together in sealed degassed Pyrex ampules prepared by freeze–pump–thaw method. The solutions were then heated at 100 °C for 2.5 h, which corresponds to five half-lives of the initiator. After reaction the tubes were quenched in ice–water and opened before GLC analyses.

Control Experiment Ruling Out Reactions of Phenyl Disulfides with Either Phenyl Radicals or BP. *p*-Chlorothiophenol (0.2 M), BP (5×10^{-3} M), and naphthalene (5×10^{-3} M; internal standard) were heated in chlorobenzene at 100 °C for 2.5 h with (2×10^{-3} M) and without addition of phenyl disulfide. The addition did not change at all the yields of benzene and benzoic acid, thus, giving invariable k_a/k_d.

Analytical Procedure. The reaction mixtures were analyzed on a 6 ft × $^1/_8$ in. stainless steel column packed with 10% OV-101 or 10% OV-17 on Chromosorb W by temperature programming from 80 to 200 °C by using Varian Vista 4600 GC equipped with FID and CDS 401 data system. Benzene and benzoic acid were separately analyzed, the latter being silylated with 1,1,1,3,3,3-hexamethyldisilazane before GLC analyses.

Analytical Method. The relative rates (k_a/k_d) for the thiophenols were obtained from the slopes of the lines attained by eq 5.

Acknowledgment. We warmly thank the Korea Science and Engineering Foundation for financial assistance. We are also very grateful to the Inha University for the generous support, to Dr. Jeffrey I. Seeman for reading the entire manuscript, and to Dr. Chawng Siek Pak for continuous assistance throughout research. Finally one of us (S.S.K.) thanks professor Cheves Walling for the numerous valuable suggestions and comments.

Registry No. *p*-$MeOC_6H_4SH$, 696-63-9; *p*-MeC_6H_4SH, 106-45-6; *p*-FC_6H_4SH, 371-42-6; PhSH, 108-98-5; *p*-ClC_6H_4SH, 106-54-7; PhC(O)O•, 1854-28-0.

[2 + 2] Cycloaddition of Dichloroketene to Allyl Ethers and Thioethers

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During the development of an efficient synthesis of the commercially valuable aggregation pheromone lineatin (1),[1] we investigated the addition of dichloroketene to allylic ether 2.[2] Initial experiments wherein dichloroketene was generated by dehydrohalogenation of dichloroacetyl chloride or by zinc dehalogenation of trichloroacetyl chloride gave only low yields of adducts. In the case of dehydrohalogenation route, the low yields were attributed to polymerization of dichloroketene by triethylammonium chloride[3] produced during ketene formation. This approach was abandoned after methods to circumvent this problem by slow addition of reagents[3] failed to give useful yields of adducts.

In the case of the dehalogenation route, low yields were attributed to $ZnCl_2$-induced side reactions. Sequestering of $ZnCl_2$ by addition of phosphorus oxychloride[4] gave a low yield (33% overall) of the desired [2 + 2] cycloadduct 3 (7%) and a moderate yield of the product 4 (26%) arising from rearrangement (Figure 1). Indeed, reaction of dichloroketene with allyl ethers and allyl sulfides 5 typically results in rearrangement (6) rather than [2 + 2] cycloaddition (7).[5,6] The proposed mechanism for the formation of the rearrangement product is a [3,3]-sigmatropic rearrangement of the initially formed dipolar intermediate 8. This process is presumably promoted by $ZnCl_2$. For the reaction of dichloroketene with allylic ether 2, the addition of phosphorus oxychloride did not provide sufficiently strong $ZnCl_2$ complexation to prevent its catalysis of this rearrangement. Substitution of 1,2-dimethoxyethane for phosphorus oxychloride efficiently suppressed the formation of 4, and a 50–60% yield of 3 could be realized. Optimum conditions were 4–6 equiv of 1,2-dimethoxyethane/equiv of trichloroacetyl chloride with the reaction carried out in refluxing ether for 4–5 days.

