References and Notes

(1) D. E. Burke, G. A. Cook, J. M. Cook, K. G. Haller, H. A. Lazar, and P. W. Le Quesne, *Phytochemistry*, **12**, 1467 (1973).
(2) P. K. Yuldashev, U. Ubaev, M. A. Kuchenkova, and S. Yu, Yunosov, *Khim. Prir. Soedin.*, **1**, 34 (1965).
(3) N. Abdurakhimova, P. K. Yuldashev, and S. Yu. Yunusov, *Dokl. Akad. Nauk SSSR*, **173**, 87 (1967).
(4) M. R. Yagudaev, Z. N. Malikov, and S. Yu. Yunosov, *Khim. Prir. Soedin.*, **10**, 260 (1974).
(5) B. Gilbert, A. P. Duarte, Y. Nakagawa, J. A. Joule, S. E. Flores, J. A. Brissolese, J. Campello, E. P. Carrazzoni, R. J. Owellen, E. C. Blossey, K. S. Brown, Jr., and C. Djerassi, *Tetrahedron*, **21**, 1141 (1965).
(6) Y. Ahmad, P. W. Le Quesne, and N. Neuss, *J. Pharm. Sci.*, **60**, 1581 (1971).
(7) J. M. Karle and P. W. Le Quesne, *J. Chem. Soc., Chem. Commun.*, 416 (1972).
(8) In $CDCl_3$, H_A appeared as a doublet (J = 8 Hz) at τ 3.0, while H_B and H_C gave superimposed signals at ca. τ 3.3. However, when the spectrum was repeated in acetone-d_6 the 1,2,4 pattern reminiscent of vindoline was quite clear (H_A, doublet, J = 8 Hz; H_B, doublet of doublets, J_{AB} = 8 Hz, J_{BC} = 2 Hz; H_C, doublet, J = 2 Hz).

Reactions of Dichlorocarbene with Methylenecyclohexan-4-one Ethylene Thioacetals

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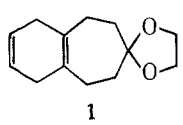
"Synergistic" carbenic cyclopropanation is dramatically illustrated by the Simmons–Smith reaction, in which a zinc carbenoid is intercepted by an hydroxyl, alkoxyl, or oxo substrate functionality, and the methylene fragment is subsequently transferred to a nearby π bond. Augmented addition rates and stereochemical control are observed in such reactions.[2,3] Substrate-assisted cyclopropanation is rarely observed with other carbenic species, however, and our attention was drawn to the suggestion that CCl_2 could be delivered to the central π bond of **1** by prior coordination to an oxygen atom, resulting in a threefold reactivity advantage of the central over the peripheral π bond.[4]



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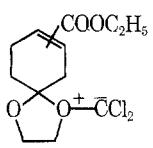

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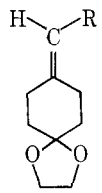


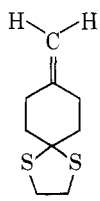
3a, R = H
b, R = $COOC_2H_5$

Unfortunately, no synergism could be detected in CCl_2 additions to various oxygen-functionalized cyclohexene derivatives,[5-7] including those in which the olefinic carbons were activated toward possible Michael addition of an anionic fragment representing a "trapped" CCl_2; cf. **2**.[7]

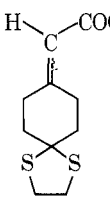
Addition–displacement cyclopropanations passing through **2**, or analogs, would require front-side displacement of the CCl_2 moiety from the oxygen carrier to complete the cyclopropanation.[8] The forbidden character of such displacements[9] could explain the observed lack of synergism. Moving the acceptor π bond from an endocyclic to an exocyclic position would obviate this problem, but CCl_2 additions to methylenecyclohexan-4-one ethylene acetals, **3**, were also found to occur without synergistic involvement of the acetal function.[10] Either oxygen atoms competed poorly with π bonds as sites for attack by the highly selective CCl_2,[11] or O-ylides which did form followed alternative, lower energy pathways in preference to addition–displacement.

On the other hand, S atoms do compete intramolecularly with π bonds for CCl_2. Whereas reaction of CCl_2 with allyl ethyl ether gave no evidence for O-ylide derived products,[12] S-ylide derived products were formed in reactions of CCl_2 with allylic sulfides.[13,14] Indeed, S-ylides formed by carbene capture have achieved substantial importance in sigmatropic rearrangement[15] and β-elimination reactions.[16]

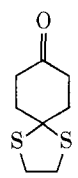
The obvious superiority of sulfur over oxygen as a site for carbene attack prompted us to prepare methylenecyclohexan-4-one ethylene thioacetals **4** and **5**, and to examine their reactions with CCl_2, in search of S-ylide mediated cyclopropanations.



