and its nmr and infrared spectra were recorded. Methyl absorptions (τ 7.8, 7.9, and 8.2 ppm) identical with those of (*E*)- and (*Z*)-1,2-diphenylpropene and 1,1-diphenylpropene, respectively, were prominent. The vinyl absorptions were partially obscured by the aromatic resonances. Several other materials were also evident in the τ 8.0-ppm region; judging from the yellow color of the solution it was presumed that azines were responsible for these absorptions.

Quenching of 1,2-Diphenyldiazopropane (1) with Dimethyl Acetylenedicarboxylate. Dimethyl acetylenedicarboxylate (DMADC) was found to be an efficient quencher of 1,2-diphenyldiazopropane (**1**); a solution of **1** was rapidly decolorized after the addition of the acetylene. Furthermore, analysis of a freshly prepared solution of **1** after quenching indicated only trace amounts of olefins relative to the 1,2-diphenylpropanone (**6**) present.

Table XX indicates that use of dimethyl acetylenedicarboxylate to quench **1** had no effect upon the products or the analyses. In each case the difference between the normal analysis and that of the quenched sample was small.

Table XX. Effect of Dimethyl Acetylenedicarboxylate upon Analyses of Products from Decomposition of **1** (Rel %)

Sample[a]	8	6	4	5	4:5	(4 + 5):8
1N	15	18	26	36	0.72	4.1
1Q	15	18	26	37	0.70	4.2
2N	19	15	22	40	0.55	3.3
2Q	19	16	21	40	0.52	3.2

[a] Sample 1 was decomposed at 75° and sample 2 at 100°; N = normal analysis, Q = dimethyl acetylenedicarboxylate added prior to analysis.

Isolation and tentative identification of the addition product of DMADC and 1,2-diphenyldiazopropane were accomplished as follows. An ethereal solution (20 ml) of dimethyl acetylenedicarboxylate (90 mg, 0.60 mmol) was gradually added to 125 mg (0.56 mmol) of freshly prepared 1,2-diphenyldiazopropane (**1**) in 35 ml of ether. The resulting colorless solution was refluxed for 10 min, and the solvent was removed on a steam bath. The residual light yellow oil would not crystallize: nmr τ 2.9 (m, 14, Ar*H*), 4.8 (q, 1, J = 7.0 Hz, C*H*CH$_3$), 6.3 (m, 15, CO$_2$C*H*$_3$), 8.2 ppm (d, 3, J = 7.0 Hz, CHC*H*$_3$). Excess DMADC accounts for the extra ester methyls; the absorption at τ 6.3 appeared to be several singlets, ir 1720–1740 cm^{-1} (C=O). The oil was vlpc collected (column E at 200°); the infrared spectrum of the collected material was nearly identical with that of the original compound. Mass spectral analysis of the vlpc collected material displayed an intense peak at *m/e* 364 in addition to an abundance of fragmentation ions (75 eV). At lower voltages (10–20 eV) the *m/e* 364 peak persisted, but fragmentation still occurred. Major ions at *m/e* 364, 349, 332, 317, 273, 260, 229, 172, and 105 (base peak).

Acknowledgment. We wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. Financial assistance by the Alfred P. Sloan Foundation is also acknowledged with pleasure.

Free-Radical Rearrangements in the Thermal Decomposition of *tert*-Butylperoxy 3-(1-Phenylcyclopropyl)propanoate, 4-(1-Phenylcyclopropyl)butanoate, and 5-(1-Phenylcyclopropyl)pentanoate

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Abstract: Decomposition of *tert*-butylperoxy 3-(1-phenylcyclopropyl)propanoate (**4**), 4-(1-phenylcyclopropyl)-butanoate (**14**), and 5-(1-phenylcyclopropyl)pentanoate (**29**) yields the corresponding alkyl radicals which are studied by esr; the barrier to rotation about C_β–C_γ for the alkyl radicals produced from **4** and **14** gives a distinct inequivalency in the β hydrogens. The yields of assigned products from thermal decomposition of **14** and **29** in benzene are greater than 84% and from **4**, greater than 93%. Products from both the cyclopropylethyl and the previously unobserved cyclopropylbutyl radical rearrangements have been detected, although in low yield. Ar_{2-5}, Ar_{2-6}, and Ar_{2-7} radical rearrangement products are formed and their yields compared to give an estimate of relative reactivity in the formation of five-, six-, and seven-membered rings. No product from the cyclopropylcarbinyl radical rearrangement, expected in the process yielding Ar_{2-n} rearrangement products, is observed; this result is discussed in terms of the requirements for the cyclopropylcarbinyl radical rearrangement. The identity and extent of hydrogen transfer reactions are also presented and discussed.

Highly strained cycloalkanes are well suited to studies of free-radical reactions at saturated carbon. In particular, substrates containing cyclopropane rings have been used extensively in studies of homoallylic rearrangements[3] and homolytic substitution reactions.[4]

The rearrangements of organic free radicals generally parallel but are less common than those of carbenium

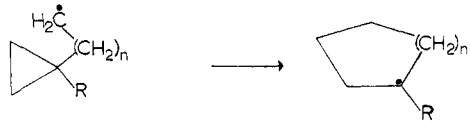
(1) (a) Author to whom inquiries should be addressed; (b) Hope College.

(2) Kansas State University.

(3) (a) D. J. Edge and J. K. Kochi, *J. Amer. Chem. Soc.*, **94**, 7695 (1972); (b) J. K. Kochi, P. J. Krusic, and D. R. Eaton, *ibid.*, **91**, 1877 (1969); (c) L. K. Montgomery and J. W. Matt, *ibid.*, **89**, 6556 (1967), and previous papers in this series; (d) S. J. Cristol and R. V. Barbour, *ibid.*, **90**, 2832 (1968); (e) J. D. Roberts, T. A. Halgren, M. E. H. Howden, and M. E. Medof, *ibid.*, **89**, 3051 (1967); (f) D. C. Neckers, A. P. Schaap, and J. Hardy, *ibid.*, **88**, 1265 (1966); (g) E. C. Friedrich and R. L. Holmstead, *J. Org. Chem.*, **37**, 2550 (1972), and references therein; (h) W. G. Dauben, L. Schutte, R. E. Wolf, and E. J. Deviny, *ibid.*, **34**, 3512 (1969); (i) R. W. Thies and D. D. McRitchie, *ibid.*, **38**, 112 (1973).

(4) (a) K. U. Ingold and B. P. Roberts, "Free-Radical Substitution Reactions," Wiley-Interscience, New York, N. Y., 1971, Chapter 5; (b) J. H. Incremona and C. J. Upton, *J. Amer. Chem. Soc.*, **94**, 301 (1972); (c) G. G. Maynes and D. E. Applequist, *ibid.*, **95**, 856 (1973).

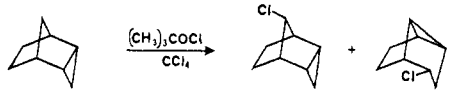
ions.[5] Olefinic cyclization reactions, for example, are well known in both homolytic[3a,b,6] and carbenium ion processes. Internal homolytic rearrangements of cyclopropylalkyl radicals (eq 1 and 2), however,


(1)


(2)

have not been thoroughly investigated. Both reactions, but especially that given in eq 1, appear feasible because of the release in strain energy accompanying rearrangement. Although radical rearrangements are usually associated with unsaturated centers, the addition of free radicals to cyclopropane compounds is well known.[7] In solvolytic studies with cyclopropylethyl substrates evidence has been presented for cyclopropyl participation accompanying rearrangement.[8] Also, Rhodes has found evidence for cyclopropyl migration in solvolytic reactions.[8d]

Recently, Freeman and coworkers presented evidence for a cyclopropylethyl radical rearrangement in the radical chlorination of *endo*-tricyclo[3.2.1.$0^{2,4}$]-octane (eq 3).[9a] Among the monochlorination prod-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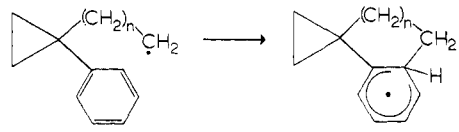
ucts they found both *anti*-8-chloro-*endo*-tricyclo[3.2.-1.$0^{2,4}$]octane and *endo*-2-chlorotricyclo[3.3.0.$0^{4,6}$]octane in varying ratios dependent on the concentrations of reactants. The formation of *endo*-2-chlorotricyclo[3.3.0.$0^{4,6}$]octane was proposed to have occurred by a cyclopropylethyl radical rearrangement analogous to eq 2. In related systems, however, no evidence for the cyclopropylethyl radical rearrangement was obtained.[5b]

By comparison with homolylic olefinic cyclization reactions, for $n = 3$ the reaction given by eq 1 is analogous to the rearrangement of the 5-hexenyl radical[6] and would provide an unambiguous example of a similar free radical rearrangement involving a saturated center. For $n = 2$ there is no evidence for the analogous cyclization of 4-pentenyl radicals;[6b] however, intramolecular cyclization leading to the formation of indene[10] and substituted indan[11] has been observed in radical processes. When $n = 1$ the olefinic analog is the homoallylic rearrangement.

To study the existence of internal homolytic rearrangements of cyclopropylalkyl radicals we chose to produce (1-phenylcyclopropyl)alkyl radicals (eq 1 and 2, R = C_6H_5) both because of the greater exothermicity for eq 1 when a tertiary benzylic radical would be produced from a primary radical, and because radical addition to the phenyl substituent (eq 4)[6a]

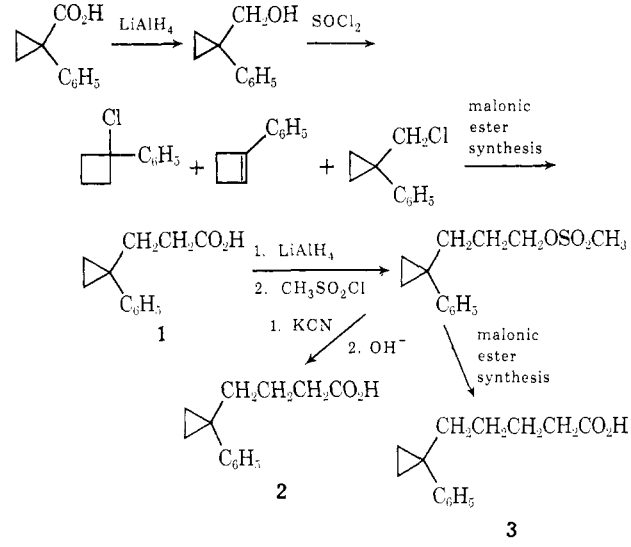

(4)

would permit the direct comparison of free-radical reactivity in additions to saturated and unsaturated centers. This paper describes the reactions and esr spectra of (1-phenylcyclopropyl)alkyl radicals (n = 1, 2, and 3), presents evidence for the existence of reaction 1 when $n = 1$ and 3, identifies free-radical processes not previously reported, and describes the cyclopropylcarbinyl radical rearrangement from the results obtained through reaction 4.

Results

Free radicals were generated in these studies by thermal decomposition of the corresponding *tert*-butylperoxy esters.[12] The carboxylic acid precursors were prepared from 1-phenylcyclopropanecarboxylic acid by the sequence given in Scheme I. Treatment

Scheme I



of (1-phenylcyclopropyl)methanol with thionyl chloride under a variety of conditions produced 1-chloro-1-phenylcyclobutane and 1-phenylcyclobutene in addition to (1-phenylcyclopropyl)methyl chloride. The cyclopropylmethyl chloride was conveniently isolated from the mixture by distillation from sodium carbonate. The *tert*-butylperoxy esters were chosen because of their demonstrated ability to produce carbon-centered

(5) (a) J. W. Wilt, "Free Radicals," Vol. I, Wiley-Interscience, New York, N. Y., 1973, Chapter 8; (b) C. Walling, "Molecular Rearrangements," Vol. 1, P. deMayo, Ed., Wiley-Interscience, New York, N. Y., 1963, Chapter 7.

(6) (a) M. Julia, *Accounts Chem. Res.*, **4**, 386 (1971); (b) C. Walling and A. Cioffari, *J. Amer. Chem. Soc.*, **94**, 6059, 6064 (1972); (c) C. Walling, J. H. Cooley, A. A. Ponaras, and E. J. Racah, *ibid.*, **88**, 5361 (1966).

(7) (a) C. Walling and P. S. Fredricks, *ibid.*, **84**, 3326 (1962); (b) D. E. Applequist, G. F. Fanta, and B. W. Henrikson, *ibid.*, **82**, 2368 (1960), and references therein; (c) A. J. Davidson and A. T. Bottini, *J. Org. Chem.*, **34**, 3642 (1969).