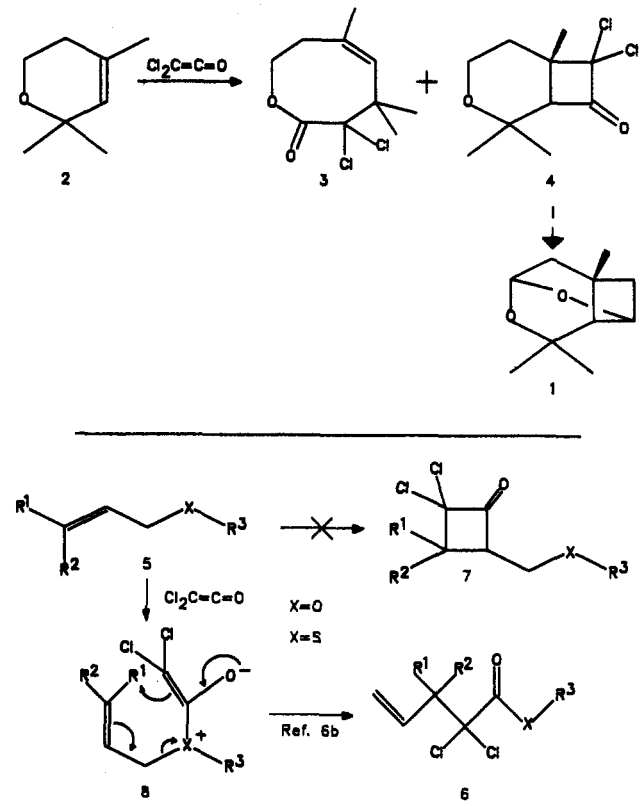


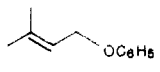
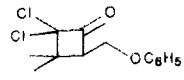
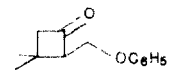
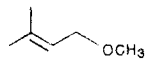
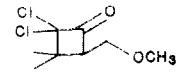
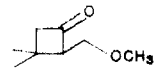
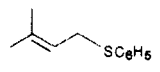
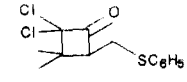
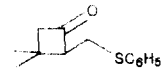
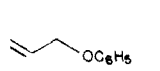
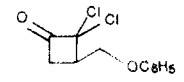
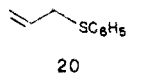
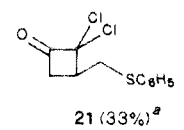
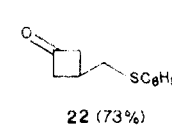
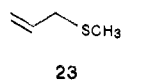
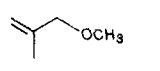
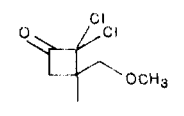
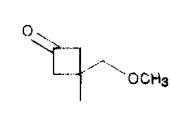
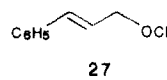
Figure 1.

In this paper, we report that the use of 1,2-dimethoxyethane as a cosolvent for [2 + 2] dichloroketene addition to allyl ethers and allyl sulfides has general utility. Addition of dichloroketene to each substrate in Table I using our modified conditions gave none of the Claisen rearrangement products. Several of these substrates have been previously shown to yield predominantly Claisen-type rearrangement products when dichloroketene was generated by the standard trichloroacetyl chloride/zinc method.[6b] For each substrate dichlorocyclobutanones were the major products. Yields of the [2 + 2] cycloadducts were, for the most part, in the range of 66–85%. Although certain of the products were unstable and tended to decompose during distillation or chromatography, dechlorination with zinc proceeded smoothly to yield the corre-

(1) (a) Skattebol, L.; Stenstrom, Y. *Acta Chem. Scand., Ser. B* **1985**, *B39*, 291. (b) *Tetrahedron Lett.* **1983**, *24*, 3021.
(2) Johnston, B. D.; Slessor, K. N.; Oehlschlager, A. C. *J. Org. Chem.* **1985**, *50*, 114.
(3) Hassner, A.; Cory, R. M.; Sartoris, N. *J. Am. Chem. Soc.* **1976**, *98*, 7698.
(4) Krepski, L. R.; Hassner, A. *J. Org. Chem.* **1978**, *43*, 2879.
(5) Brady, W. T. In *The Chemistry of Ketenes, Allenes and Related Compounds*, Part I; Patai, S., Ed.; Wiley: New York, 1980; pp 279–308.
(6) (a) Malherbe, R.; Bellus, D. *Helv. Chim. Acta* **1978**, *61*, 3096. (b) Malherbe, R.; Rist, G.; Bellus, D. *J. Org. Chem.* **1983**, *48*, 860.

0022-3263/87/1952-3693$01.50/0

Table I. Reaction of Dichloroketene with Allyl Ethers and Sulfides

allyl derivative	dichlorocyclobutanone (% yield)	cyclobutanone (% yield)
 9	 10 (65%)	 11 (89%)
 12	 13 (76%)	 14 (73%)
 15	 16 (66%)	 17 (69%)
 18	 19 (86%)[a]	
 20	 21 (33%)[a]	 22 (73%)
 23	complex mixture	
 24	 25 (28%)[a]	 26 (87%)
 27	slow reaction	

[a] Unstable product.

sponding cyclobutane derivatives.