4



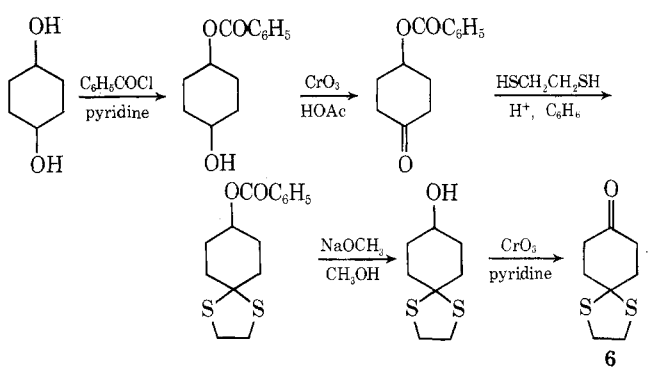
5



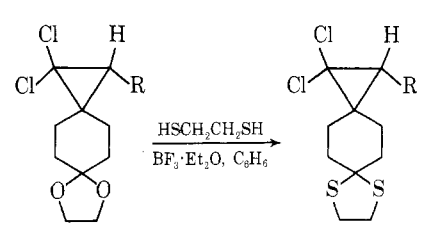
6

Olefinic thioacetals **4** and **5** were prepared by appropriate Wittig reactions on 1,4-cyclohexanedione monoethylene thioacetal (**6**), which was itself obtained from 1,4-cyclohexanediol by the procedure of Scheme I.

Scheme I



The CCl_2 adducts of **4** and **5** (**7** and **8**, respectively) were most readily prepared by acetal–thioacetal exchange reactions on oxygen analogs **7**-Ox and **8**-Ox, which were available in quantity from a previous study; cf. eq 1.[17]



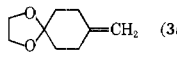
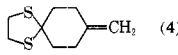
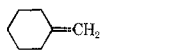
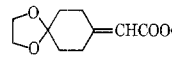
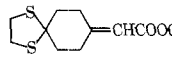
(1)

7-Ox, R = H
8-Ox, R = $COOC_2H_5$

7, R = H
8, R = $COOC_2H_5$

Mercurial-based CCl_2 precursors[12] did not convert **4** to **7**. However, **4** with sodium trichloroacetate in refluxing monoglyme[18] afforded **7** and a yet unidentified isomer in low yield. Similar attempts to add CCl_2 to **5** were fruitless. Cyclopropane **8** could not be obtained; rather, substrate **5** was *destroyed*, leaving behind a black, high-boiling tar. Control experiments showed that authentic **8** was stable to the reaction conditions, and could be readily detected by GC in the control product mixtures.

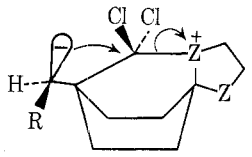
Table I
Relative Reactivities toward CCl_2 (80–85°)

Substrate	Reactivity
 (3a)	0.65
 (4)	0.79
	1.00
 (3b)	0.045
 (5)	*a*

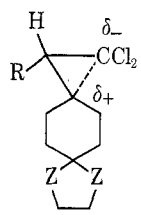
[a] The expected addition product, 8, could not be obtained; see text.

Relative to *cyclohexene*, the reactivity of **4** toward CCl_2 addition was found to be 3.60 ± 0.18[2] by the competition technique.[3] Previous data[10] allows us to write the relative reactivity sequence (80–85°) **3a**:**4**:methylenecyclohexane, 0.65:0.79:1.00. On this scale, the relative reactivity toward CCl_2 of **3b** is 0.045,[10] whereas that of **5** cannot be determined. For convenience, the reactivity data are gathered in Table I.

The quantitative data establish the absence of any kinetic advantage resulting from ylide-mediated addition–displacement cyclopropanation, with olefins **4**, **5**, **3a**, and **3b**, which could occur via intermediates such as **9** (Z = S or O; R = H or $COOC_2H_5$). The data suggest, instead, a normal cyclopropanation passing through transition state **10T**, in which partial positive charge resides mainly on the tertiary carbon of the methylenecyclohexane.[3,7,10] The inductively



9



10T

withdrawing heteroatoms of the remote acetal functions destabilize **10T**, and the reactivity order **3a** < **4** < methylenecyclohexane is quite reasonable. $\sigma_I(SCH_3)$ is smaller than $\sigma_I(OCH_3)$;[19] **10T** should be less destabilized when Z = S than when Z = O; hence thioacetal **4** is less deactivated toward CCl_2 addition than is acetal **3a**.