(8) (a) R. R. Sauers and R. W. Ubersax, *ibid.*, **31**, 495 (1966); (b) Y. E. Rhodes and T. Takino, *J. Amer. Chem. Soc.*, **90**, 4469 (1968); (c) M. J. S. Dewar and J. M. Harris, *ibid.*, **90**, 4468 (1968); **92**, 6557 (1970); (d) Y. E. Rhodes and T. Takino, *ibid.*, **92**, 5270 (1970).

(9) (a) P. K. Freeman, R. S. Raghavan, and G. L. Fenwick, *ibid.*, **94**, 5101 (1972); (b) P. K. Freeman and R. S. Raghavan, *J. Org. Chem.*, **37**, 3670 (1972).

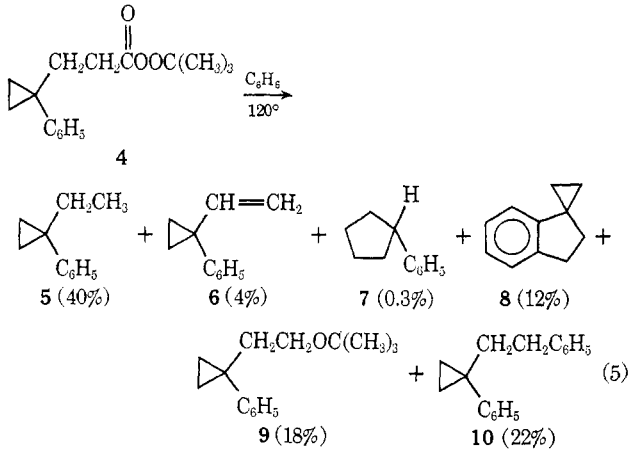
(10) (a) W. S. Trahanovsky and C. C. Ong, *J. Amer. Chem. Soc.*, **92**, 7174 (1970); (b) J. W. Wilt, L. L. Maravetz, and J. F. Zawadzki, *J. Org. Chem.*, **31**, 3018 (1966).

(11) E. W. Valyocsik and P. Sigal, *ibid.*, **36**, 66 (1971).

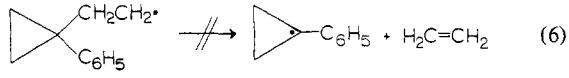
(12) P. D. Bartlett and R. R. Hiatt, *J. Amer. Chem. Soc.*, **80**, 1398 (1958), and subsequent papers in this series.

radicals under mild conditions,[12] and because, unlike the carbon radicals produced by tin hydride reductions of alkyl halides or by methods utilizing *tert*-butyl hypochlorite, reactions of the produced radical with the reagents used to generate that radical are limited.[5]

2-(1-Phenylcyclopropyl)ethyl Radical. The thermal decomposition of thoroughly degassed solutions of *tert*-butylperoxy 3-(1-phenylcyclopropyl)propanoate (**4**) in benzene at 120° gave the products listed in eq 5. Ben-



zene was used as the solvent to minimize hydrogen abstraction from the solvent; dilute solutions (0.05–0.02 *M*) were employed to minimize bimolecular reactions. The sum of the yields of products from duplicate runs was between 93 and 98%.[13] With the possible exception of the coupling product from **11**, no hydrocarbon products derived from **4** other than those listed in eq 5 were observed; although their yields were not determined, small amounts of **1** and the methyl ester of **1** were observed. No evidence for the presence of phenylcyclopropane that could arise from β scission of the 2-(1-phenylcyclopropyl)-ethyl radical (eq 6) was obtained. No attempt was



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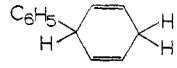
made to measure the yields of *tert*-butyl alcohol, acetone, and carbon dioxide in these reactions. Toluene, xylene, biphenyl (2%), and a dihydrobiphenyl (2%), believed to be **12** by pmr and ir analysis,[14] were



12

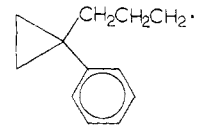
detected. With the exception of phenylcyclopentane, whose low yield discouraged isolation, each product was isolated and analyzed by spectral methods. Phenylcyclopentane was detected by glpc retention times and peak enhancement on five separate columns and by mass spectral analysis of the product mixture; 1-phenylcyclopentene was not detected in the product mixture.

(13) The yield of each product was averaged from duplicate runs. The precision of the reported yields at each concentration was within ±2%.

(14) This compound has been observed as a product from the thermal decomposition of benzoyl peroxide in benzene: (a) D. F. DeTar and R. A. J. Long, *J. Amer. Chem. Soc.*, **86**, 5251 (1964); (b) D. F. DeTar, R. A. J. Long, J. Rendleman, J. Bradley, and P. Duncan, *ibid.*, **89**, 4051 (1967).

Except for the yield of **10**, which increased from 18 to 26% as the perester (**4**) was diluted from 0.05 to 0.02 *M* in benzene, the yields of products were invarient within experimental error over the range of concentrations used. Phenylcyclopentane was also observed when **4** was thermally decomposed in chlorobenzene, but was present in somewhat lower yield (<0.3%).

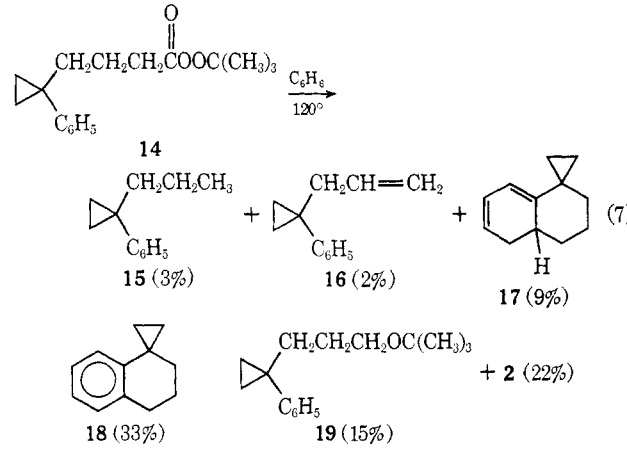
3-(1-Phenylcyclopropyl)propyl Radical. Inspection of models shows that the radical center can interact with the cyclopropane ring at a closer distance when the next higher homolog of **11** is produced. However, **13**



13

would also be expected to have a greater tendency to react with the phenyl substituent (eq 4).[3a,6a]

Thermal decomposition of *tert*-butylperoxy 4-(1-phenylcyclopropyl)butanoate (**14**) yielded the products given in eq 7.[13] Phenylcyclohexane and 1-



phenylcyclohexene were not observed under conditions where 0.1% could be detected. Several minor products with glpc retention times comparable to that of **2** were observed; one of these products was identified as the methyl ester of **2**, but its yield was not determined. Toluene, xylene, biphenyl (1%), and **12** (1%) were also detected. Each product was isolated and analyzed by spectral methods. With the possible exception of the coupling product from **13**, no hydrocarbon products derived from **14** other than those listed in eq 7 were observed. 3-(1-Phenylcyclopropyl)propylbenzene (the homolog of **10**), if present, was not a major product; no glpc peak that would correspond to this product was detected. The sum of the yields of identified products from the decomposition of **14** in benzene, averaged from three runs, was 84 ± 3%.

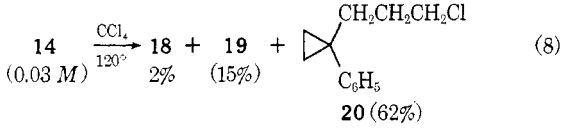
The relative yields of hydrocarbon products from thermal decomposition of perester **14** in a variety of solvents are given in Table I. The relative yields of 5,10-dihydro- and spiro(cyclopropane-1,1′-tetralin) (**17** + **18**) are greatest in chlorobenzene and least in cumene, indicating that the extent of homolytic addition varies with the hyrogen-donating properties of the solvent. Within the limited range of perester concentrations employed, the yields of products do not appear to be sensitive to changes in concentration.

Table I. Product Yields from Thermal Decomposition of *tert*-Butylperoxy 4-(1-Phenylcyclopropyl)butanoate (**14**) in Various Solvents at 120°[a]

Solvent	14, *M*	Actual yield, %[b] 15–18	19	Relative yield, %[c] 15	16	17	18	17 + 18
Benzene	0.042	47	15	7	4	19	70	89
Chlorobenzene	0.010	33	12	3	5	2	90	92
Toluene[d]	0.039	53	23	15	6	11	68	79
Cyclohexane	0.028	39	18	15	5	8	72	80
	0.013	39	19	15	5	3	77	80
Acetonitrile	0.027	43	12	15	1	4	80	84
Cumene	0.008	47	21	34	6	9	51	60

[a] Except for decomposition of **14** in cumene, yields are reported as average values from duplicate or triplicate runs. Per cent yields were determined by comparison of the area of the glpc peak of the product with that of an added standard and corrected for the sensitivity of the detector for each product. [b] Maximum variation in per cent yield was ±2%. The carboxylic acid, **2**, was detected in each run but its yield was not determined, except in benzene runs. [c] ±4% of reported yields. [d] Bibenzyl was obtained in 11% yield.

Thermal decomposition of **14** in carbon tetrachloride gave the products listed in eq 8. Hexachloroethane



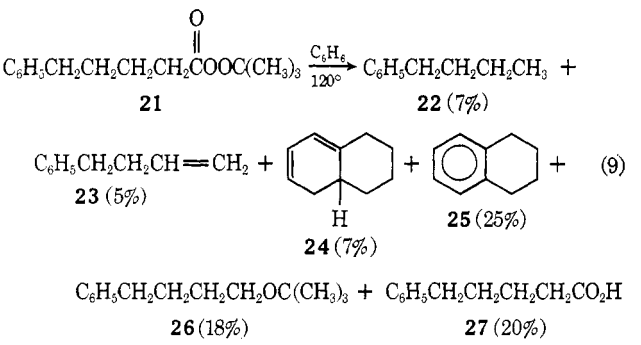
(8)

was also present, but its yield was not determined. No evidence was obtained for compounds **15**, **16**, or **17**. Although the ir and pmr spectra of the product mixture suggest the presence of a carboxylic acid, neither **2** nor its acid chloride was present. Additionally, the pmr spectrum of the reaction solution after removal of the solvent shows that not all of the products contain the cyclopropyl group.

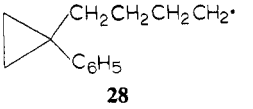
Compound **17** was not expected even though similar dihydrobenzene products have been detected in homolytic reactions;[14] no similar product was observed from thermal decomposition of **4**. In initial attempts to isolate **17** by glpc methods we observed that **17** was converted to **18**. Decreasing the retention time and the temperatures used for the collection of **17**, however, permitted its isolation with only minor contamination by **18**.

The unexpected observation of **17** prompted us to investigate the thermal decomposition of *tert*-butylperoxy 5-phenylpentanoate (**21**). No evidence has been reported for the formation of a compound analogous to **17** in previous studies using a variety of methods for generating the 4-phenylbutyl radical.[15] The products resulting from thermal decomposition of dilute solutions (0.03–0.05 *M*) of **21** at 120° in benzene (eq 9), however, were distinctly similar to those formed from **14**. In addition, the yields of these products correspond well to those observed from the decomposition of **14** in benzene (eq 7), indicating that there is not a significant effect on the cyclization reaction due to the cyclopropane ring. Both biphenyl (1%) and **12** (1%) were also detected.

(15) (a) S. Winstein, R. Heck, S. Lapporte, and R. Baird, *Experientia*, **12**, 138 (1956); (b) D. F. DeTar and C. Weis, *J. Amer. Chem. Soc.*, **79**, 3041, 3045 (1957); **78**, 4296 (1956); (c) H. Pines, N. C. Sih, and D. B. Rosenfield, *J. Org. Chem.*, **31**, 2255 (1966); (d) M. Julia and B. Malassine, *Tetrahedron Lett.*, 987 (1971).