The [2 + 2] cycloaddition of dichloroketene to thioketal and ketal derivatives of α,β-unsaturated ketones would constitute a formal nonphotochemical method for the cycloaddition of a ketene to α,β-unsaturated ketones. Since preparation of ketals of many, α,β-unsaturated ketones results in mixtures in which the unsaturation is α,β and β,γ, we centered our attention on thioketals. These substrates are known to undergo ring expansion of the dithiolane moiety when treated with dichloroketene[7] under ordinary conditions. Thus, addition of dichloroketene to **28**, has previously been reported to yield **29**.[7]

When we reacted dichloroketene with **28** in the presence of 1,2-dimethoxyethane, we obtained a diminished yield of **29** and concomitant formation of a second more polar component **30** (~26% yield), whose elemental composition and spectral characteristics (IR ν_{max} 1690, 1710 cm^{-1}) indicated it was a 2:1 adduct of dichloroketene and **28** (Figure 2).

The structure of **30** was deduced by a series of ^{13}C and ^{1}H NMR experiments involving selective decoupling of ^{1}H signals and observation of their effect on long-range $^{1}H/^{13}C$ couplings. Thus, irradiation of the signals due to the hydrogens on the C_{10} methyl caused decoupling of C_9 (CCl_2, δ 98.20), but not C_2(CCl_2, δ 91.10). Disappearance of long-range $^{1}H/^{13}C$ coupling at C_{14} (δ 131.55, —CH=) was also observed in this experiment, while the ^{13}C signals of both carbonyl groups (C_3, C_8) remained unchanged. Irradiation of the signal due to the vinyl hydrogen on C_{14} did not result in decoupling of either carbonyl carbon resonance but did decouple C_2 (CCl_2, δ 91.10). Irradiation of the signals due to the hydrogens on C_5 and C_6 caused decoupling of both carbonyl carbon resonances. These experiments establish the atom connectivity of the 11-membered ring of **30**. The ^{1}H NMR spectrum of **30** shows additional signals due to the isolated CH_2 groups (C_{11} and C_{13}) and two quaternary methyls (on C_{12}). Given the symmetry of the C_{11}–C_{13} fragment and its required connectivity to C_1 and C_{10}, the substitution pattern of the cyclohexenyl ring of **30** is apparent.

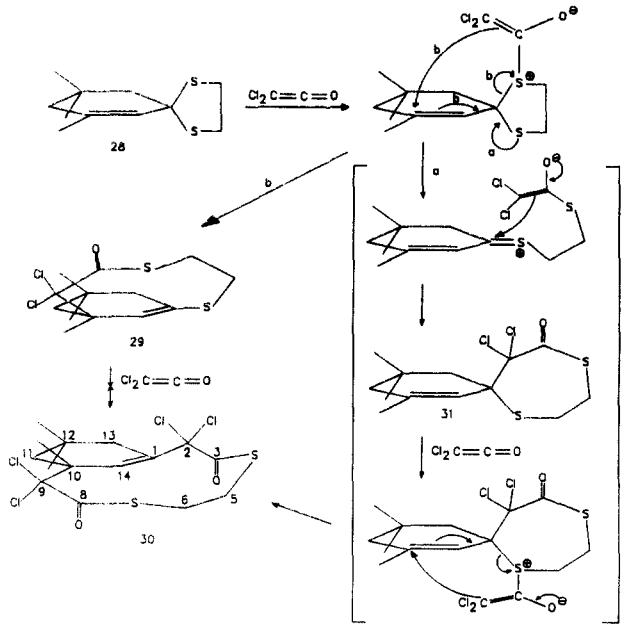


Figure 2.

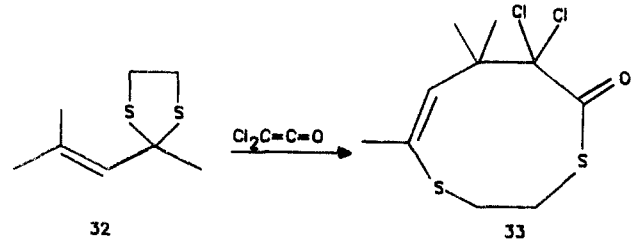
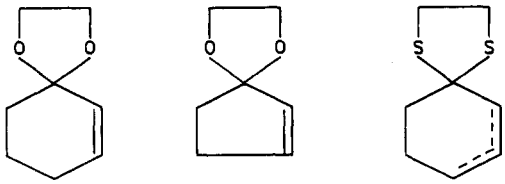


Figure 3.