Although ylide-mediated cyclopropanation does not seem to occur, the thioacetal function must capture CCl_2 competitively with CCl_2 addition to π bonds. This is clearly seen on comparison of olefinic ester acetals **3b** and **5**. The former has a low reactivity toward CCl_2 addition because of the combined deactivating effects of its carboethoxy and ethylene acetal groups. However, the reactivity of the π bond in **5** is even lower, despite the fact that the ethylene thioacetal group (of **5**) should be *less* deactivating than the ethylene acetal function (of **3b**); see **3a** vs. **4**, above.

This is understandable if S atoms capture CCl_2 at rates similar to those of the π bonds of disubstituted alkenes, and then nonproductively dispose of CCl_2. Because the substitution of a carboethoxy group on the exo methylene position of methylenecyclohexane decreases π-bond reactivity toward CCl_2 by ~17-fold,[10] the additionally deactivated double bond of **5** will not be able to compete for CCl_2 with the S atoms of the thioacetal group.

Further evidence on this point was obtained from experiments in which **5** and 4-methylcyclohexanone ethylene thioacetal (**11**) were shown to *inhibit* CCl_2 addition to cyclohexene; cf. Table II.

Table II
Inhibition of Dichloronorcarane Formation from Cyclohexene by Thioacetals[a]

Run	Thioacetal	Mg	Mmol (× 10)	7,7-Dichloronorcarane formed, mg	Residual thioacetal, mg
1	None	0	0.0	14.4	
2	**5**	20	0.78	6.8	0.0
3	**5**	39	1.5	4.9	0.0
4	**5**	58	2.2	3.4	0.0
5	**5**	82	3.2	1.8	0.0
6	**11**	21	1.1	6.7	0.03
7	**11**	42	2.2	2.9	5.2
8	**11**	60	3.2	1.9	15

[a] Conditions: 50 mg (0.61 mmol) of cyclohexene and 110 mg (0.60 mmol) of $NaOOCCCl_3$ were heated in monoglyme at 85° for 30 min. Product and residual thioacetals were analyzed by GC, relative to an internal *n*-dodecane standard.

When [thioacetal]/[cyclohexene] ~ 0.5, **5** inhibits CCl_2 addition to cyclohexene by 88% (run 5 vs. run 1), and **11** inhibits by 86% (run 8 vs. run 1). These results parallel those of Parham and Groen, who showed that *n*-butyl phenyl sulfide inhibited the addition of CCl_2 to cyclohexene.[13]

Table II also shows that, although **5** and **11** are similarly effective as inhibitors, **11** was only partially destroyed (75%) by 2 equiv of CCl_2 precursor, whereas **5** was totally destroyed (runs 8 and 5). This suggests that there *is* a synergistic relation between the conjugated ester and thioacetal functions of **5** (toward CCl_2), but that it leads to accelerated substrate destruction rather than to accelerated cyclopropanation.[13a]

By analogy,[13–16] the initial product formed from CCl_2 and an ethylene thioacetal should be a sulfonium ylide. Attempts to "trap" the CCl_2 moiety of such an ylide by generating CCl_2 in the presence of **11** and either pentanal or methyl acrylate have led only to unidentified products derived solely from thioacetal **11**.[20]

Finally, why are allylic sulfides good substrates for *S*-ylide mediated CCl_2 reactions, whereas "remote" olefinic substrates such as **4** and **5** are "poor"? The activation energy for the [2,3] sigmatropic rearrangement of an ylide formed by addition of CCl_2 to an allylic sulfide must be very low; such ylides are rapidly consumed by the rearrangement process.[21] On the other hand, substrate-assisted cyclopropanation of **5** would require passage through **9** (R = $COOC_2H_5$; Z = S), the formation of which involves a Michael addition to a tetrasubstituted alkene. The activation energy for this process appears to be high enough to permit alternative, intermolecular reactions (polymerization) to occur in preference to self-cyclopropanation.