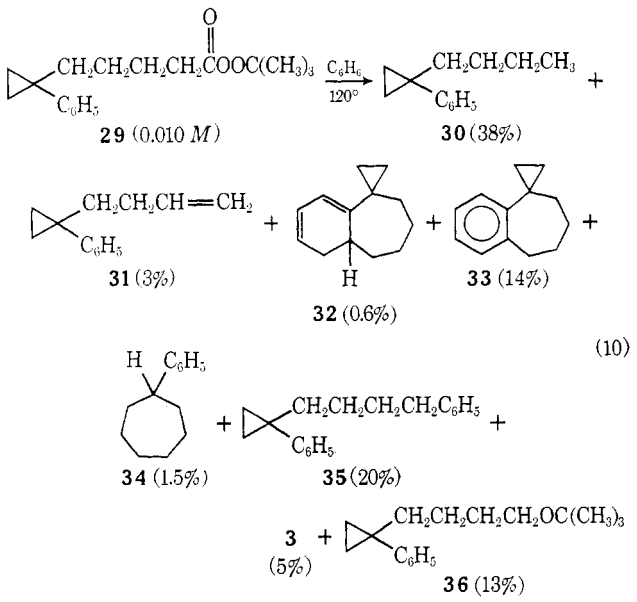


4-(1-Phenylcyclopropyl)butyl Radical. Unlike radical **13**, for which reaction 4 is the predominant process, we expected that the cyclopropylbutyl radical, **28**,



would not possess the same tendency to undergo intramolecular addition to the benzene ring. No analogous cyclization reaction in which a benzosuberan is formed has been reported.

Results from the thermal decomposition of *tert*-butylperoxy 5-(1-phenylcyclopropyl)pentanoate (**29**) in benzene (eq 10) are analogous to those from the decomposi-



tion of **4** under the same conditions. With the possible exception of the coupling product from **28**, no hydrocarbon products derived from **29** other than those listed in eq 10 were observed; neither 1-benzylcyclohexane or 1-methyl-1-phenylcyclohexane could be detected. A small amount of the methyl ester of **3** was detected, but its yield was not determined. Toluene, xylene, biphenyl (2%), and **12** (2%) were detected. With the exception of **32** and **34**, each of the products from thermal decomposition of **29** was isolated and analyzed by spectral methods. Phenylcycloheptane (**34**) was identified by glpc retention times and peak enhancement on four different columns and by mass spectral analysis. 6,11-Dihydrospiro(cyclopropane-1,1′-benzosuberan) (**32**) was inferred by glpc retention times and by comparison of its mass spectrum with that of its homolog (**17**).

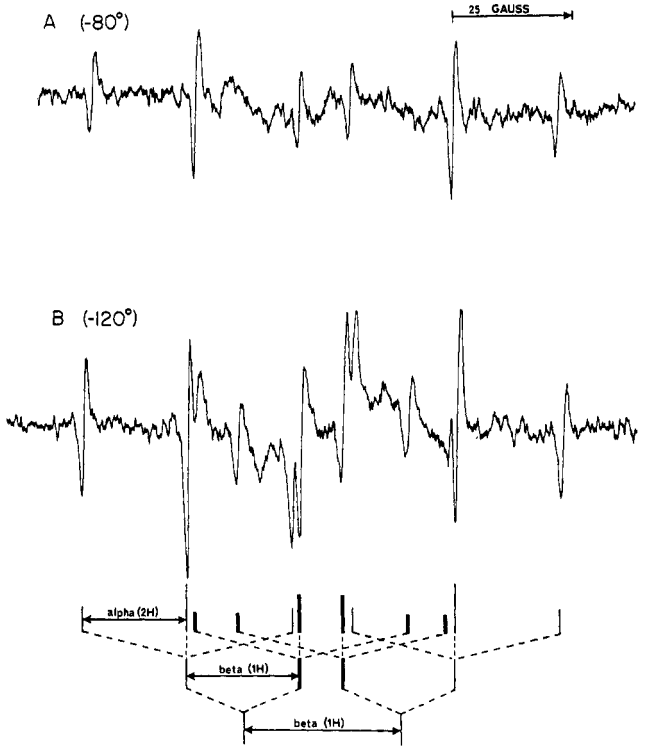


Figure 1. Esr spectra of **11** obtained by photolysis of **4** in cyclopropane solution. Spectrum A was obtained at −80° at which the $M_I = 0$ lines for the β protons are broadened almost beyond detection. Spectrum B was recorded at −140° and shows the inequivalency of the β protons. The slightly broadened peaks which would correspond to the $M_I = 0$ lines in the case of equivalent β protons are illustrated with somewhat heavier marks of reduced height in the stick diagram.

Electron Spin Resonance Studies. Cyclopropane solutions of the peresters **4, 14,** and **29** were prepared at reduced temperatures, thoroughly degassed by freeze–thawing at least three times on a vacuum line, and then photolyzed while held in the cavity of the esr spectrometer. Spectra of the corresponding radicals **11** and **13** were recorded at various temperatures; the limited solubility of **29** in cyclopropane allowed the observation of radical **28** at only the higher temperature. The esr spectra were readily interpreted as resulting from the unrearranged radicals **11, 12,** and **28** although small amounts of other paramagnetic species, presumably produced in secondary reactions, were evident under some conditions.

The hyperfine coupling constants for the α and β hydrogens are very similar for all three radicals at −40° but at lower temperatures the spectra of **11** and **13** exhibit line width alternation effects as a result of the β hydrogens becoming nonequivalent on the esr time scale (*cf.* Figure 1). The factors responsible for this behavior are discussed below. The esr parameters for **11, 13,** and **28** are recorded in Table II.

Discussion

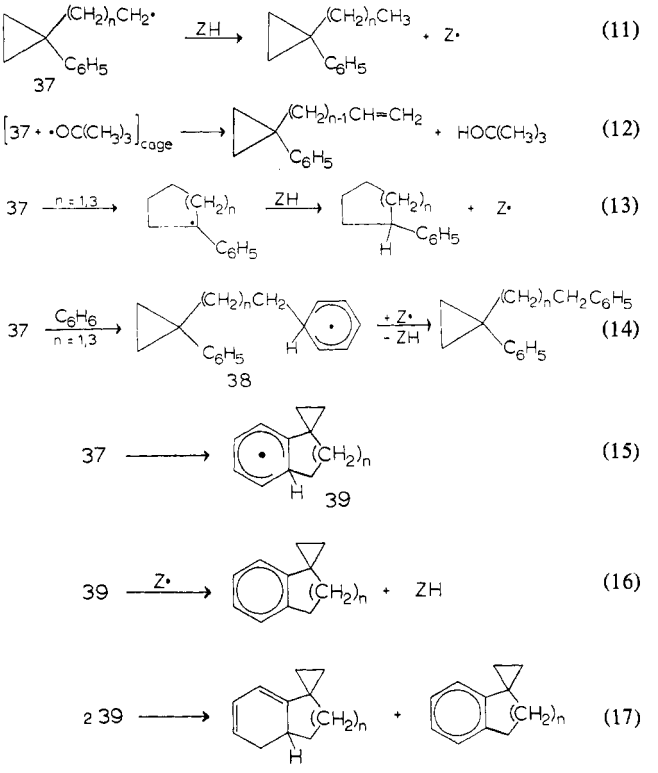
The accountability of the yields of products from thermal decomposition of peresters **4** and **29** in benzene is approximately 94%, and for **14** is greater than 84%. The high material balance indicates that no significant radical processes were undetected in the analysis. The hydrocarbon products from decomposition of peresters **4, 14,** and **29** in benzene can be explained by the reactions depicted in Scheme II.

Table II. Electron Spin Resonance Hyperfine Coupling Constants and *g* Values for **11, 13,** and **28**[a]

Perester	Radical	Temp, °C	Coupling constants, G[b]	*g* value[c]
4	**11**	−140	22.2 (2 H)	2.0028
			34.0 (1 H)	
			23.6 (1 H)	
		−40	22.2[d] (2 H)	
			27.0[d] (2 H)	
14	**13**	−120	22.1 (2 H)	2.0027
			28.3 (1 H)	
			30.5 (1 H)	
			1.0 (2 H)	
		−40	22.4[d] (2 H)	
			28.5[d] (2 H)	
29	**28**	−40	22.1[d] (2 H)	2.0024
			28.8[d] (2 H)	

[a] Cyclopropane solvent. [b] Estimated accuracy ±0.1 G except where noted. [c] Estimated accuracy ±0.0001. [d] Estimated accuracy ±0.2 G due to low signal to noise ratio and high modulation amplitude required to obtain spectrum.

Scheme II



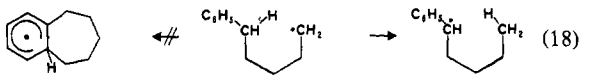
Cyclopropylethyl and Cyclopropylbutyl Radical Rearrangements. Results from the three radical systems reported in this study demonstrate that rearrangement of cyclopropylalkyl radicals according to eq 13 does occur, but not as a favored process. Rearrangement of the 2-(1-phenylcyclopropyl)ethyl radical to the 1-phenylcyclopentyl radical occurs to the extent of only 0.3%, the corresponding rearrangement of the 3-(1-phenylcyclopropyl)propyl radical was not observed, and the rearrangement of the 4-(1-phenylcyclopropyl)butyl radical to the 1-phenylcycloheptyl radical accounts for only 1.5% of the reaction process. The absence of 1-phenylcyclopentene from the decomposition of perester **4** suggests that phenylcyclopentane is produced in reaction 1 rather than from 1-phenylcyclopropylethene (**6**) in the vinylcyclopropane–cyclopentene rearrange-

ment.[16] No product or products from the rearrangement process given by eq 2 were observed.

The low yield of products from cyclopropylethyl radical rearrangement is in accord with previously reported results and also with unreported results from our laboratory. Freeman and coworkers observed cyclopropylethyl radical rearrangement in the radical chlorination of *endo*-tricyclo[3.2.1.$0^{2,4}$]octane[9a] but not in the corresponding reaction with the exo isomer[9a] nor with *exo*- and *endo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene,[9b] deltacyclene,[9b] or bicyclo[3.1.0]hexane.[17] Similarly, Bergman prepared the isomeric 1-ethyl-2-methylcyclopropanes by tri-*n*-butyltin hydride reduction of the corresponding ethyl bromides without observing rearrangement.[18] We were not able to detect phenylcyclopentane in the triphenyltin hydride reduction of 2-(1-phenylcyclopropyl)ethyl bromide; only 1-ethyl-1-phenylcyclopropane (**5**) was formed. Also, irradiation of 1-phenylcyclopropylmethyl hypochlorite did not yield 2-chloro-2-phenyltetrahydrofuran or either of the 2-phenyldihydrofurans; the major product was (1-phenylcyclopropyl)methyl 1-(phenylcyclopropane)carboxylate.

Although phenylcycloheptane is formed in low yield, its presence demonstrates that a free-radical rearrangement analogous to the rearrangements of the 5-hexenyl and 4-phenylbutyl radicals can occur at saturated carbon centers. However, rearrangement involving addition to an unsaturated center is highly favored. In the 4-(1-phenylcyclopropyl)butyl radical system formation of phenylcycloheptane can occur by a homolytic displacement reaction[4b] involving a six-membered ring transition state, whereas for the formation of spiro(cyclopropane-1,1′-benzosuberan) (**33**) a seven-membered ring transition state would be invoked.[19] An estimate of the relative ability of **28** to undergo addition to cyclopropane compared to benzene using similar transition state geometries can be obtained by comparing the yield of phenylcycloheptane with those of the phenyl addition products from decomposition of **14** (**17** + **18**). This value, calculated from the relative yields of hydrocarbon products, is less than 0.03.

Ar_{2-n} Radical Rearrangements. Intramolecular cyclization of alkyl radicals by addition to the phenyl substituent (eq 15) occurred with all of the (1-phenylcyclopropyl)alkyl radicals examined. Both Ar_{2-5}[10,11] and Ar_{2-6}[15] cyclization reactions have been observed in other radical reactions. However, previous studies have not reported evidence for a Ar_{2-7} cyclization reaction;[20] the 5-phenyl-1-pentyl radical preferentially undergoes internal hydrogen abstraction to give a benzylic radical (eq 18).[21] Since there is no hydrogen


(18)

α to the phenyl substituent in the 4-(1-phenylcyclopropyl) radical, reaction by eq 15 is favored for this system. Comparison of the relative yields of the products from Ar_{2-n} cyclization (n = 5, 6, and 7), given in Table III, shows that Ar_{2-6} cyclization is favored over

Table III. Relative Yields of Ar_{2-n} Cyclization Reactions

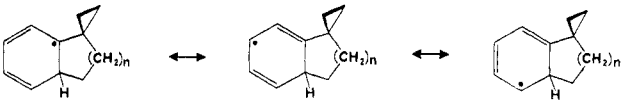
Radical	Relative yield Ar_{2-n} cyclization, %	n	Ar_{2-n}/Ar_{2-5}
11	15[a]	5	1.0
13	89[b]	6	5.9
28	18[c]	7	1.2

[a] % = **8/5** + **6** + **8** + **10**. [b] Data from Table I. [c] % = **32** + **33/30** + **31** + **32** + **33** + **34** + **35**.

Ar_{2-5} cyclization by only a factor of 6 and that there is little difference in the relative yields from Ar_{2-5} and Ar_{2-7} cyclization.