Although an attractive route to **30** is via dichloroketene addition to **29** (Figure 2, route **b**), this reaction does not give more than trace quantities of components with thin-layer chromatographic behavior similar to **30**. An alternative process for the formation of **30** involves route a shown in Figure 2. This pathway would be expected to increase in importance if zinc ion activity were decreased by complexation with 1,2-dimethoxyethane. A search of the reaction mixture of the reaction of **28** with dichloroketene for the intermediate **31** proposed in route a revealed only **29** in the chromatographic region expected of 1:1 dichloroketene adducts of **28**.

Reaction of **32** with dichloroketene under our modified conditions gave a 44% yield of **33** (Figure 3). We were similarly unsuccessful at suppressing the 3,3-sigmatropic rearrangement during addition of dichloroketene to **34–36** (Figure 4). Analysis of (GC/FTIR) of the reaction mix-

(7) Rosini, G.; Spineti, G. G.; Foresti, E.; Pradella, G. *J. Org. Chem.* **1981**, *46*, 2228.



34 35 36

Figure 4.

tures from reactions of **34–36** with dichloroketene failed to reveal any evidence for cyclobutanone formation.

Experimental Section

NMR spectra were recorded on a Bruker WM400 spectrometer unless otherwise stated. ^1H NMR spectra (60 and 100 MHz) were recorded with Varian EM-360 and Bruker SY100 instruments. Infrared spectra were recorded as neat films between NaCl plates on a Perkin-Elmer 599B spectrophotometer unless otherwise noted. Mass spectra were obtained with a Hewlett-Packard 5985B GC/MS/DS system operating at 70 eV. Gas chromatographic analysis utilized a Hewlett-Packard 5880A operated with a J&W fused silica DB-1 capillary column (15 m × 0.25 mm), a flame-ionization detector, and a suitable linear oven temperature program. Elemental analyses were performed by M. Yang of the Department of Biological Sciences, Simon Fraser University, with a Perkin-Elmer Model 240 elemental analyzer.

Solvents and reagents were used as supplied from commercial sources with the following exceptions. Chromatography solvents were distilled before use. Anhydrous ether was obtained from freshly opened cans (Fisher Scientific) or by distillation from lithium aluminum hydride. Tetrahydrofuran (THF) was distilled from sodium or potassium benzophenone ketyl immediately prior to use. 1,2-Dimethoxyethane was distilled from lithium aluminum hydride immediately prior to use. Zinc was activated by the method of Krepski and Hassner.[4] All reactions involving air- or moisture-sensitive reagents were performed under an argon atmosphere.

Synthesis of Allyl Ethers and Allyl Sulfides. Allyl phenyl ether (**18**) allyl methyl sulfide (**23**) were commercial products (Aldrich). Cinnamyl methyl ether (**27**) and 2-methyl-2-propenyl methyl ether (**24**) were prepared by methylation of the corresponding alcohols with dimethyl sulfate.[8] Allyl phenyl sulfide (**20**) was prepared from allyl bromide and thiophenol.[9]

Preparation of 3-Methyl-2-butenyl Phenyl Ether (9). Phenol (10.0 g, 106 mmol) was added to a stirred mixture of acetone (50 mL) and K_2CO_3 (17.0 g, 123 mmol) at room temperature. After 10 min, 1-bromo-3-methyl-2-butene (14.9 g, 100 mmol) was added and the mixture stirred at room temperature for 16 h. After filtration and solvent removal in vacuo, the residue was dissolved in hexane (100 mL) and washed with water (2 × 50 mL). Drying (anhydrous $MgSO_4$), solvent removal, and distillation yielded **9**: 10.2 g, 63%; bp 60–63 °C (0.1 mmHg); ^1H NMR ($CDCl_3$) δ 7.28 (2 H, phenyl, m), 6.93 (3 H, phenyl, m), 5.51 (1 H, C=CH, tm, J_{vic} = 7 Hz), 4.51 (1 H, OCH_2, d, J_{vic} = 7 Hz), 1.80 (3 H, CH_3, s), 1.74 (3 H, CH_3, s).