Experimental Section[22]

4-Benzoyloxycyclohexanone. 1,4-Cyclohexanediol (250 g, 2.15 mol), benzoyl chloride (295 g, 2.10 mol), and pyridine (600 ml) in 1400 ml of chloroform gave 275 g (58%) of 4-benzoyloxycyclohexanol, bp 175–178° (0.2 Torr) [lit.[23] bp 175–178° (0.2 Torr)], according to the procedure of Jones and Sondheimer.[23] The product (260 g, 1.18 mol) was oxidized with 115 g (1.15 mol) of CrO_3 in 700 ml of acetic acid and 67 ml of water.[23] There was isolated 140 g (54%) of 4-benzoyloxycyclohexanone: mp 58–60° (lit.[23] mp 63°); NMR δ 8.20–7.93 and 7.63–7.23 (m's, 2 H + 3 H, aryl), 5.60–5.27 (m, 1 H, carbinyl), and 2.73–1.97 (m, 8 H, cyclohexyl).

4-Benzoyloxycyclohexanone Ethylene Thioacetal. The above keto ester (70 g, 0.32 mol), 30 g (0.32 mol) of ethane-1,2-dithiol, 200 mg of *p*-toluenesulfonic acid, and 600 ml of benzene were heated to reflux for 20 hr, during which time ~5.7 ml of water collected in a Dean-Stark trap. Removal of the benzene gave a white

solid which was used without further purification. A small sample was recrystallized from benzene–petroleum ether (bp 30–60°): mp 73–76°; NMR δ 8.23–7.90 and 7.67–7.20 (m's, 2 H + 3 H, aryl), 5.30–4.87 (m, 1 H, carbinyl), 3.27 (s, 4 H, thioacetal), and 2.43–1.73 (m, 8 H, cyclohexyl).

Anal. Calcd for $C_{15}H_{18}O_2S_2$: C, 61.2; H, 6.12. Found: C, 61.2; H, 6.15.

4-Hydroxycyclohexanone Ethylene Thioacetal. The crude ester thioacetal (90 g, 0.31 mol), 2 g of sodium methoxide, and 300 ml of methanol were refluxed for 15 hr. Methanol was distilled away; the solid residue was shaken twice with 2 × 500 ml of acetone. Each acetone extract was filtered, acetone was stripped from the combined filtrate, and the residue was distilled. Methyl benzoate was removed at ~31° (0.25 Torr). The pot residue was cooled and recrystallized from benzene–petroleum ether to give three crops (total yield ~50 g, 85%) of the desired product: mp 83.5–85°; NMR ($CDCl_3$) δ 3.93–3.53 (m, 1 H, carbinyl), 3.27 (s, 4 H, thioacetal), and 2.40–1.47, including a superimposed singlet (OH) at 1.57 (m, 9 H, cyclohexyl and OH).

Anal. Calcd for $C_8H_{14}OS_2$, C, 50.5; H, 7.36. Found: C, 50.7; H, 7.50.

1,4-Cyclohexanedione Monoethylene Thioacetal (6). CrO_3 (28.0 g, 280 mmol) was cautiously added to 300 ml of pyridine, followed by a solution of 21 g (110 mmol) of the above alcohol thioacetal in 100 ml of pyridine.[24] After the reaction mixture was stirred for 3 days at 25°, it was diluted with 500 ml of ether and filtered. The ethereal filtrate was washed with 3 × 150 ml of water and 3 × 150 ml of 2 *N* H_2SO_4, dried (Na_2SO_4), and stripped of solvent. The residue was maintained at 0.2 Torr for 12 hr, and then distilled to give 7 g (33%) of **6**: bp 102° (0.13 Torr); ir (film) 5.83 μ (s, C=O); NMR δ 3.33 (s, 4 H, thioacetal) and 2.40 ("s", 8 H, cyclohexyl[25]).

Anal. Calcd for $C_8H_{12}OS_2$: C, 51.0; H, 6.39. Found: C, 51.3; H, 6.46.