As contrasted to the results of DeTar and Weis for Ar_{2-6} cyclization of the 4-phenyl-1-butyl radical,[15b] a small amount of spiro(cyclopropane-1,1′-tetralin) (**18**) is formed when carbon tetrachloride is used as the solvent (eq 8). If, as has been proposed,[15b] only cage reactions compete with chlorine atom abstraction in carbon tetrachloride, this small amount of **18** may have been formed in a cage reaction and might represent an upper limit to phenyl participation in the decomposition of **14**.[22] Further experimentation, however, is required to test this hypothesis.

Cyclopropylcarbinyl Radical Rearrangements. Reaction 15 produces a cyclopropylcarbinyl radical that can be described by three resonance contributing structures (**39a–c**). The orientation of the cyclopropane


39a **39b** **39c**

ring with respect to the benzene ring for compounds **8**, **18**, and **33** has been given by Hahn and Howard.[23] For **39** (n = 1) the angle made by the plane of the benzene ring with the cyclopropyl CH_2–CH_2 bond can be estimated from the angle reported for **8** and from a Dreiding model to be 90°; the corresponding angle for **39** (n = 2) is near 80° and for **39** (n = 3) is approximately 25°. Although models indicate a considerable

(16) (a) J. S. Swenton and A. Wexler, *J. Amer. Chem. Soc.*, **93**, 3066 (1971); (b) P. H. Mazzocchi and H. J. Tambarin, *ibid.*, **92**, 7220 (1970); (c) M. R. Willcott and V. H. Cargle, *ibid.*, **91**, 4310 (1969), and references therein; (d) M. J. Jorgenson, *ibid.*, **88**, 3463 (1966), and references therein.

(17) P. K. Freeman, F. A. Raymond, J. C. Sutton, and W. R. Kuidley, *J. Org. Chem.*, **33**, 1448 (1968).

(18) R. G. Bergman, *J. Amer. Chem. Soc.*, **91**, 7405 (1969).

(19) Alternatively, Ar_{1-6} participation would require a six-membered ring transition state from which the products from the Ar_{2-7} rearrangement (**32** and **33**) could be formed by simultaneous breaking of the C_1–C_6 bond and formation of the C_2–C_7 bond. This reaction process has not been excluded in previous studies of Ar_{1-5} participation;[18d] there is, however, no evidence for its existence.

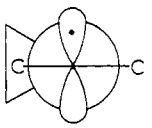
(20) Ar_{2-6} and Ar_{2-7} cyclizations have been observed recently in rearrangements of silyl radicals: H. Sakurai and A. Hosomi, *J. Amer. Chem. Soc.*, **92**, 7507 (1970), and references therein.

(21) C. A. Grob and H. Kammüller, *Helv. Chim. Acta*, **40**, 2139 (1957).

(22) No kinetic evidence has been obtained for phenyl participation in the decomposition of *tert*-butylperoxy 3-phenylpropanoate or 4-phenylbutanoate: (a) M. M. Martin, *J. Amer. Chem. Soc.*, **84**, 1986 (1962). However, the reactivity of the carbon–carbon double bond toward addition of the trichloromethyl radical to $C_6H_5(CH_2)_nCH{=}CR_2$ does exhibit a rate increase when n = 1 or 2, compared to n > 2. (b) M. M. Martin and G. J. Gleicher, *ibid.*, **86**, 239 (1964).

(23) R. C. Hahn and P. H. Howard, *J. Amer. Chem. Soc.*, **94**, 3143 (1972).

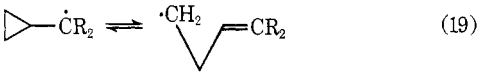
degree of flexibility for **39** (n = 3), the homologous radicals (**39**, n = 1 and 2) are relatively inflexible. The rigid geometry of structure **39** (n = 1 and 2) locks the cyclopropylcarbinyl radical in the more stable[3b,24] bisected conformation (**40**). Radical **39** (n = 3), al-



40

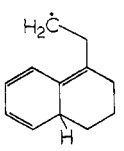
though not locked in the bisected conformation, is sufficiently flexible to adopt the bisected conformation. Contrary to our expectations no product from ring opening, characteristic of cyclopropylcarbinyl radicals,[3] was observed. Three explanations can be advanced to explain this result.

An argument might be presented that the equilibrium[3c] between the cyclopropylcarbinyl and homoallylic radicals (eq 19) favors the cyclopropylcarbinyl



(19)

radical because of the stability of **39**. Roberts observed that the diphenylcyclopropylcarbinyl radical (eq 19, R = C_6H_5), formed in cyclohexane from the corresponding *tert*-butyl perester at 35°, gave diphenylcyclopropylmethane and 1,1-diphenyl-1-butene in a ratio of 10:1.[3e] When the γ,γ-diphenylalkylcarbinyl radical was generated from the corresponding perester in cyclohexane at 128°, however, the ratio of diphenylcyclopropylmethane to 1,1-diphenyl-1-butene was 1:10; the difference in the observed product ratios was attributed to the change in the position of equilibrium for eq 19 with temperature.[3e] Even in 1,4-cyclohexadiene, a good hydrogen donor solvent, the yield of 1,1-diphenyl-1-butene was from 3 to 100 times greater than that of diphenylcyclopropylmethane. If **39** were of comparable stability to the diphenylcyclopropylcarbinyl radical, we would have expected that at 120°, the decomposition temperature used for **14**, the ratio of (**17** + **18**) to products from the homoallylic radical, **41**, would be as high as 1:10. In our analysis we would have been able to detect at least 0.2% of hydrocarbon products arising from **41**, or of products resulting from internal homolytic addition by **41**, radical **42**.



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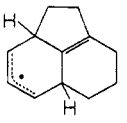


42

Although Carlsson and Ingold have shown that the rearrangement of the cyclopropylcarbinyl radical is an exceedingly fast process,[25] hydrogen-abstraction processes such as that given by eq 16 may be faster than rearrangement of **39**. The spin density at the cyclopropylcarbinyl carbon (*i.e.*, **39a**) is much less in these cyclohexadienyl radical systems than in other cyclopropylcarbinyl radicals reported to rearrange. Fessenden and Schuler have determined the values of the spin densities at carbon for the cyclohexadienyl radical from esr data;[26] by analogy to this simple system the spin density at the cyclopropylcarbinyl carbon of **39** is expected to be 0.35 (**39a**). The spin density at the methyl carbon of the diphenylmethyl radical, also from esr data, has been determined to be 0.60.[27] If the spin density at the carbinyl carbon of the diphenylcyclopropylcarbinyl radical, whose rearrangement was examined by Roberts,[3e] can be related to that of the diphenylmethyl radical, there is a significant difference in the spin densities at the carbinyl carbon between **39a** and the diphenylcyclopropylcarbinyl radical. Other cyclopropylcarbinyl radicals that have been reported to rearrange have even higher spin densities at the carbinyl carbon; for example, a reasonable estimate of the spin density at the α carbon of the benzyl radical is 0.77.[29] If the rate of the cyclopropylcarbinyl radical rearrangement is dependent on the spin density at the carbinyl carbon, radical **39** would be expected to have the slowest rate for rearrangement of the systems previously examined. Bimolecular reactions, such as those of eq 16 and 17, may occur at a faster rate than formation of **41**.

We would advance a third explanation: that *the cyclopropylcarbinyl radical rearrangement preferentially occurs from the perpendicular conformation.* Previous studies[3] of the cyclopropylcarbinyl radical rearrangement have either produced this radical in the perpendicular conformation or yielded a cyclopropylcarbinyl radical that could adopt the perpendicular conformation. Radical **39** is fixed in the bisected conformation and yields no detectable rearranged product during its lifetime. A rationalization of this preference for the perpendicular conformation would be that the rearrangement requires the interaction of the p orbital containing the odd electron with the ring antibonding orbital symmetric with respect to the plane of symmetry of the molecule. The same rationalization has been used by Kochi, Krusic, and Eaton to explain the apparent activation energy required for conversion of the cyclopropylcarbinyl radical to the homoallylic radical.[30] However, with the radical systems that we have examined it is impossible to distinguish with certainty whether rearrangement was not observed due to the low spin density at the carbinyl carbon in **39a** or because of a conformational preference for rearrangement.

Hydrogen-Abstraction and Hydrogen-Donation Reactions. The low yields of biphenyl and **12** in the decompositions of the *tert*-butylperoxy esters in benzene indicate that hydrogen abstraction from the solvent is only a minor process. Although we did not determine the existence or yields of terphenyl and quater-

(24) (a) L. M. Stock and P. E. Young, *J. Amer. Chem. Soc.*, **94**, 7686 (1972); (b) P. J. Krusic, P. Meakin, and J. P. Jesson, *J. Phys. Chem.*, **75**, 3438 (1971); (c) G. A. Russell and H. Malkus, *J. Amer. Chem. Soc.*, **89**, 160 (1967); (d) C. E. Hudson and N. L. Bauld, *ibid.*, **94**, 1158 (1972).

(25) D. J. Carlsson and K. U. Ingold, *ibid.*, **90**, 7047 (1968).

(26) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

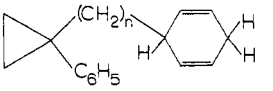
(27) (a) D. R. Dalton, S. A. Liebman, H. Waldman, and R. S. Sheinson, *Tetrahedron Lett.*, 145 (1968); (b) D. R. Dalton and S. A. Liebman, *Tetrahedron*, **26**, 3265 (1970). Although the assignment of the diphenylmethyl radical is in question and is most likely the 1,1,2,2-tetraphenylethyl radical,[28] this structural reassignment does not seriously change the spin density determination of Dalton.

(28) F. A. Neugebauer and W. R. Groh, *Tetrahedron Lett.*, 1005 (1973).

(29) (a) A. Carrington and I. C. P. Smith, *Mol. Phys.*, **9**, 137 (1965); (b) R. V. Lloyd and D. E. Wood, *ibid.*, **20**, 735 (1971).

(30) J. K. Kochi, P. J. Krusic, and D. R. Eaton, *ibid.*, **91**, 1897 (1969).

phenyl components, their yields are not expected to be more than twice as large as those of the biphenyl components.[14b] Solvent addition (eq 14) is the favored reaction of the primary radicals with benzene. For the decompositions of **4** and **29**, however, hydrogen-abstraction processes are predominant. Reactions 11 and 17 can be explained if the source of hydrogen atoms (ZH in Scheme II) is **38** and/or **39**. This would also explain our inability to observe **43** and the greater



43

yields of **8**, **18**, and **33** than their corresponding dihydro compounds. However, we cannot exclude **17**, **43**, or similar dihydrobenzene compounds as hydrogen atom sources for reaction 11; Roberts and coworkers have observed that 1,4-cyclohexadiene is a good hydrogen donor for primary free radicals.[3e]

If **38** and **39** are the only hydrogen atom donors in Scheme II, we can predict that the yields of products formed from hydrogen atom abstraction should equal the yields of products from hydrogen atom donation. These yields may be compared from the data in Table IV. Excellent agreement is found for the products

Table IV. Comparison of Product Yields for Compounds Requiring Hydrogen Atom Abstraction and Hydrogen Atom Donation[a]

Radical	Products requiring H abstraction, *A*	% yield, *A*	Products requiring H donation, *B*	% yield, *B*	% *A* − *B*
11	**5** + **7**	40	**8** + **10**	34	6
13	**2** + **15** + **17**	34	**18**	33	1
28	**3** + **30** + **32** + **34**	45	**33** + **35**	34	11

[a] Data taken from decompositions in benzene.

from radical **13**, indicating that Scheme II accurately accounts for hydrogen-transfer reactions. The results for radicals **11** and **18**, although showing that more than 75% of the hydrogen-transfer reactions are attributable to reactions with **38** and **39**, indicate that other hydrogen atom donors are operable in the thermal decomposition of **4** and **29** in benzene. Since toluene was observed as a product from thermal decomposition of each of the peresters in benzene, the cyclohexadienyl radical precursor of toluene may be reasonably assumed to be a hydrogen atom donor in reactions involving **11** and **28**.

The observation of **17**, and similar compounds from the thermal decomposition of peresters **21** and **29**, is consistent with the disproportionation reaction 17. No other radical or hydrocarbon species formed in the thermal decompositions of **14** other than **39** ($n = 2$) could reasonably serve as a hydrogen atom donor to **39**. Biphenyl and **12** are only minor products in this reaction, and reaction 14 was not observed for the thermal decomposition of **14**.