Preparation of 3-Methyl-2-butenyl Methyl Ether (12). 1-Bromo-3-methyl-2-butene (7.45 g, 50.0 mmol) was added dropwise to a solution of $NaOCH_3$ (61 mmol) in anhydrous methanol with stirring over 10 min. After a further 0.5 h, the reaction mixture was poured into pentane (75 mL) and water (100 mL). The pentane layer was separated and dried over anhydrous $MgSO_4$. Careful removal of the pentane at atmospheric pressure through a Vigreux column followed by distillation of the residue yielded **12**: 2.3 g, 46%; bp 104–105 °C (760 mmHg); a forerun [1.2 g; bp 80–104 °C (760 mmHg)] was contaminated with ~20% of the tertiary ether resulting from S_N2' reaction; ^1H NMR ($CDCl_3$) δ 4.95 (1 H, C=CH, s), 4.89 (1H, C=CH, s), 3.82 (2 H, OCH_2, s), 3.32 (3 H, OCH_3, s), 1.73 (3 H, CH_3, s).

Preparation of 3-Methyl-2-butenyl Phenyl Sulfide (15). This compound was prepared in 50% yield by the ZnI_2-catalyzed reaction of 2-methyl-3-buten-2-ol with thiophenol:[10] bp 75–78 °C (0.2 mmHg); ^1H NMR (100 MHz, $CDCl_3$) δ 7.6–7.1 (5 H, aromatic, m), 5.41 (1 H, vinyl H, t, J = 8 Hz), 3.63 (2 H, SCH_2, d, J = 8 Hz), 1.83 (3 H, CH_3, s), 1.70 (3 H, CH_3, s).

General Procedure for the Cycloaddition of Dichloroketene with Allyl Ethers or Allyl Sulfides. A solution of the allyl ether or sulfide (20 mmol) in anhydrous ether (75 mL) and 1,2-dimethoxyethane (10 mL) containing activated zinc (4.0 g, 62 mmol) and trichloroacetyl chloride (6.0 mL, 54 mmol) was refluxed under an argon atmosphere for 40–60 h. The reaction mixture was filtered and the excess Zn rinsed with anhydrous ether (3 × 25 mL). The ether was removed in vacuo and the residue dissolved in hexane (100 mL). Insoluble material was removed by filtration and the filtrate washed with saturated $NaHCO_3$ solution (2 × 100 mL) and with brine (50 mL). After drying (anhydrous $MgSO_4$), the solvent was removed in vacuo and the crude product purified by distillation or chromatography on silica gel.

General Procedure for Reductive Dechlorination of the Dichlorocyclobutanone Adducts. A solution of the dichloro cycloadduct (5 mmol) in methanol (20 mL) saturated with NH_4Cl was stirred with Zn powder (2 g) at room temperature for 1–3 h. Filtration and solvent removal in vacuo yielded a mixture of the product with Zn salts. The residue was partitioned between ether (75 mL) and water (25 mL). After further washing with water (2 × 25 mL), the ether solution was dried (anhydrous $MgSO_4$) and concentrated to yield the product. Final purification consisted of bulb-to-bulb distillation at reduced pressure.

Preparation of 2,2-Dichloro-3,3-dimethyl-4-(phenoxymethyl)cyclobutanone (10). Reaction of dichloroketene with **9** yielded **10** (65%) after purification by distillation [bp 110–115 °C (0.1 mmHg)]. The distillate slowly crystallized, and an analytical sample was obtained by recrystallization from pentane: mp 46–47 °C; ^1H NMR ($CDCl_3$) δ 7.3–6.8 (5 H, phenyl, m), 4.28 (1 H, OCH, dd, J_{gem} = 10 Hz, J_{vic} = 5 Hz), 4.11 (1 H, OCH′, t, J = 10 Hz), 3.97 (1 H, C_4 H, dd, $J_{OCH'}$ = 10 Hz, J_{OCH} = 5 Hz), 1.61 (3 H, CH_3, s), 1.32 (3 H, CH_3, s); mass spectrum, EI m/e (relative intensity) 274, 272 (2, M^+), 148 (32), 107 (14), 94 (16), 79 (7), 77 (15), 55 (100). Anal. Calcd for $C_{13}H_{14}O_2Cl_2$: C, 57.16; H, 5.17. Found: C, 57.35; H, 5.06.

Preparation of 3,3-Dimethyl-2-(phenoxymethyl)cyclobutanone (11). Dechlorination of **10** yielded **11** in 89% yield after bulb-to-bulb distillation: bp 90–100 °C (0.2 mmHg); ^1H NMR ($CDCl_3$) δ 7.3–6.8 (5 H, phenyl, m), 4.19 (1 H, OCH, dd, J_{gem} = 10 Hz, J_{vic} = 4 Hz), 4.07 (1 H, OCH′, t, J = 10 Hz), 3.45 (1 H, C_2 H, m), 2.92 (1 H, C_4H, dd, J_{gem} = 17 Hz, J_{C_2H} = 3 Hz), 2.69 (1 H, C_4 H, dd, J_{gem} = 17 Hz, J_{C_2H} = 2 Hz), 1.50 (3 H, CH_3, s), 1.26 (3 H, CH_3, s); mass spectrum, EI m/e (relative intensity) 204 (7, M^+), 111 (37), 95 (12), 94 (100), 78 (10), 69 (80), 55 (48), 41 (15). Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H 7.90. Found: C, 76.80; H, 7.82.