Methylenecyclohexan-4-one Ethylene Thioacetal (4).[26] Dimsyl sodium was prepared in a 100-ml, three-neck flask. NaH, 0.90 g of a 61% dispersion in mineral oil (22.9 mmol), was washed with petroleum ether, dried of solvent under vacuum, covered with N_2, and treated with 20 ml of DMSO (dried over 3A molecular sieves, and then distilled) at 65–70°, with stirring for ~30 min. After H_2 evolution ceased, the reaction mixture was cooled to 25°, and a solution of methyltriphenylphosphonium bromide (8.5 g, 23.8 mmol) in 30 ml of DMSO was added via syringe. After 10 min, 4.3 g (22.8 mmol) of ketone **6** was added. The orange ylide turned brown. The solution was heated to 70° for 3 hr, cooled, and diluted with 30 ml of petroleum ether and 60 ml of water. The aqueous layer was extracted with 3 × 20 ml of petroleum ether, and the combined organic extracts were washed with 30 ml of water, dried over Na_2SO_4, and stripped. Distillation of the residue gave 2.1 g (52%) of pure **4**: bp 55° (0.03 Torr); ir (CCl_4) 6.05 μ (m, C=C); NMR δ 4.60 ("s", 2 H, vinyl), 3.23 (s, 4 H, thioacetal), and 2.47–1.90 (m, 8 H, cyclohexyl).

Anal. Calcd for $C_9H_{14}S_2$: C, 58.1; H, 7.53; S, 34.4. Found: C, 58.1; H, 7.75; S, 34.1.

Carboethoxymethylenecyclohexan-4-one Ethylene Thioacetal (5).[27] NaH, 0.628 g of a 61% dispersion in mineral oil (15.9 mmol), was placed in a dry, 25-ml, three-neck flask equipped with a thermometer, N_2 inlet, addition funnel, and stirring bar. Dry benzene (10 ml) was added and stirring commenced. This was followed slowly by the addition of 3.58 g (15.9 mmol) of triethyl phosphonoacetate via the addition funnel. The temperature was kept at <35° during the addition. After an additional 1 hr of stirring, 3.0 g (15.9 mmol) of ketone **6** was added over 20 min. During the addition, the reaction mixture became very viscous, and was then warmed to 60°. Heating was continued for 30 min after the addition of **6** was completed. The reaction mixture was then cooled, benzene was decanted, and the residue was leached with 4 × 10 ml of hot benzene. All benzene fractions were combined and stripped; the residue was distilled to give 0.8 g of a mixture of **5** and **6** (95:5), bp 140–143° (0.3 Torr), followed by 1.85 g of GC-pure **5**, bp 143–146° (0.3 Torr). The overall yield was 63%: ir (film) 5.85 (s, C=O) and 6.16 μ (s, C=C); NMR δ 5.58 ("s", 1 H, vinyl), 4.10 (q, *J* = 7 Hz, 2 H, OCH_2), 3.28 (s, 4 H, thioacetal), 3.05 ("t", *J* = 7 Hz, 2 H, allylic CH_2 cis to carboethoxy), 2.58–1.98 (m, 6 H, other cyclohexyl), and 1.25 (t, *J* = 7 Hz, 3 H, methyl).

Exact mass. Calcd for $C_{12}H_{18}S_2O_2$: 258.074. Found: 258.072.[22]

1,1-Dichlorospiro[2.5]octan-6-one Ethylene Thioacetal (7) and 1,1-Dichloro-2-carboethoxyspiro[2.5]octan-6-one Ethylene Thioacetal (8). These compounds were prepared from their (oxy) acetal analogs, **7**-Ox and **8**-Ox, respectively.[17] The preparation of **7** is illustrative. In a test tube was placed 120 mg (0.51 mmol) of **7**-Ox, 0.2 ml of 1,2-ethanedithiol, and 0.2 ml of $BF_3 \cdot (C_2H_5)_2O$. The mixture was shaken, 2 ml of ether was added, and the solution was placed on a small alumina column (3 g). Elution with 10 ml of ether, followed by stripping of the eluate, gave an oil which was purified by GC,[28] retention time 13.5 min (the retention time of **8** was 22 min) on a 5 ft × 0.25 in., 15% SE-30 on 45/60 GCR column at 210°, He flow rate 70 ml/min. Both **7** and **8** were white solids. For **7**: NMR δ 3.23 (s, 4 H, thioacetal), 2.28–1.67 (m, 8 H, cyclohexyl), 1.20 (s, 2 H, cyclopropyl).

Exact mass. Calcd for $C_{10}H_{14}Cl_2S_2$: 267.991. Found: 267.989.[22]

For **8**: ir (CCl_4) 5.75 μ (C=O); NMR δ 4.13 (q, *J* = 7 Hz, 2 H, OCH_2), 3.23 (s, 4 H, thioacetal), 2.3–1.73 [m, with superimposed s at 1.98, 9 H, cyclohexyl and cyclopropyl (s)], and 1.27 (t, *J* = 7 Hz, 3 H, methyl).