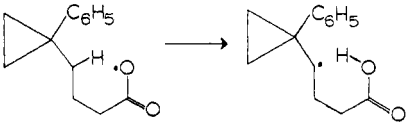
Despite the differences in the reaction processes for the radicals studied, the yield of olefin produced in the thermal decomposition of *tert*-butylperoxy esters in benzene is relatively constant. Additionally, decomposition of **14** in the solvents listed in Table I produces 3-(1-phenylcyclopropyl)prop-1-ene (**16**) in yields that are constant within experimental error. These observations are consistent with the formation of alkene products by disproportionation of the alkyl radical–*tert*-butoxy radical pair within the solvent cage (eq 12).[31] In a similar manner, the relative constancy of the yields of *tert*-butyl ethers (15 ± 2%) indicates that the formation of these products is due to recombination of the alkyl and *tert*-butoxy radicals within the solvent cage.[31]

Thermal decomposition of **4** yields, at most, 2% of the carboxylic acid, **1**, and less than 7% of the product composition is not accountable. Similarly, **29** yields only 5% of **3** with less than 6% of the products not identified. However, thermal decomposition of **14** gives 22% of **2**, while more than 15% of the product yield is not assigned. The formation of carboxylic acids in the thermal decomposition of *tert*-butylperoxy esters has been attributed to hydrolysis of the peresters by traces of water.[32] However, the solvents used in this study were carefully purified by methods that remove small amounts of water, and the same solvents were used in the thermal decompositions of **4**, **14**, and **29** with greatly differing yields of the corresponding carboxylic acids. Additionally, carboxylic acid product or products were detected in experiments in which **14** was thermally decomposed in carbon tetrachloride; this carboxylic acid, however, was not **2**.

Several investigators have shown that *tert*-butylperoxy esters of *n*-alkanoic acids undergo thermal decomposition in two steps (eq 20).[12,22a] The high yields

$$\underset{\textbf{44}}{RCH_2\overset{O}{\overset{\|}{C}}OOC(CH_3)_3} \longrightarrow RCH_2CO_2\cdot + \cdot OC(CH_3)_3 \longrightarrow RCH_2\cdot + \cdot OC(CH_3)_3 + CO_2 \quad (20)$$

of carboxylic acid products that have been observed in several studies[33] indicate that **44** has a sufficient lifetime or reactivity to abstract a hydrogen atom. The yields of carboxylic acid from the peresters examined in this study are compatible with hydrogen abstraction from **39** or analogous hydrogen donors. The formation of carboxylic acid products other than **2** in carbon tetrachloride and the relatively large amount of products not accounted for from the thermal decomposition of **14** suggest that intramolecular hydrogen abstraction by **44** from the γ position (eq 21) is a likely process. The



(21)

product from hydrogen abstraction from the γ position for perester **14** is a cyclopropylcarbinyl radical and would be expected to give rearranged products. Intramolecular hydrogen abstraction reactions involving six-membered transition states are relatively common.[5]

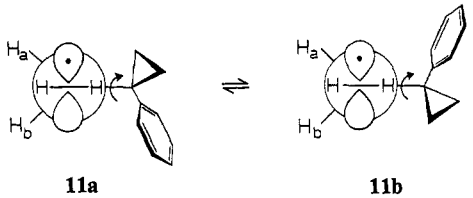
(31) Sheldon and Kochi obtained similar results for the photolysis of peresters: R. A. Sheldon and J. K. Kochi, *J. Amer. Chem. Soc.*, **92**, 5175 (1970).

(32) W. S. Trahanovsky and M. P. Doyle, *J. Org. Chem.*, **32**, 146 (1967).

(33) (a) M. Trachtman and J. G. Miller, *J. Amer. Chem. Soc.*, **84** 4828 (1962); (b) W. H. Starnes, Jr., *ibid.*, **85**, 3708 (1963).

Electron Spin Resonance Studies. The esr results from the photolytic decomposition of peresters **4, 14,** and **29** in cyclopropane are in complete accord with the thermolytic product studies in benzene insofar as production of radical **37** (n = 1, 2, and 3) appears to be the initial homolytic reaction in both. There is no evidence for participation by either the benzene or cyclopropane ring in a concerted decomposition of any of the precursor peresters. The esr results indicate that radicals **11, 13,** and **28** are rather typical substituted alkyl radicals and there is no evidence for delocalization of any significant amount of spin density into either the cyclopropyl group or benzene ring.

The temperature effect of the β hydrogen hyperfine coupling constant in **11** and **13** deserves comment. From the data in Table II it may be noted that at $-40°$ all three radicals exhibit very similar hyperfine interactions with both the α hydrogens (21.9–22.1 G) and β hydrogens (27.7–28.8 G). Moreover, these couplings are quite similar to that observed for the ethyl radical, $CH_3\dot{C}H_2$ (a_α = 22.30 G, a_β = 26.81 G, $-85°$),[34] indicating that, on the esr time scale of *ca.* 10^{-7} sec^{-1}, there is a rapid rotation about both the C_α–C_β and C_β–C_γ bonds in all the radicals. Upon lowering the temperature, however, rather dramatic changes take place in the spectra for **11** and **13** indicating that conformational interchanges are occurring which render either the α or β protons magnetically nonequivalent. Examination of the spectra reveals that the central lines (M_I = 0) of the triplet corresponding to the two β protons broaden as the temperature is lowered and essentially disappear (*cf.* Figure 1A). Lowering the temperature even further results in the appearance of two magnetically nonequivalent β protons (*cf.* Figure 1B and Table II). This type of esr behavior is not unique; Krusic and Kochi[35] and others have described such line-broadening effects in detail in terms of the dynamic equilibrium conformations of the radical structures. Our results on **11** and **13** can be explained in a manner analogous to that for the *n*-butyl radical. An internal rate process in these radicals exchanges the β protons between different environments. Hindered rotation about the C_β–C_γ bond as depicted below for **11** is consistent with this exchange and is supported



11a **11b**

by an examination of molecular models. Such a conformational movement results in the two β protons, H_a and H_b, being exchanged between two different environments; broadening of the M_I = 0 component for these hydrogens indicates that this rotation is occurring at a rate comparable to the difference in the splittings for two sites (*ca.* 10^{-7}–10^{-8} sec^{-1} at *ca.* $-80°$). The observation that the triplet due to the two α protons remains sharp over the temperature ranges investigated indicates that rotation about the C_α–C_β bond in both **11** and **13** is rapid on the esr time scale at these temperatures.

The barrier to rotation about C_β–C_γ for **11** and **13** must be greater than that for the corresponding rotation in the *n*-butyl radical[35] since at $-105°$ the M_I = 0 components for the β protons of this radical are only broadened while in **11** and **13** distinct inequivalency of the β protons is apparent. Higher barriers to rotation in **11** and **13** are realistic since the bulky phenyl and cyclopropyl groups cause considerably larger moments of inertia as compared to the *n*-butyl case. The large difference in hyperfine interaction for the two β protons in **11** at $-140°$ is notable, reflecting considerably different magnetic environments for H_a and H_b. This is presumably due to the proximities of the cyclopropyl and phenyl rings to these protons, but to ascribe a particular type of interaction to one or the other of these groups would be purely speculative on the basis of the present data.

Experimental Section

General. Instrumentation has been described.[36] Mass spectra were obtained using a Finnigan Model 1015 gas chromatograph–mass spectrometer operated at 70 eV. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. *tert*-Butyl hydroperoxide was purified according to the procedure of Trahanovsky and Doyle.[32] Phenylcyclopropane was prepared by the method of Shank and Shechter.[37] Phenylcyclopentane was synthesized from cyclopentanol by a Friedel–Crafts reaction with benzene.[38] Phenylcycloheptane was prepared by triethylsilane reduction[39] of 1-phenylcycloheptene, which was prepared from cycloheptanone and phenylmagnesium bromide. Phenylcyclohexane, 1-phenylcyclohexene, and 1-phenylcyclopentene were commercially available. 1-Phenylcyclopropanecarboxylic acid was synthesized in two steps from phenylacetonitrile using the procedure of Case.[40]

(1-Phenylcyclopropyl)methyl Chloride. (1-Phenylcyclopropyl)-methanol[41] (102 g, 0.69 mol) was dissolved in a constantly stirred solution of 102 g (0.84 mol) of *N*,*N*-diethylaniline in 500 ml of reagent grade benzene, and the resulting solution was cooled in an ice bath. Thionyl chloride (165 g, 1.39 mol) was added dropwise over a period of 1 hr at such a rate that the temperature of the solution remained below 10°. Following complete addition, the solution was allowed to warm to room temperature. After stirring for 3 hr at room temperature, 100 ml of 15% aqueous hydrochloric acid was added, and after thorough mixing the benzene layer was separated and washed three times with 100-ml portions of 15% aqueous hydrochloric acid, twice with 30% sodium hydroxide, and twice with water. The benzene solution was passed through anhydrous magnesium sulfate and the benzene removed under reduced pressure. A pmr spectrum of the crude mixture (119 g) exhibited absorptions due to (1-phenylcyclopropyl)methyl chloride (61%), 1-phenylcyclobutyl chloride (36%), and 1-phenylcyclobutene (3%). Neither changes in the reaction temperature (-15 to 55°) nor variation of the relative amount of thionyl chloride added, nor using pyridine instead of *N*,*N*-diethylaniline had a beneficial effect on the relative yield of (1-phenylcyclopropyl)methyl chloride.

To 119 g of the product mixture in a 500-ml round-bottomed flask equipped with a reflux condensor was added 18.5 g (0.175 mol) of anhydrous sodium carbonate. The resulting mixture was heated with stirring at 165° for 30 min, then cooled, washed with water to remove inorganic salts, and dried by passing the organic liquid through anhydrous magnesium sulfate. Distillation of the resulting liquid at 0.3 Torr through a 10-cm column of glass beads gave two fractions with boiling points of 37.5–38.5° and 52.5–53.5°, respectively. The first fraction was identified as 1-phenylcyclobutene (20.0 g, 0.15 mol, 22% yield): pmr (CCl_4) δ 7.45–7.10 (m, 5 H), 6.21 (t, J = 1.2 Hz, 1 H), and 2.9–2.4 (m, 4 H). The second fraction was (1-phenylcyclopropyl)methyl chloride (56.5 g, 0.34 mol, 49% yield): pmr (CCl_4) δ 7.27 (s, 5 H), 3.59 (s, 2 H), and 0.93 (br s, 4 H).

(34) J. K. Kochi and P. H. Krusic, *J. Amer. Chem. Soc.*, **91**, 3940 (1969).
(35) P. J. Krusic and J. K. Kochi, *ibid.*, **93**, 846 (1971), and references cited therein.
(36) M. P. Doyle and W. Wierenga, *ibid.*, **94**, 3896 (1972).
(37) R. S. Shank and H. Shechter, *J. Org. Chem.*, **24**, 1825 (1959).
(38) P. V. Hai, N. P. Buu-Hoi, and N. O. Xuong, *ibid.*, **23**, 39 (1958).
(39) F. A. Carey and H. S. Tremper, *ibid.*, **36**, 758 (1971).
(40) F. H. Case, *J. Amer. Chem. Soc.*, **56**, 715 (1934).
(41) J. W. Wilt and D. D. Roberts, *J. Org. Chem.*, **27**, 3430 (1962).

Anal. Calcd for $C_{10}H_{11}Cl$: C, 72.07; H, 6.66; Cl, 21.27. Found: C, 71.80; H, 6.68; Cl, 21.14.

3-(1-Phenylcyclopropyl)propanoic Acid (1). Diethyl (1-phenylcyclopropyl)methylmalonate was prepared by an adaption of the method of Shoppe and Stephenson.[42] Freshly cut sodium (7.13 g, 0.31 mol) was added to a 2-l. flask fitted with a reflux condenser and addition funnel, and containing 500 ml of ethanol that had been dried by distillation from sodium ethoxide. After the formation of sodium ethoxide was complete, diethyl malonate (86 g, 0.54 mol) was added in one portion to the hot liquid. After refluxing this solution for 15 min, (1-phenylcyclopropyl)methyl chloride (45 g, 0.27 mol) was added in one portion, and refluxing was continued for 16 hr. After cooling the mixture, 150 ml of water was added and the solution reduced in volume to 200 ml by distillation under reduced pressure. The resulting mixture was extracted with three 100-ml portions of ether. The combined ether extract was washed twice with water and dried by passing through anhydrous magnesium sulfate, and the ether was removed under reduced pressure. The resulting thick oil was fractionally distilled through a 7-cm Vigreux column to give 51.2 g (0.18 mol, 65% yield) of diethyl (1-phenylcyclopropyl)methylmalonate (bp 131–133° (0.3 Torr)): pmr (CCl_4) δ 7.45–7.05 (m, 5 H), 4.08 (q, 4 H), 3.20 (t, J = 7 Hz, 1 H), 2.17 (d, J = 7 Hz, 2 H), 1.20 (t, 6 H), and 0.72 (br s, 4 H); ir (film) 1736 cm^{-1} (C=O).