Preparation of 2,2-Dichloro-3,3-dimethyl-4-(methoxymethyl)cyclobutanone (13). Reaction of **12** with dichloroketene yielded **13** (76%) after vacuum distillation: bp 65–67 °C (0.1 mmHg); IR 2970 (m), 2930 (m), 2880 (m), 2825 (m), 1805 (s), 1466 (m), 1390 (m), 1245 (m), 1202 (m), 1178 (m), 1130 (s), 1103 (s), 932 (m), 860 (m), 808 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.72 (1 H, OCH, dd, J_{gem} = 9 Hz, J_{vic} = 5 Hz), 3.62 (1 H, C_4 H, dd, J = 10, 5 Hz), 3.56 (1 H, OCH′, dd, J_{gem} = 9 Hz, J_{vic} = 10 Hz), 3.32 (3 H, OCH_3, s), 1.53 (3 H, CH_3, s), 1.27 (3 H, CH_3, s); mass spectrum, EI m/e (relative intensity) 139/141 (23), 125 (15), 119/121 (100), 45 (12); CI (isobutane) 213/211 (100, M^+ + 1).

Preparation of 3,3-Dimethyl-2-(methoxymethyl)cyclobutanone (14). Dechlorination of **13** yielded **14** (73%) after bulb-to-bulb distillation: bp 65–75 °C (15 mmHg); IR 2960 (m), 2920 (m), 2865 (m), 1775 (s), 1460 (m), 1380 (m), 1370 (m), 1248 (m), 1190 (m), 1123 (m), 1085 (m), 1040 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.52 (2 H, OCH_2, m), 3.31 (3 H, OCH_3, s), 3.19 (1 H, C_2H, m), 2.83 (1 H, C_4H, dd, J_{gem} = 17 Hz, J_{C_2H} = 3 Hz), 2.62 (1 H, C_4 H′, dd, J_{gem} = 17 Hz, J_{C_2H} = 2 Hz), 1.42 (3 H, CH_3, s), 1.22 (3 H, CH_3, s); mass spectrum, EI m/e (relative intensity) 110 (15), 85 (100), 83 (13), 82 (30), 69 (23), 67 (12), 45 (15), 41 (20); mass spectrum, CI (isobutane) m/e 143 (10, M^+ + 1) 111 (100).

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Preparation of 2,2-Dichloro-3,3-dimethyl-4-[(phenylthio)methyl]cyclobutanone (16). Reaction of **15** with dichloroketene yielded **16** (66%) after distillation: bp 135–140 °C (0.3 mmHg); ^{1}H NMR ($CDCl_3$) δ 7.5–7.3 (5 H, phenyl, m), 3.69 (1 H, C_4 H, dd, $J_{SCH'}$ = 10 Hz, J_{SCH} = 6 Hz), 3.49 (1 H, SCH, dd, J_{gem} = 14 Hz, J_{vic} = 6 Hz), 3.00 (1 H, SCH′, dd, J_{gem} = 14 Hz, J_{vic} = 10 Hz), 1.65 (3 H, CH_3, s), 1.38 (3 H, CH_3, s). Anal. Calcd for $C_{13}H_{14}Cl_2OS$: C, 53.99; H, 4.88. Found: C, 54.15; H, 5.10.

Preparation of 3,3-Dimethyl-2-[(phenylthio)methyl]-cyclobutanone (17). Dechlorination of **16** yielded **17** (69%) after bulb-to-bulb distillation: bp 105–110 °C (0.2 mmHg); ^{1}H NMR ($CDCl_3$) δ 7.3–6.8 (5 H, phenyl, m), 3.25 (1 H, SCH, dd, J_{gem} = 13 Hz), 2.85 (1 H, C_2 H, dm, $J_{SCH'}$ = 11 Hz), 2.70 (1 H, SCH′, dd, J_{gem} = 13 Hz, J_{vic} = 11 Hz), 2.31 (1 H, C_4 H, dd, J_{gem} = 16.5 Hz, J_{C_2H} = 2.2 Hz), 2.15 (1 H, C_4 H, dd, J_{gem} = 16.5 Hz, J_{C_2H} = 1.8 Hz), 1.09 (3 H, CH_3, S), 0.88 (3 H, CH_3, s); mass spectrum, EI m/e (relative intensity) 220 (100, M^+ + 1), 178 (10), 111 (42), 110 (35), 69 (39), 45 (20). Anal. Calcd for $C_{13}H_{16}OS$: C, 70.87; H, 7.32. Found: C, 71.03; H, 7.42.