Exact mass. Calcd for $C_{13}H_{18}Cl_2S_2O_2$: 340.012. Found: 340.012.[22]

4-Methylcyclohexanone Ethylene Thioacetal (11) was prepared from 10.0 g (89.5 mmol) of 4-methylcyclohexanone, 8.0 g (85 mmol) of 1,2-ethanedithiol, and 300 mg of *p*-toluenesulfonic acid in 50 ml of refluxing benzene, with azeotropic removal of water. Removal of solvent, followed by distillation afforded 13 g (81%) of the product, bp 81° (0.4 Torr). The thioacetal was GC pure and showed no carbonyl band in its ir spectrum: NMR δ 3.23 (s, 4 H, thioacetal) and 2.33–0.80 (m, with methyl signal superimposed at ~0.97, 12 H, cyclohexyl and methyl).

Exact mass. Calcd for $C_9H_{16}S_2$: 188.069. Found: 188.074.[22]

Relative Reactivity Experiments. Weighed samples of olefin A and olefin B were diluted with 3 ml of monoglyme (distilled from Na) and injected into a nitrogen-blanketed flask containing ~0.1 equiv of sodium trichloroacetate and *n*-hexadecane (~80 mg) as an internal standard. The reaction mixture was stirred magnetically and heated with an oil bath to 80–85° for 1 hr. The reaction mixture was then cooled and filtered; the filtrate was analyzed on either an 8 ft × 0.25 in. 10% or a 5 ft × 0.25 in. 15% SE-30 on 45/60 GCR column programmed between 100 and 200°. The relative reactivity toward CCl_2, k_A/k_B, was calculated in the normal manner from $(P_A/P_B)(O_B/O_A)$ where the *P* factor represents the product ratio and the *O* factor represents the initial olefin ratio.[3] Olefins were present in tenfold excess over carbene precursor. Data appear in Table III.

Table III
Relative Reactivity Experiments

Olefin A/olefin B	$(O_A/O_B)^a$	$(P_A/P_B)^b$	$k_A/k_B{}^c$	$k_A/k_B{}^d$
4/cyclohexene	0.266	1.01	3.80	3.46
4/cyclohexene	0.522	2.15	4.12	3.75
4/methylenecyclohexane	0.972	0.735	0.756[e]	

[a] Mole ratio. [b] From integration of GC product peaks. [c] Uncorrected for relative thermal conductivity detector responses. [d] The detector response, C_K = (moles of **7**/moles of dichloronorcarane)/(GC response of **7**/GC response of dichloronorcarane), was 0.91. Crude k_A/k_B was multiplied by 0.91 to obtain the corrected k_A/k_B. The average corrected value is 3.60 ± 0.18. [e] From $(k_4/k_{cyclohexene})(k_{cyclohexene}/k_{methylenecyclohexane}) = 3.60 \times 1/4.57$,[10] we calculate $k_4/k_{methylenecyclohexane} = 0.788$, in good agreement with the observed cross-check value.

Inhibition of CCl_2 Additions. Conditions and results of these experiments are described in Table II and its note.

Control Experiments. To establish the stability of **8**, a solution of ~15 mg (0.044 mmol) of **8**, 10 μl of *n*-hexadecane, 80 mg (0.95 mmol) of cyclohexene, and 15 mg (0.081 mmol) of sodium trichloroacetate in 2 ml of glyme was heated for 1 hr at 85°. GC analysis gave the ratios, **8**/*n*-hexadecane, as 0.465 (before reaction) and 0.460 (after reaction). Dichloronorcarane *was* formed in this experiment.

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Registry No.—**3a**, 51656-90-7; **3b**, 51656-91-8; **4**, 54531-72-5; **5**, 54531-73-6; **6**, 54531-74-7; **7**, 54531-75-8; **7**-Ox, 51656-93-0; **8**, 54531-76-9; **8**-Ox, 51656-92-9; **11**, 41158-95-6; dichlorocarbene, 1605-72-7; 4-benzoyloxycyclohexanone, 23510-95-4; 1,4-cyclohex-

anediol, 556-48-9; benzoyl chloride, 98-88-1; 4-benzoyloxycyclohexanol, 6308-92-5; 4-benzoyloxycyclohexanone ethylene thioacetal, 54531-77-0; ethane-1,2-dithiol, 540-63-6; 4-hydroxycyclohexanone ethylene thioacetal, 22428-86-0; 4-methylcyclohexanone, 589-92-4.