Diethyl (1-phenylcyclopropyl)methylmalonate (25.0 g, 0.086 mol) was added to 500 ml of 13% aqueous sodium hydroxide, and the solution was refluxed for 8 hr. After cooling, the homogeneous yellow alkaline solution was washed three times with ether to remove any impurities not soluble in the alkaline solution. Hydrochloric acid was then added to the aqueous solution until the pH was less than one; a white solid formed which dissolved when ether was added. The solution was worked up in the usual manner to give 17.5 g (0.075 mol, 87% yield) of a white solid: mp 154–155° dec; ir (KBr) 3500–2300 (broad, OH) and 1700 cm^{-1} (C=O).

(1-Phenylcyclopropyl)methylmalonic acid (38.7 g, 0.165 mol) was added to a flask equipped with a reflux condenser and heated at 160–170° for 30 min. Distillation of the resulting dark liquid under reduced pressure gave 29.7 g (0.156 mol, 94% yield) of **1** (bp 117–119° (0.2 Torr)): ir (film) 3500–2300 (broad), 1705 (C=O), 1600, 1490, 1440, 1305 (broad), 758, 700 cm^{-1}; pmr (CCl_4) δ 12.8 (s, 1 H, COOH), 7.35–7.05 (m, 5 H), 2.45–1.70 (sym m centered at 2.08, 4 H), and 0.85–0.60 (sym m centered at 0.73, 4 H).

Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.86; H, 7.50.

4-(1-Phenylcyclopropyl)butanoic Acid (2). 3-(1-Phenylcyclopropyl)propan-1-ol was prepared by the hydride reduction of **1**. In a typical run 8.97 g (0.236 mol) of lithium aluminum hydride was added to 500 ml of anhydrous ethyl ether in a 1-l. flask equipped with an addition funnel, reflux condenser, and mechanical stirrer. **1** (29.8 g, 0.156 mol) in 200 ml of anhydrous ethyl ether was added dropwise at a rate sufficient to produce moderate refluxing. After complete addition of **1** the mixture was stirred for 3 hr. Excess lithium aluminum hydride was destroyed by careful dropwise addition of ice–water. After the evolution of hydrogen subsided, 200 ml of 20% sulfuric acid was added and the mixture was stirred for 2 hr. The solution was worked up in the usual manner to give 25.6 g (0.145 mol, 93% yield) of 3-(1-phenylcyclopropyl)propan-1-ol (bp 86–88° (0.2 Torr)): pmr (CCl_4) δ 7.35–7.00 (m, 5 H), 3.42 (t, 2 H), 2.3 (s, OH), 1.7–1.3 (m, 4 H), and 0.9–0.6 (m, 4 H); ir (film) 3280 cm^{-1} (OH).

3-(1-Phenylcyclopropyl)prop-1-yl methanesulfonate was prepared from the corresponding alcohol and methanesulfonyl chloride in pyridine:[43] pmr (CCl_4) δ 7.40–7.05 (m, 5 H), 4.08 (distorted t, 2 H), 2.80 (s, 3 H), 2.0–1.5 (m with intense absorption at 1.67, 4 H), and 0.88–0.63 (m, 4 H); ir (film) 1345 and 1175 cm^{-1} (RSO_3R').

4-(1-Phenylcyclopropyl)butyronitrile was prepared in 89% yield by refluxing 3-(1-phenylcyclopropyl)prop-1-yl methanesulfonate with potassium cyanide in 70% aqueous acetonitrile for 20 hr:[44] bp 91–94° (0.2 Torr); pmr (CCl_4) δ 7.35–7.00 (m, 5 H), 2.17 (t, 2 H), 1.9–1.4 (m, 4 H), and 0.85–0.60 (m, 4 H); ir (film) 2220 cm^{-1} (C≡N).

The nitrile (12.5 g, 0.068 mol) was hydrolyzed by refluxing with 500 ml of 10% sodium hydroxide for 20 hr. After work-up the resulting brown liquid was distilled under reduced pressure to give 11.0 g (0.054 mol, 80% yield) of **2** (bp 122–123° (0.2 Torr)): pmr (CCl_4) δ 11.3 (s, 1 H, COOH), 7.4–7.0 (m, 5 H), 2.26 (distorted t, 2 H), 1.58 (distorted t, 4 H), and 0.86–0.62 (m, 4 H); ir (film) 3500–2300 (broad), 1705 (C=O), 1605, 1490, 1450, 1285 (broad), 762, 700 cm^{-1}.

Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.39; H, 7.96. Found: C, 76.40; H, 7.95.

5-(1-Phenylcyclopropyl)pentanoic Acid (3). The malonic ester synthesis used in the preparation of **1** was employed without change, except that 3-(1-phenylcyclopropyl)prop-1-yl methanesulfonate was treated instead of (1-phenylcyclopropyl)methyl chloride. Diethyl 3-(1-phenylcyclopropyl)prop-1-yl malonate was synthesized in 71% yield: bp 147–149° (0.2 Torr); pmr (CCl_4) δ 7.4–7.0 (m, 5 H), 4.12 (q, 4 H), 3.12 (t, 1 H), 2.05–0.95 (m, 6 H), 1.22 (t, 6 H), and 0.85–0.60 (m, 4 H); ir (film) 1735 cm^{-1} (C=O).

Basic hydrolysis of the malonate ester followed by acidification and thermal decomposition yielded **3** in 79% yield: bp 148–149° (0.3 Torr); pmr (CCl_4) δ 11.7 (s, 1 H, COOH), 7.4–7.0 (m, 5 H), 2.23 (distorted t, 2 H), 1.9–1.0 (m, 6 H), and 0.8–0.5 (m, 4 H); ir (film) 1706 cm^{-1} (C=O).

Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 76.91; H, 8.36.

***tert*-Butylperoxy esters** of **1, 2, 3,** and 5-phenylpentanoic acid were prepared by the method of Bartlett and Gortler.[45] The yield, elemental analysis, and carbonyl stretching frequency of each perester are given in Table V. Pmr (CCl_4): **4**, δ 7.4–7.0 (m, 5 H), 2.4–1.7 (symmetrical m, 4 H), 1.24 (s, 9 H), and 0.88–0.70 (m, 4 H); **14**, δ 7.3–7.0 (m, 5 H), 2.16 (distorted t, 2 H), 1.59 (distorted t, 4 H), 1.22 (s, 9 H), and 0.88–0.63 (m, 4 H); **21**, δ 7.3–7.0 (m, 5 H), 2.60 (distorted t, 2 H), 2.21 (distorted t, 2 H), 1.80–1.45 (m, 4 H), and 1.25 (s, 9 H); **29**, δ 7.35–7.05 (m, 5 H), 2.13 (distorted t, 2 H), 1.8–1.1 (m, 6 H), 1.25 (s, 9 H), and 0.85–0.55 (m, 4 H).

Table V. Preparation and Properties of *tert*-Butylperoxy Esters

Perester	% yield	Empirical formula	Anal. Calcd, % C	Calcd, % H	Found, % C	Found, % H	$\nu_{C=O}$,[a] cm^{-1}
4	79	$C_{16}H_{22}O_3$	73.25	8.45	73.04	8.47	1776
14	83	$C_{17}H_{24}O_3$	73.87	8.75	74.08	8.91	1776
21	85	$C_{15}H_{22}O_3$	71.96	8.86	71.82	8.87	1780
29	81	$C_{18}H_{26}O_3$	74.44	9.03	74.54	9.05	1775

[a] Spectra taken in carbon tetrachloride.

Purification of Solvents. Benzene was purified by distilling spectrometric grade benzene from calcium hydride and was stored over molecular sieves Type 4A. Acetonitrile was twice distilled[36] and reagent grade toluene distilled once from calcium hydride. Carbon tetrachloride was purified by the method of DeTar and Weis.[15b] Chlorobenzene and cumene were purified by the procedures given by Perrin.[46] Spectrometric grade cyclohexane was used without prior purification.

Thermal decomposition of peresters was carried out in sealed Kontes drying ampoules. The perester and solvent were weighed into the rigorously cleaned, dry ampoule and the solution was degassed under vacuum (<2 Torr) through three freeze–thaw cycles before the ampoule was sealed. The concentrations of peresters are given in the Results; generally the amount of perester used was less than 2 mmol and the volume of solvent less than 40 ml. The sealed ampoule was placed in an oil bath at 115–125°. After 24 hr the ampoule was cooled and opened. The reaction mixture was transferred to a round-bottomed flask, and approximately three-fourths of the solvent was removed by distillation through a Vigreux column. The solvent distillate was shown to contain no products from perester decomposition other than *tert*-butyl alcohol, acetone, and toluene by glpc analysis. Complete perester decomposition was indicated by the absence of the characteristic C=O stretching absorption at approximately 1780 cm^{-1}.

Identification of Products from Thermal Decomposition of 4. Glpc analysis of the product mixture from **4** was obtained on several columns. As an example of the separation obtained, identified

(42) C. W. Shoppe and R. J. Stephenson, *J. Chem. Soc.*, 2230 (1954).
(43) A. Streitwieser and W. D. Schaeffer, *J. Amer. Chem. Soc.*, **79**, 6233 (1957).
(44) W. S. Trahanovsky, M. P. Doyle, P. W. Mullen, and C. C. Ong, *J. Org. Chem.*, **34**, 3679 (1969).
(45) P. D. Bartlett and L. B. Gortler, *J. Amer. Chem. Soc.*, **85**, 1864 (1963).
(46) D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, "Purification of Laboratory Chemicals," Pergamon Press, New York, N. Y., 1966.

products were observed with the following retention times (given in parentheses and expressed in minutes) from 5-ft columns of 20% Carbowax 20M on Chromosorb P: toluene (2.8), xylene (4.2), **5** (7.7), **6** (10.1), **8** (21.6), **7** (24.8), **12** (27.3), **9** (38.1), biphenyl (50.1), methyl ester of **1** (54.1), and **10** (65.1). No other peak was observed throughout this time period. With the exception of toluene, xylene, and **8**, each product was isolated by glpc collection. Toluene and xylene were determined by comparison of glpc retention times and by comparison of their mass spectra with authentic samples. Individual analyses are given below.

5: pmr (CCl_4) δ 7.35–7.05 (m, 5 H, phenyl), 1.57 (q, J = 7 Hz, 2 H, CH_2), 0.83 (t, J = 7 Hz, 3 H, CH_3), and 0.80–0.55 (m, 4 H, cyclopropyl); mass spectrum,[47] *m/e* (rel intensity) 146 (7, parent ion), 145 (2), 132 (1), 131 (6), 130 (1), 129 (3), 128 (3), 127 (1), 118 (11), 117 (100), 116 (11), 115 (38), 105 (2), 104 (3), 103 (5), 102 (4), 92 (3), 91 (45).

6: pmr (CCl_4) δ 7.4–7.1 (m, 5 H, phenyl), 5.71 (1 H, RC*H*=CH_2, J_{trans} = 17 Hz, J_{cis} = 11 Hz), 4.86 (*trans*-RCH=C*H*$_2$, J_{cis} = 11 Hz, J_{gem} = 2 Hz), 4.54 (*cis*-RCH=C*H*$_2$, J_{trans} = 17 Hz, J_{gem} = 2 Hz), 1.15–0.55 (m, 4 H, cyclopropyl); ir (CCl_4) cm^{-1}, 3070, 3050, 3008, 2996. 2947, 2908, 2860, 1622 (C=C stretching), 1594, 1488, 1440, 1420, 1282, 1243, 1117, 1070, 1048, 1018, 958, 940, and 900; mass spectrum[47] *m/e* (rel intensity) 144 (25, parent ion), 143 (26), 132 (0), 131 (2), 130 (6), 129 (100), 128 (72), 127 (9), 118 (2), 117 (38), 116 (11), 115 (95), 105 (2), 104 (10), 103 (14), 102 (7), 92 (2), 91 (58).

7 was identified by comparison of retention times and peak enhancement using an authentic sample of phenylcyclopentane on 5-ft columns of 10% Carbowax 20M, 20% SE-30, and 20% diisodecylphthalate, all on Chromosorb P, and on 5-ft columns of 10% QF-1 and 10% DEGS, both on Chromosorb W. The mass spectrum of **7** in the product mixture from decomposition of **4** exhibited *m/e* values with the relative intensities of authentic phenylcyclopentane:[47] *m/e* (rel intensity) 146 (32, parent ion), 145 (3), 132 (1), 131 (8), 130 (0.3), 129 (2), 128 (3), 127 (1), 118 (15), 117 (100), 116 (6), 115 (16), 105 (15), 104 (92), 103 (11), 102 (3), 92 (14), 91 (58).