Preparation of 2,2-Dichloro-3-(phenoxymethyl)cyclobutanone (19). Reaction of **18** with dichloroketene yielded **19** (86%) after vacuum distillation: bp 103–110 °C (0.1 mmHg); ^{1}H NMR ($CDCl_3$) δ 7.3–6.8 (5 H, phenyl, m), 4.38 (1 H, OCH, dd, J_{gem} = 10 Hz, J_{vic} = 6 Hz), 4.23 (1 H, OCH′, dd, J_{gem} = 10 Hz, J_{vic} = 6 Hz), 3.58 (1 H, C_4 H, dd, J_{gem} = 17 Hz, J_{vic} = 9 Hz), 3.40 (1 H, C_3 H, m), 3.28 (1 H, C_4 H′, dd, J_{gem} = 17 Hz, J_{vic} = 9 Hz). This compound proved to be unstable in air and decomposed over a period of several days.

Preparation of 2,2-Dichloro-3-[(phenylthio)methyl]-cyclobutanone (21). Reaction of **20** with dichloroketene yielded **21** (33%) after purification by silica gel chromatography (hexane/ethyl acetate, 4:1). The chromatography caused extensive decomposition, and the yield of crude product was much greater: IR 3060 (m), 2930 (m), 1810 (s), 1584 (m), 1483 (m), 1440 (m), 1390 (m), 1258 (m), 1215 (m), 1180 (m), 1088 (m), 1060 (m), 1027 (m), 983 (m), 746 (m), 695 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.2–7.5 (5 H, phenyl, m), 3.43 (2 H, C_2H, C_3H, m), 3.08 (3 H, C_2H′, SCH_2, m). This adduct was further characterized after dehalogenation because of its unstable nature.

Preparation of 3-[(Phenylthio)methyl]cyclobutanone (22). Dechlorination of **21** yielded **22** (73%) after bulb-to-bulb distillation: bp 80–90 °C (0.2 mmHg); IR 3050 (m), 2960 (m), 2910 (m), 1780 (m), 1578 (m), 1476 (m), 1433 (m), 1378 (m), 1255 (m), 1229 (m), 1085 (m), 1020 (m), 737 (s), 688 (m) cm^{-1}; ^{1}H NMR (C_6D_6) δ 7.3–6.9 (5 H, phenyl, m), 2.65–2.55 (2 H, C_2 H, 19-line multiplet), 2.46 (2 H, SCH_2, d, J = 7.5 Hz), 2.37–2.27 (2 H, C_2 H′, C_4 H′, 14-line multiplet), 2.05–1.92 (1 H, C_3 H, 28-line multiplet); mass spectrum, EI m/e (relative intensity) 192 (100), 150 (75), 149 (33), 148 (46), 135 (95), 130 (27), 123 (48), 117 (60), 110 (20), 109 (26), 83 (23), 69 (20), 65 (15), 55 (19), 45 (15), 41 (18). Anal. Calcd for $C_{11}H_{12}OS$: C, 68.71; H, 6.29. Found: C, 68.88; H, 6.40.

Preparation of 2,2-Dichloro-3-methyl-3-(methoxymethyl)cyclobutanone (25). Reaction of **24** with dichloroketene yielded **25** (28%) after distillation. The yield of crude product was better, but extensive decomposition occurred during the distillation: bp 70–80 °C (0.1 mmHg); IR 2985 (m), 2930 (m), 2890 (m), 2825 (m), 1815 (s), 1460 (m), 1400 (m), 1202 (m), 1118 (s), 985 (m), 756 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.60 (1 H, OCH, d, J_{gem} = 9.5 Hz), 3.50 (1 H, OCH′, d, J_{gem} = 9.5 Hz), 3.37 (3 H, OCH_3, s), 3.23 (1 H, C_4 H, d, J_{gem} = 17 Hz), 3.01 (1 H, C_4 H′, d, J_{gem} = 17 Hz), 1.44 (3 H, CH_3, s); mass spectrum, CI (isobutane) m/e (relative intensity) 197/199 (80, M^+ + 1).

