)-dibenzo[*a*,*c*]-6-cycloocten-5-one (43) and 7,7-(Ethylenedioxy)-6-methylenedibenzo[*a*,*c*]cycloheptan-5-one (44). The telluroester **40** (0.1873 g, 0.373 mmol) was dissolved in benzene (20 mL) and photolyzed in the usual manner at 8 °C for 5.5 h (shorter photolysis times resulted in incomplete conversion) and then concentrated to dryness. At this stage ^1H NMR spectroscopy revealed the complete absence of olefinic signals. The residue was taken up in THF (4 mL) and stirred with 30% H_2O_2 (0.5 mL) for 1 h at room temperature. After concentration under vacuum the residue was filtered on silica gel, eluting with hexane/ether 3:2, to give the crude product which consisted of a 3.7:1 mixture of the cyclooctenone **43** and the cycloheptanone **44** (65 mg, 63%). Careful preparative TLC of this mixture (eluent hexane/benzene/ether/Et_3N 70:20:10:1) enabled the isolation of pure samples of **43** and **44**. The faster eluting cycloheptanone (**44**) had mp 135–136 °C: δ_H 3.95 (4H, m), 6.01 (1H, d, J = 1.9 Hz), 6.38 (1H, d, J = 1.9 Hz), 7.36–7.51 (5H, m), 7.60 (1H, m), 7.65 (1H, m), and 7.76 (1H, m). This compound was unstable and decomposed on standing in $CDCl_3$ which prevented further characterization. The slower eluting cyclooctenone (**43**) had mp 159–161 °C: δ_H 3.38 (1H, m), 3.68–3.83 (2H, m), 4.00 (1H, m), 6.34 (1H, d, J = 13.0 Hz), 6.87 (1H, d, J = 13.0 Hz), 7.23 (1H, m), 7.35 (3H, m), 7.43 (3H, m), and 7.62 (1H, m); δ_C 63.32, 64.20, 106.97, 125.04, 127.46, 127.98, 128.35, 128.40, 129.97, 132.14, 133.63, 136.56, 138.71, 140.11, 140.25, 145.41, and 196.72; ν 1731 cm^{-1}. Anal. Calcd for $C_{18}H_{14}O_3$: C, 77.68; H, 5.07. Found: C, 77.77; H, 5.00.

Ethyl 2-Methylene-4-phenyl-4-oxobutanoate (58). A solution of telluroester **2** (15 mg, 0.044 mmol) and alkene **57**[50] (34 mg, 0.17 mmol) in $CDCl_3$ (0.6 mL) was photolyzed at 8 °C under nitrogen in a cold water bath with a 250 W tungsten lamp. The reaction was monitored periodically by ^1H NMR. After **2** had been totally consumed, evaporation of the solvent and preparative TLC on silica gel eluting with 1:9 ethyl acetate/hexanes gave **58** as a colorless oil (5 mg, 52%): δ_H 1.26 (3H, t, J = 7.2 Hz), 4.00 (2H, s), 4.21 (2H, q, J = 7.2 Hz), 5.90 (1H, s), 6.41 (1H, s), 7.47 (2H, dd, J = 7.8 and 7.3 Hz), 7.56 (1H, tt, J = 7.8 and 1.3 Hz), and 7.99 (2H, dd, J = 7.3 and 1.3 Hz); δ_C 14.11, 41.67, 61.04, 128.29, 128.38, 128.65, 133.24, 134.85, 136.53, 166.42, and 196.95; ν (film) 1720, 1689, and 1640 cm^{-1}; HRMS calcd for $C_{13}H_{14}O_3$ 218.0943, found 218.0942.

Reaction of 27 with Tributyltin Hydride and Methyl Acrylate. Isolation of 59 and 60. A freshly prepared solution of tributyltin hydride (130 mg, 0.45 mmol), AIBN (2 mg), and methyl acrylate (520 mg, 0.9 mmol) in benzene (2.0 mL) was added portionwise (0.4 mL/h) to a solution of **27** (60 mg, 0.15 mmol) and methyl acrylate (40 mg, 0.45 mmol) at reflux in benzene (5 mL) over a period of 4 h. After 2 h of further heating to reflux (total = 6 h) the solvent was removed under vacuum. Chromatography of the residue on silica gel, eluting with a gradient of ethyl acetate in hexane (1:9 to 1:4) gave **59** as a colorless oil (21 mg, 53%) and **60** also as a colorless oil (7 mg, 18%): the chromanone **59**, δ_H 1.17 (3H, s), 1.64 (4H, m), 2.29 (2H, t, J = 6.5 Hz), 3.63 (3H, s), 4.15 (1H, d, J = 8.6 Hz), 4.26 (1H, d, J = 8.6 Hz), 6.95 (1H, d, J = 8.3 Hz), 7.02 (1H, dd, J = 7.0 and 7.9 Hz), 7.46 (1H, ddd, J = 7.0, 8.4, and 1.4 Hz), and 7.89 (1H, dd, J = 1.4 and 7.9 Hz); δ_C 17.52, 19.29, 33.25, 34.25, 44.66, 51.55, 74.94, 117.60, 119.70, 121.52, 127.78, 135.63, 161.07, 173.58, and 196.67; ν (film) 1739 and 1690 cm^{-1}; HRMS calcd for $C_{15}H_{18}O$ 262.1205, found 262.1209; the ketone **60**, δ_H 1.08 (3H, s), 1.82 (1H, ddd, J = 7.3, 9.3, and 14.0 Hz), 1.95 (1H, ddd, J = 7.7, 8.9, and 14.0 Hz), 2.42 (2H, m), 2.57 (1H, d, J = 11.3 Hz), 2.85 (1H, d, J = 11.3