8 was identified from its pmr spectrum, which was identical with that observed by Hahn,[48] and by its ir and mass spectra: ir (CCl_4) cm^{-1}, 3064, 3040, 3015, 2992, 2940, 2882, 2858, and 2842; mass spectrum[47] *m/e* (rel intensity) 144 (40, parent ion), 143 (14), 132 (0), 131 (1), 130 (10), 129 (100), 128 (53), 127 (15), 118 (1), 117 (11), 116 (13), 115 (62), 105 (1), 104 (3), 103 (6), 102 (1), 92 (1), 91 (17).

9: pmr (CCl_4) δ 7.35–7.00 (m, 5 H, phenyl), 3.22 (t, J = 7 Hz, 2 H, $-CH_2O-$), 1.75 (t, J = 7 Hz, 2 H, $-CH_2CH_2O-$), 1.06 (s, 9 H, $OC(CH_3)_3$), and 0.71 (broadened s, 4 H, cyclopropyl); mass spectrum[49] *m/e* (rel intensity) 162 (22, M − C_4H_8), 161 (2), 145 (7), 144 (12), 143 (30), 132 (13), 131 (15), 130 (8), 129 (32), 128 (21), 117 (68), 115 (55), 91 (100).

10: pmr (CCl_4) δ 7.5–7.0 (m with most intense absorptions at 7.25 and 7.08, 10 H, phenyl), 2.75–1.70 (symmetrical m centered at 2.2, 4 H, $-CH_2CH_2-$), and 0.87–0.60 (m, 4 H, cyclopropyl).

Biphenyl was confirmed by comparison of retention times and peak enhancement using an authenic sample and after isolation by pmr analysis.

Although isolated **12** was contaminated with biphenyl, the sample gave an ir spectrum comparable to that previously reported.[14] The pmr spectrum of the dilute sample (CCl_4) showed multiplets at δ 7.0–7.5, 5.7–5.4, 4.6–4.9, and 2.8–2.6 in the approximate ratio of 6.5:4.0:0.8:2.3.[50] The mass spectrum of **12** obtained from the reaction mixture from decomposition of **4** prior to glpc collection, although exhibiting *m/e* values at 152–155 characteristic of biphenyl, showed intense *m/e* values at 94 (45), 93 (100), 92 (23), 91 (85), 79 (75), 78 (38), and 77 (95). Above *m/e* 94 only low intensity masses (<15% of 93) were observed, and at *m/e* 156 the parent ion was <0.5% of 93. With the exception of the peak at 77 the *m/e* values from 78 to 94 were not intense in the mass spectrum of biphenyl.

The methyl ester of **1** was observed as a minor product (<2%): pmr (CCl_4) δ 7.4–7.0 (m, 5 H, phenyl), 3.53 (s, 3 H, OCH_3), 2.45–1.65 (symmetrical multiplet centered at 2.05, 4 H, $-CH_2CH_2-$), and 0.85–0.60 (m, 4 H, cyclopropyl).

1 (<2%) was detected by glpc retention times and peak enhancement on 5-ft 20% Carbowax 20M columns and from the pmr spectrum of the isolated product.

Identification of Products from Thermal Decomposition of 14. Glpc analysis of the product mixture from **14** was obtained from several columns. As an example of the separation obtained, identified products were observed with the following retention times (given in parentheses and expressed in minutes) from 5-ft columns of 20% Carbowax 20M on Chromosorb P: toluene (2.1), xylene (3.8), **15** (13.7), **16** (17.0), **17** (20.8), **12** (28.5), **18** (36.8), **19** (46.8), and biphenyl (54.3). Neither phenylcyclohexane (26.0) nor 1-phenylcyclohexene (43.9) was detected in amounts ≥0.1% by glpc analysis. No other peak was observed throughout this time period. With the exception of toluene, xylene, **12**, and biphenyl, each product was isolated by glpc collection. Toluene, xylene, and biphenyl were identified by comparison of glpc retention times and by comparison of their mass spectra with authentic samples. **12** was shown to be identical with **12** from thermal decomposition of **4** by glpc retention times and by mass spectral analysis.[51] Individual analyses of the products from thermal decomposition of **14** are given below.

15: pmr (CCl_4) δ 7.4–7.0 (m, 5 H, phenyl), 1.8–1.0 (m, 4 H, $-CH_2CH_2-$), 0.82 (distorted t, 3 H, CH_3), and 0.80–0.55 (m, 4 H, cyclopropyl); mass spectrum[47] *m/e* (rel intensity) 160 (5, parent ion), 159 (0.5), 145 (0.6), 132 (7), 131 (18), 130 (2), 129 (6), 128 (5), 127 (2), 118 (12), 117 (100), 116 (11), 115 (33), 105 (3), 104 (6), 103 (8), 102 (5), 92 (5), 91 (55).

16: pmr (CCl_4) δ 7.4–7.0 (m, 5 H, phenyl), 6.1–4.7 (m characteristic of CH_2CH=CH_2, 3 H), 2.32 (broadened d, 2 H, $-CH_2-$), and 0.85–0.60 (m, 4 H, cyclopropyl); mass spectrum[47] *m/e* (rel intensity) 158 (4, parent ion), 157 (3), 143 (25), 132 (7), 131 (10), 130 (12), 129 (35), 128 (28), 127 (6), 118 (10), 117 (100), 116 (11), 115 (75), 105 (7), 104 (8), 103 (13), 102 (10), 92 (9), 91 (75).

17:[52] pmr (CCl_4) δ 5.55 (broad s, 2 H, =CHCH=), 5.27 (broad s, 1 H, =CH–), 2.61 (broad s, 3 H, =CHCH_2CH–), 2.0–1.6 (m, 4 H, CH_2CH_2CH_2), 1.5–1.15 (m, 2 H, $CH_2CH_2CH_2$), and 1.1–0.7 (m, 4 H, cyclopropyl); ir[53] (CCl_4) cm^{-1} 3063 (m), 3015 (m), 2995 (w), 2920 (s), 2873 (w), 2845 (s), 2817 (m), 1595 (w), 1490 (w), 1440 (m), 1420 (w), 1035 (w), 1007 (m), 951 (m), 889 (w), 853 (w), and 700 (δ); mass spectrum[47] *m/e* (rel intensity) 160 (9, parent ion), 159 (2), 145 (5), 132 (15), 131 (37), 130 (4), 129 (10), 128 (9), 127 (2), 118 (9), 117 (68), 116 (9), 115 (25), 105 (15), 104 (37), 103 (11), 102 (4), 92 (15), 91 (100).

18 was identified from its pmr and ir spectra, which were identical with those reported by Hahn,[48] and by its mass spectrum:[47] *m/e* (rel intensity) 158 (20, parent ion), 157 (8), 143 (9), 142 (4), 141 (8), 132 (1), 131 (15), 130 (100), 129 (95), 128 (55), 127 (19), 118 (0.5), 117 (5), 116 (12), 115 (62), 105 (1), 104 (5), 103 (4), 102 (9), 92 (2), 91 (60).

19: pmr (CCl_4) δ 7.4–7.0 (m, 5 H, phenyl), 3.20 (t, 2 H, $-CH_2O-$), 1.7–1.3 (m, 4 H, $-CH_2CH_2-$), 1.10 (s, 9 H, $OC(CH_3)_3$), and 0.85–0.55 (m, 4 H, cyclopropyl); mass spectrum[49] *m/e* (rel intensity) 176 (5, M − C_4H_8), 175 (7), 157 (18), 145 (8), 144 (2), 143 (11), 132 (71), 131 (13), 130 (24), 129 (63), 128 (18), 117 (73), 115 (52), 91 (100).

2 was identified as a component of the product mixture from thermal decomposition of **14** in benzene by its retention time on 5-ft 20% Carbowax 20M columns and after glpc collection from its pmr spectrum.

The methyl ester of **2** (<2%) was identified from its pmr spectrum which, except for the presence of the methoxy absorption at δ 3.55 and the absence of an acid proton absorption, was identical with that of **2**.

Products from the thermal decomposition of **14** in the solvents listed in Table I were identified from their glpc retention times by comparison with those of products formed in the decomposition of **14** in benzene. Bibenzyl was identified as a product from thermal decomposition of **14** in toluene by glpc retention times and peak enhancement and after glpc collection from its pmr spectrum.

With the exception of **20** products from thermal decomposition

(47) The mass spectrum was found to be particularly diagnostic in the *m/e* 132–127, 118–115, and 105–102 ranges. All *m/e* values are included for these regions despite the low relative intensity for most compounds. Intensities are relative to the most intense *m/e* value ≤91.

(48) R. C. Hahn, P. H. Howard, S.-M. Kong, G. A. Lorenzo, and N. L. Miller, *J. Amer. Chem. Soc.*, **91**, 3558 (1969).

(49) No parent ion was observed for the *tert*-butyl ethers.

(50) The pmr spectrum of **12** has been reported: L. J. Durham, J. Studebaker, and M. J. Perkin, *Chem. Commun.*, 456 (1965).

(51) No product corresponding to **12** was observed from thermal decomposition of **14** in solvents other than benzene.

(52) **17** was isolated with glpc injector, column, and detector ovens set at approximately 150°. The collected sample was contaminated with less than 12% of **18**. Pmr data are given after subtraction of absorptions due to **18**.

(53) Sample was the same as that used to obtain the pmr spectrum. No absorptions characteristic of an aromatic nucleus (1600–1450 cm^{-1}) were observed as moderately intense. Absorptions are listed with respect to that at 2920 cm^{-1} (rel intensity): s = strong (≥60%), m = moderate (≥30 and <60%), w = weak (≥10 and <30%).

of **14** in carbon tetrachloride were confirmed by comparison of glpc retention times with those from decompositions in benzene and from their mass spectra. Hexachloroethane was confirmed by comparison of retention times and peak enhancement using an authentic sample and by its mass spectrum. 3-(1-Phenylcyclopropyl)propyl chloride (**20**): pmr (CCl_4) δ 7.4–7.0 (m, 5 H, phenyl), 3.40 (distorted t, 2 H, CH_2Cl), 1.85–1.45 (m, 4 H, $-CH_2CH_2-$), and 0.85–0.55 (m, 4 H, cyclopropyl); mass spectrum[47] *m/e* (rel intensity) 196 (0.3, parent ion ^{37}Cl), 194 (1.0, parent ion ^{35}Cl), 159 (0.2), 158 (0.1), 157 (0.2), 145 (1), 132 (12), 131 (6), 130 (3), 129 (9), 128 (7), 127 (3), 118 (11), 117 (100), 116 (10), 115 (29), 105 (2), 104 (3), 103 (10), 102 (5), 92 (4), 91 (50). Carboxylic acid product(s) were indicated by the ir spectrum of the product mixture (ν_{OH} as a broad absorption, 3300–2400 cm^{-1}, and $\nu_{C=O}$ at 1704 cm^{-1}) and by the presence of an acidic proton by pmr analysis. Glpc analysis using authentic samples showed the absence of **2** or the acid chloride of **2**.

Identification of Products from Thermal Decomposition of 21. Glpc analysis of the product mixture from **21** was obtained on 5-ft 20% Carbowax 20M columns. As an example of the separation obtained, identified products were observed with the following retention times (given in parentheses and expressed in minutes): toluene (0.95), xylene (1.3), **22** (2.3), **23** (2.6), **24** (3.2), **25** (5.2), **12** (7.7), **26** (10.7), and biphenyl (21.0). 1-Phenylbutane (**22**), 1,2,3,4-tetrahydronaphthalene (**25**), and biphenyl were identified by comparison of glpc retention times and peak enhancement with authentic samples. In addition, **22** and **25** were isolated and their pmr and mass spectral were compared to authentic compounds. **12** was shown to be identical with **12** from thermal decompositon of **4** by glpc retention times and after isolation from its pmr and mass spectra. 5-Phenylpropanoic acid was identified by pmr analysis. Individual analyses of the remaining products from thermal decomposition of **21** are given below.

23: pmr (CCl_4) δ 7.13 (s, 5 H, phenyl), 6.0–4.7 (m characteristic of $CH_2CH{=}CH_2$, 3 H), and 2.9–2.0 (m, 4 H, $-CH_2CH_2-$); mass spectrum *m/e* (rel intensity) 132 (7, parent ion), 105 (3), 104 (9), 92 (17), 91 (100).