References and Notes

(1) (a) Fellow of the Alfred P. Sloan Foundation; (b) University Fellow, Rutgers University.
(2) H. E. Simmons, T. L. Cairns, S. A. Vladuchick, and C. M. Hoiness, *Org. React.*, **20**, 1 (1973).
(3) R. A. Moss, "Carbenes", Vol. 1, M. Jones, Jr., and R. A. Moss, Ed., Interscience, New York, N.Y., 1973, p 153 ff.
(4) W. Grimme, J. Reisdorff, W. Jünemann, and E. Vogel, *J. Am. Chem. Soc.*, **92**, 6335 (1970).
(5) D. Seyferth and V. A. Mai, *J. Am. Chem. Soc.*, **92**, 7412 (1970).
(6) M. A. Tobias and B. E. Johnston, *Tetrahedron Lett.*, 2703 (1970).
(7) R. A. Moss, *J. Am. Chem. Soc.*, **94**, 6004 (1972).
(8) See ref 7, p 6008.
(9) L. Tenud, S. Farooq, J. Seibl, and A. Eschenmoser, *Helv. Chim. Acta*, **53**, 2059 (1970), and references cited therein.
(10) R. A. Moss and C. B. Mallon, *Tetrahedron Lett.*, 4481 (1973).
(11) More reactive carbenic species do attack the oxygen atoms of allylic and homoallylic ethers. See ref 10, notes 17–20.
(12) D. Seyferth, J. M. Burlitch, R. J. Minasz, J. Y.-P. Mui, H. D. Simmons, Jr., A. J. H. Treiber, and S. R. Dowd, *J. Am. Chem. Soc.*, **87**, 4259 (1965).
(13) (a) W. E. Parham and S. H. Groen, *J. Org. Chem.*, **29**, 2214 (1964). (b) A referee has suggested that ". . .the total destruction of **5** does (not) imply that there is a synergistic relation but rather that now one has introduced a Michael acceptor into the system for an alternate intermolecular pathway". The introduction of a Michael acceptor group per se does not cause destructive intermolecular reactions in CCl_2-generating systems (cf. **3b**). The presence of *both* an ethylene thioacetal and a carboethoxyethylene function in the same substrate molecule (e.g., **5**), however, does lead to an alternative, fast (relative to cyclopropanation), presumably intermolecular destructive process. In the sense of "cooperative behavior", this result is an example of synergism because neither the ethylene thioacetal (cf. **4**) nor the carboethoxy function[10] *alone* prevents cyclopropanation or induces destructive intermolecular reactions. Unfortunately, the synergism is not a desirable one.
(14) W. E. Parham and S. H. Groen, *J. Org. Chem.*, **30**, 728 (1965); **31**, 1694 (1966).
(15) W. Ando, Y. Saiki, and T. Migita, *Tetrahedron*, **29**, 3511 (1973); G. Andrews and D. A. Evans, *Tetrahedron Lett.*, 5121 (1972); M. Yoshimoto, S. Ishihara, E. Nakayama, and N. Soma, *ibid.*, 2923 (1972); I. Ojima and K. Kondo, *Bull. Chem. Soc. Jpn.*, **46**, 1539 (1973); K. Kondo and I. Ojima, *J. Chem. Soc., Chem. Commun.*, 62 (1972).
(16) W. Ando, H. Fujii, T. Takeuchi, H. Higuchi, Y. Saiki, and T. Migita, *Tetrahedron Lett.*, 2117 (1973), and references cited therein. Review: A. P. Marchand and N. M. Brockway, *Chem. Rev.*, **74**, 431 (1974). See also M. Numata, Y. Imashiro, I. Minamida, and M. Yamaoka, *Tetrahedron Lett.*, 5097 (1972); M. Yoshimoto, S. Ishihara, E. Nakayama, E. Shoji, H. Kuwano, and N. Soma, *ibid.*, 4387 (1972).
(17) See ref 10. Experimental details for the preparation of **7**-Ox and **8**-Ox will appear in the Ph.D. Thesis of C. B. Mallon, and are available, on request, from the authors.
(18) W. M. Wagner, *Proc. Chem. Soc., London*, 229 (1959).
(19) The σ_I values are 0.23 and 0.27, respectively: S. Ehrenson, R. T. C. Brownlee, and R. W. Taft, *Prog. Phys. Org. Chem.*, **10**, 1 (1973).
(20) R. A. Moss and C. B. Mallon, unpublished work.
(21) Attempts to construct stabilized allylic sulfonium ylides lead to [2,3] sigmatropic rearrangement products under even extremely mild conditions: J. E. Baldwin and W. F. Erickson, *Chem. Commun.*, 359 (1971).
(22) Boiling points and melting points are uncorrected. NMR spectra were determined in CCl_4 (unless otherwise indicated) with a Varian T-60 spectrometer. Chemical shifts are given in δ units, relative to an internal Me_4Si standard. Exact mass determinations employed an Hitachi Perkin-Elmer RMU-7E mass spectrometer. Exact mass calculations, and exclusion of possible alternative elemental compositions within ±5 mmu, were done using the computer program described by S. R. Shrader, "Introductory Mass Spectrometry", Allyn and Bacon, Boston, Mass., 1971, p 233 ff. Microanalyses were done by Micro-Tech Laboratories, Skokie, Ill.
(23) E. R. H. Jones and F. Sondheimer, *J. Chem. Soc.*, 615 (1949).
(24) T. Reichstein, *Helv. Chim. Acta*, **40**, 1621 (1957), employs a similar method for oxidation of the (oxy) acetal analog.
(25) In benzene solvent, the cyclohexyl "singlet" is a broad multiplet, δ 2.57–1.90.
(26) This procedure was adapted from the work of Corey et al.: E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84**, 866 (1962); **87**, 1345 (1965); R. Greenwald, M. Chaykovsky, and E. J. Corey, *J. Org. Chem.*, **28**, 1128 (1963).
(27) This procedure was adapted from W. S. Wadsworth, Jr., and W. D. Emmons, *J. Am. Chem. Soc.*, **83**, 1733 (1961).
(28) Conversions of **7**-Ox and **8**-Ox to **7** and **8** were apparently quantitative.