(68) (a) Tour, J. M.; Negishi, E. *J. Am. Chem. Soc.* **1985**, *107*, 8289. (b) Echavarren, A. M.; Stille, J. K. *J. Am. Chem. Soc.* **1988**, *110*, 1557.

Hz), 3.69 (3H, s), 3.78 (1H, d, J = 12.4 Hz), 4.04 (1H, d, J = 12.4 Hz), 7.03 (1H, dd, J = 1.5 and 8.5 Hz), 7.06 (1H, ddd, J = 1.9, 7.3, and 8.0 Hz), 7.39 (1H, ddd, J = 1.9, 7.3, and 8.5 Hz), and 7.73 (1H, dd, J = 1.9 and 8.0 Hz); δ_C 22.14, 29.0, 34.12, 41.08, 51.82, 52.54, 83.12, 119.88, 122.35, 127.94, 129.23, 133.50, 163.91, 173.76, and 198.71; υ (film) 1734 and 1684 cm^{-1}; HRMS calcd for $C_{15}H_{18}O$ 262.1205, found 262.1207.

3-[(Phenylseleno)methylene]-4-chromanone (61). The vinyl telluride **31** (35 mg, 0.092 mmol, cis/trans 1:5) and diphenyl diselenide (0.28 g, 0.90 mmol) in $CDCl_3$ (5 mL) were photolyzed at 8 °C with the 250 W GE sunlamp for 6 h with periodic monitoring by ^1H NMR after which the ratio of **31** to **61** was 1:5. The solvent was then evaporated to give a yellow solid which was purified by careful chromatography on silica gel, eluting with 7:1 hexane/ethyl acetate, to give **61** as a yellow solid (21.6 mg, 75%) with mp 75.5–77 °C (hexane): δ_H 4.98 (2H, d, J = 1.4 Hz), 6.97 (1H, d, J = 8.2 Hz), 7.08 (1H, t, J = 8.0 Hz), 7.37 (3H, m), 7.48 (1H, t, J = 7.3 Hz), 7.63 (2H, m), 7.73 (1H, t, J = 3.7 Hz), and 8.01 (1H, dd, J = 7.8 and 1.76 Hz); δ_C 71.54, 117.67, 122.05, 122.58, 126.95, 127.64, 128.40, 129.41, 133.21, 133.46, 135.56, 144.56, 160.95, and 182.20; υ 1642 cm^{-1}. Anal. Calcd for $C_{16}H_{12}O_2Se$: C, 60.96; H, 3.84. Found: C, 60.74; H, 3.85.

Cuprate Addition to the Vinyl Telluride 31. Methyllithium (1.05 mL of 1.4 M in Et_2O, 1.5 mmol) was added at −78 °C to a stirred suspension of copper(I) cyanide (70 mg, 0.75 mmol) in THF (12 mL), and the reaction mixture was stirred at that temperature for 10 min and then allowed to come to −20 °C over 1 h and, finally, recooled to −78 °C. The vinyl telluride **31** (58 mg, 0.15 mmol, 2:1 E/Z mixture) in THF (2 mL) was then added, and the reaction was maintained at −78 °C for 0.5 h before gradual warming to room temperature overnight. Saturated aqueous ammonium chloride solution (10 mL) was then added and after stirring for 2 h the reaction mixture was extracted with diethyl ether (3 × 20 mL). After drying ($MgSO_4$) and evaporation, a 69:31 mixture of the adduct **25** (1:1 mixture of isomers) and the ethylidene chromanone **26** (44:56 mixture of geometric isomers) was revealed by ^1H-NMR examination of the extract. The extracts were taken up in THF (2 mL) and stirred at room temperatrure for 10 min with 30% hydrogen peroxide (5 drops) before treatment with Na_2SO_3 and drying (Na_2SO_4). Chromatography on silica gel, eluting with ethyl acetate/hexane (1:4) gave the ethylidenechromanone **26** (17.5 mg, 67%) as a 77:23 mixture of E/Z isomers. The major isomer was identical to the one described above. The minor isomer was characterized by δ_H 1.31 (3H, d, J = 6.5 Hz), 5.30 (2H, s), and 6.97–7.98 (5H, m).