24: pmr (CCl_4) δ 5.52 (broad s, 2 H, =CHCH=), 5.30 (broad s, 1 H, =CH–), 2.8–2.4 (m with most intense absorption at δ 2.60, 5 H), and 2.0–1.1 (m, 6 H); mass spectrum[54] *m/e* (rel intensity) 134 (5, parent ion), 132 (3), 105 (3), 104 (4), 92 (29), 91 (100).

26: pmr (CCl_4) δ 7.25–7.05 (m, 5 H, phenyl), 3.28 (t, 2 H, $-CH_2O-$), 2.57 (distorted t, 2 H, $C_6H_5CH_2$), 1.8–1.3 (m, 4 H, $-CH_2CH_2-$), and 1.13 (s, 9 H, $OC(CH_3)_3$); mass spectrum[49] *m/e* (rel intensity) 150 (10, M – C_4H_8), 131 (22), 103 (20), 91 (100).

Identification of Products from Thermal Decomposition of 29. Glpc analysis of the product mixture from **29** was obtained from 5-ft columns of 20% Carbowax 20M on Chromosorb P. As an example of the separation obtained, identified products were observed with the following retention times (given in parentheses and expressed in minutes): toluene (1.2), xylene (1.7), **30** (4.5), **31** (5.5), **32** (8.0), **12** (8.8), **34** (9.6), **33** (10.6), **36** (24.1), biphenyl (26.4), methyl ester of **3** (42.1), and **35** (49.0). No other peak was observed prior to 30 min. 1-Phenylcycloheptene was shown to be absent by glpc analysis. With the exception of toluene, xylene, **32**, **12**, **34**, and biphenyl, each product was isolated by glpc collection. Identifications of toluene, xylene, **12**, and biphenyl were similar to those reported previously. Individual analyses of the products from thermal decomposition of **29** are given below.

30: pmr (CCl_4) δ 7.4–7.0 (m, 5 H, phenyl), 1.8–1.0 (m, 6 H, $-CH_2CH_2CH_2-$), 0.83 (distorted t, 3 H, methyl), and 0.80–0.55 (m, 4 H, cyclopropyl); mass spectrum[47] *m/e* (rel intensity) 174 (4, parent ion), 173 (0.3), 145 (3), 132 (12), 131 (8), 130 (2), 129 (5), 128 (4), 127 (1), 118 (11), 117 (100), 116 (9), 115 (30), 105 (3), 104 (8), 103 (9), 102 (4), 92 (4), 91 (45).

31: pmr (CCl_4) δ 7.4–7.0 (m, 5 H, phenyl), 6.0–4.7 (m characteristic of $CH_2CH{=}CH_2$, 3 H), 2.2–1.3 (m, 4 H, $-CH_2CH_2-$), and 0.85–0.55 (m, 4 H, cyclopropyl); mass spectrum[47] *m/e* (rel intensity) 172 (1, parent ion), 171 (0.7), 157 (3), 143 (10), 132 (5), 131 (29), 130 (25), 129 (23), 128 (20), 127 (4), 118 (12), 117 (70), 116 (20), 115 (45), 105 (3), 104 (22), 103 (22), 102 (8), 92 (12), 91 (100).

32: mass spectrum[47] *m/e* (rel intensity) 174 (3, parent ion), 159 (3), 146 (10), 145 (6), 132 (13), 131 (17), 130 (6), 129 (15), 128 (10), 127 (3), 118 (14), 117 (80), 116 (7), 115 (32), 105 (14), 104 (22), 103 (10), 102 (4), 92 (14), 91 (100).

33 was identified from its pmr spectrum, which was identical with that reported by Hahn and Howard,[23] and by its mass spectrum:[47] *m/e* (rel intensity) 172 (9, parent ion), 171 (6), 157 (6), 144 (20), 143 (68), 142 (8), 141 (13), 132 (6), 131 (22), 130 (78), 129 (100), 128 (70), 127 (19), 118 (6), 117 (50), 116 (21), 115 (80), 105 (7), 104 (9), 103 (9), 102 (9), 92 (7), 91 (85).

34 was identified by comparison of retention times and peak enhancement using an authentic sample of phenylcycloheptane on 5-ft columns of 20% Carbowax 20M, 20% OV-17, 10% DEGS, and 20% Carbowax 4000, all on Chromosorb P. The mass spectrum of **33** in the product mixture from thermal decomposition of **29** was identical with that of authentic phenylcycloheptane:[47] *m/e* (rel intensity) 174 (21, parent ion), 159 (0.4), 145 (2), 132 (2), 131 (5), 130 (1), 129 (3), 128 (3), 127 (1), 118 (10), 117 (55), 116 (4), 115 (12), 105 (14), 104 (100), 103 (8), 102 (3), 92 (21), 91 (73).

35: pmr (CCl_4) δ 7.4–6.9 (m with most intense absorptions at 7.23 and 7.12, 10 H, phenyl), 2.52 (t, 2 H, $CH_2C_6H_5$), 1.8–1.2 (m, 6 H, $-CH_2CH_2CH_2-$), and 0.85–0.50 (m, 4 H, cyclopropyl).

36: pmr (CCl_4) δ 7.4–7.0 (m, 5 H, phenyl), 3.18 (distorted t, 2 H, $-CH_2O-$), 1.7–1.1 (m, 6 H, $-CH_2CH_2CH_2-$), 1.10 (s, 9 H, $OC(CH_3)_3$), and 0.80–0.50 (m, 4 H, cyclopropyl); mass spectrum[49] *m/e* (rel intensity) 190 (4, M – C_4H_8), 189 (2), 171 (5), 161 (5), 145 (4), 144 (4), 143 (16), 132 (9), 131 (10), 130 (9), 129 (29), 128 (9), 117 (71), 115 (29), 91 (100).

The methyl ester of **3** (<2%) and **3** were identified as components of the product mixture from thermal decomposition of **29** in benzene after glpc collection by pmr analysis. Except for the presence of the methoxy absorption at δ 3.52 and the absence of an acid proton absorption, the pmr spectrum of the methyl ester of **3** was identical with that of **3**.

Product Analyses. Following distillation of the solvent after thermal decomposition of the perester a weighed amount of an internal standard was added to the distillation residue. For quantitative decomposition studies of the following peresters the internal standard is given in parentheses: **4** (*o*-dichlorobenzene), **14** (bibenzyl),[56] **21** (*p*-chloroacetophenone), and **29** (α-tetralone). The areas of the product peaks from glpc analysis were compared with the area of the standard peak, and the absolute yields of products were determined with the use of experimentally determined thermal conductivity ratios. Thermal conductivity ratios for products were determined from collected samples when authentic samples were not available. Olefinic products **6**, **16**, **23**, and **31** were assumed to have the same thermal conductivity ratio as their corresponding alkane counterparts. Similarly, **12**, **17**, **24**, and **32** were assumed to have the same thermal conductivity ratio as their corresponding dehydro products. Product yields are usually given as an average of two or more decompositions. The yields of *tert*-butyl ethers, **18** and **20**, were also determined by pmr spectroscopy directly from the reaction mixtures and were within 2% of the yields calculated by glpc analysis.

Esr Spectra. All esr spectra were obtained on a Varian Model 4502 X-Band spectrometer equipped with a dual cavity and standard variable-temperature apparatus. Hyperfine splitting constants (hfsc) and *g* values of the radicals were obtained by comparing with the hfsc and *g* value of Fremy's salt taken to be 13.09 ± 0.04 G and 2.00550 ± 0.00005, respectively.[57,58] Samples were prepared by dissolving 10–30% by volume of the perester in cyclopropane at low temperature in Suprasil quartz sample tubes (3.5 mm i.d.). All samples were deoxygenated in the sample tubes by at least three freeze–pump–thaw cycles utilizing standard vacuum line techniques.

All photolyses were carried out using a 2000-W high-pressure mercury capillary lamp (PEK A-1-B or AH6-2b) located outside the magnet and focused on the sample by means of a series of suprasil lenses.

The esr spectra were obtained with experimental samples in the front cavity modulated at 100 kHz and an aqueous Fremy's salt solution in the rear cavity modulated at 200 or 400 Hz. Spectra of experimental samples and Fremy's salt were recorded simultaneously on a Varian G-22 dual channel recorder.

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(54) Isomerization of **24** may have occurred under the conditions used to take the mass spectrum.[55] Patterns characteristic of tetralin were observed at *m/e* 126–131 with relative intensity <1.

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Radical Addition of Trimethyltin Hydride to Conjugated Enynes

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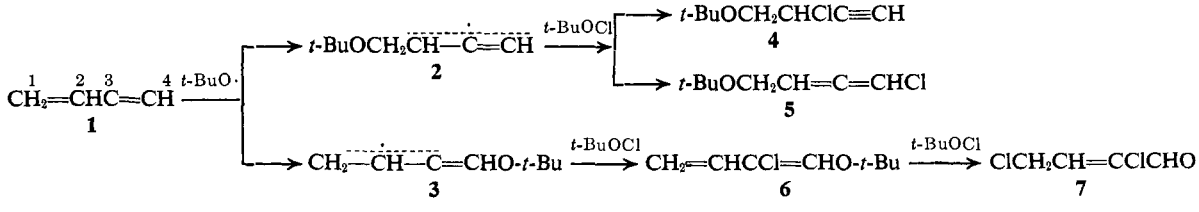
Abstract: The addition of trimethyltin hydride (**8**) to 1-penten-3-yne (**9a**) at 60–85° with AIBN catalysis gives a mixture of 1,2 adduct **10**, 4,3 adducts **11** and **12**, 4,1 adduct **13**, and probably 1,4 adduct **14**, as well as telomeric adducts. Monoadduct composition and total yield are dependent both on the ratio **9a**/**8** and on the concentration of **8**. The addition of stannane **8** to 2-methyl-1-buten-3-yne (**9b**) gives 1,2 adduct **16**, 1,4 adduct **17**, and 4,3 adducts **18** and **19**. Similar treatment of *cis*- and *trans*-3-penten-1-yne (**9c**) gives largely mixed 4,3 adducts **21** while the 2-hexen-4-ynes (**9d**) gave largely the corresponding adducts **23**; in the latter case, addition is accompanied by geometrical isomerization of **9d**. These results are discussed (Scheme I) in terms of a free-radical chain mechanism in which the intermediate propargylic (**24**) and methyleneallylic radicals (**25**) formed by attack of trimethylstannyl radicals on enyne **9** undergo not only product formation but also competitive telomerization and reversal of addition. This situation is to be contrasted with addition of *tert*-butyl hypochlorite wherein neither telomerization nor reversibility is a serious complication.

We have described[1] the photoinitiated addition of *tert*-butyl hypochlorite to vinylacetylene (**1**) and its monomethylated homologs in terms of a free-radical chain mechanism involving both propargylic[2] and methyleneallylic[2b–d] radical intermediates. Attack of *tert*-butoxy radical at the olefinic terminus of parent enyne **1** to form propargylic radical **2** was favored over attack at the acetylenic terminus to form methyleneallylic radical **3** by a factor of ~4 at ambient temperatures. This ratio was moderately sensitive to the position of methyl substitution in the enyne, being >10 for 1-penten-3-yne and 1–1.5 for the 3-penten-1-ynes, but did not fall below unity in the C_5H_6 series.



The propargylic radical intermediates underwent atom transfer to give mixtures of 1,2 and 1,4 adducts, the ratio being 10:1 for adducts **4** and **5** derived from radical **2** but again depending on the substitution pattern[2a] for the other enynes. The methyleneallylic radicals gave in all cases largely 4,3 adducts[2b,d] such as **6**, isolated as aldehyde **7**; no conclusive evidence was obtained for 4,1 adducts.

In a less detailed study of the addition of *N*-chloropiperidinium ion to enynes,[3] we also observed a preference for initial radical attack at the olefinic terminus.

Concurrent with these studies, several reports from Mal'tseva and coworkers[4] appeared which described the addition of triethyltin hydride to alkylated conjugated enynes at 80–120°. Moderate yields of monoadducts were obtained along with unidentified higher boiling products. The distilled monoadduct fractions were never separated into individual components but adduct structures were assigned on the basis of glpc, spectral, and chemical properties. In all cases, regardless of the substitution pattern of the enyne, the major product was a 4,3 adduct, although lesser amounts of 1,2, 1,4 and/or 4,1, and 3,4 adducts were reported as well as minor amounts of substitution products in which a terminal acetylenic hydrogen atom was replaced by a triethylstannyl group. These hydrostannation reactions were reported to be only mildly accelerated by azobisisobutyronitrile (AIBN) and unaffected by hydroquinone. The yield and composition of monoadducts were rather insensitive to the initial ratio of enyne/stannane which was varied from 10:1 to 1:1.

In spite of the somewhat equivocal response of the

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