Communications

Heteroatom Directed Photoarylation. Photochemistry of Aryloxyenones

Summary: Aryloxyenones **1a** and **1b** undergo photocyclization–rearrangement to give dihydrofurans **2** and **7**, respectively.

Sir: Reported photoreactions of aryl ethers have been limited to (1) cleavage of the ether bond(s) followed by hydrogen abstraction from solvent to give phenols and (2) photorearrangement to give ortho- and para-substituted hydroxybiphenyls.[1] Photocyclization of unsubstituted diaryl ethers or aryl vinyl ethers to annelated dihydrofurans apparently has not been observed;[2,3] however, photocyclization–elimination of *o*-methoxyphenyl phenyl ethers[2] and *o*-chlorophenyl 1-naphthyl ether[3] to annelated furans in low to moderate yield has been reported. Herein, we communicate the photochemistry of 2-phenoxy-3,5,5-trimethylcyclohexen-2-one (**1a**), which represents the first report of nearly exclusive photochemical carbon–carbon bond formation from an unsaturated ether, to give an annelated dihydrofuran.

Aryloxyenone **1a** was prepared by the potassium hydride (0.1 equiv) assisted reaction of isophorone oxide[4] with 1.1 equiv of phenol in refluxing tetrahydrofuran solution containing 0.75 equiv of hexamethylphosphoramide (91% isolated yield, mp 104–105°). Pyrex-filtered photolysis of **1a** (20 g) was performed in benzene–methanol–acetic acid solution (2000 ml, equal portions of each solvent component) while purged with argon. After 23 hr irradiation with a 450-W high-pressure mercury arc lamp, <2% **1a** remained in the nearly colorless reaction mixture; formation of dihydrofuran **2** (95%), rearranged phenol **3** (~2%), and trace amounts of phenol and isophorone was observed (vpc analysis). Evaporation of solvent and partition of the reaction components between ether and 1 *N* sodium hydroxide solution gave nearly pure dihydrofuran **2** (88% yield) in the organic layer. Two crystallizations from ether–petroleum ether produced analytically pure **2** (80% yield, mp 85–87°, *m/e* 230).

Acidification of the sodium hydroxide layer gave, after ether extraction and crystallization from ether–petroleum ether, pure **3** (2% yield, mp 172–175°, *m/e* 230). The nmr spectrum of **3** in $CDCl_3$ above 5 ppm is nearly identical with that of **1** and displays singlets at 1.11 (6 protons, *gem*-dimethyl), 1.83 (3 protons, vinyl methyl), and 2.42 ppm (4 protons, two methylene groups). The phenolic proton in **3** appears as a broadened singlet at 5.8 ppm and exchanges with deuterium oxide, while the four aromatic protons appear as a complex multiplet at 6.8 to 7.4 ppm. Para aromat-