Preparation of 3-Methyl-3-(methoxymethyl)cyclobutanone (26). Dechlorination of **25** yielded **26** (87%) after bulb-to-bulb distillation: bp 80–90 °C (15 mmHg); IR 2960 (m), 2920 (m), 2870 (m), 1780 (s), 1460 (m), 1383 (m), 1275 (m), 1185 (m), 1105 (m), 962 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.40 (3 H, OCH_3, s), 3.39 (2 H, OCH_2, s), 3.02 (2 H, C_2 H, C_4 H, dm, J_{gem} = 20 Hz), 2.67 (2 H, C_2 H′, C_4 H′, dm, J_{gem} = 20 Hz), 1.33 (3 H, CH_3, s); mass spectrum, CI (isobutane) m/e (relative intensity) 129 (90, M^+ + 1), 97 (100). Anal. Calcd for $C_7H_{12}O_2$: C, 65.60; H 9.44. Found: C, 65.55; H, 9.37.

Reaction of Dichloroketene with 23 and 27. Reaction of dichloroketene with allyl methyl sulfide (**23**), using the standard protocol, rapidly produced a complex mixture of products, which promptly decomposed. Reaction with cinnamyl methyl ether (**27**), on the other hand, went extremely slowly with over 70% enreacted allyl ether left after 48 h. ^{1}H NMR analysis of the crude reaction mixture indicated that the major product was the result of Claisen rearrangement rather than [2 + 2] cycloaddition. Neither of these reactions was investigated further.

Preparation of the Ketals and Thioketals. 7,9,9-Trimethyl-1,4-dithiaspiro[4.5]dec-6-ene (**28**) was prepared according to the procedure in ref 7. 1,4-Dioxaspiro[4.5]dec-6-ene (**34**) was prepared according to the procedure in ref 11. 1,4-Dioxaspiro-[4.4]non-6-ene (**35**) was purchased from Aldrich and distilled prior to use. Preparation of 1,4-dithiaspiro[4.5]dec-6-ene (**36**), using the standard BF_3·Et_2O method, gave a mixture of α,β- and β,γ-unsaturated ketals.

Preparation of Dichloroketene with 7,9,9-Trimethyl-1,4-dithiaspiro[4.5]dec-6-ene (28). The mixture obtained from reaction of dichloroketene with **28**,[7] under the conditions described above (Table I) for allyl ethers and thioethers (reflux 20 h), was subjected to chromatography on silica gel with hexane/ethyl acetate (95:5) as eluent. This separation gave a 33% yield of 2,2-dichloro-3-keto-4,7-dithia-1,10,10-trimethylbicyclo[6.3.1]dodec-8(12)-ene [**29**; mp 94–95 °C (lit.[7] mp 90–92 °C] and 10% of 2,2,9,9-tetrachloro-3,8-dioxo-4,7-dithia-10,12,12-trimethylbicyclo[8.3.1]tetradec-1(14)-ene (**30**). **30**: mp 162–164 °C; IR (Nujol) 1690 (s), 1710 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.00 (3 H, CH_3, s), 1.13 (3 H, CH_3, s), 1.43 (1 H, C_{11} H, br d J_{gem} = 14 Hz), 1.49 (3 H, CH_3, d, J = 3.5 Hz), 2.03 (1 H, C_{13}H, br dd, J_{gem} = 17 Hz, $J_{C_{14}H}$ = 2 Hz), 2.45 (1 H, C_{11} H, d, J_{gem} = 14 Hz), 2.49 (1 H, C_{13} H, dd J_{gem} = 17 Hz, $J_{C_{14}H}$ = 2.5 Hz), 3.08 (1 H, $C_{5,6}$ H, d, J = 14 Hz), 3.13 (1 H, $C_{5,6}$ H, dt J = 2.5, 14.5 Hz), 3.46 (1 H, $C_{5,6}$ H, td, J = 2.5, 14 Hz), 3.59 (1 H, $C_{5,6}$ H, m), 5.97 (1 H, C_{14} H, br d J = 2 Hz); ^{1}H NMR (C_6D_6) δ 0.79 (3 H, CH_3, s), 0.94 (3 H, CH_3, s), 1.31 (1 H, C_{11} H, br d, J_{gem} = 14 Hz), 1.35 (3 H, CH_3, d, J = 1 Hz), 1.91 (1 H, $C_{5,6}$ H, br d, J = 14 Hz), 2.03 (1 H, $C_{5,6}$ H, J = 14 Hz), 2.18 (1 H, C_{13} H, br d, J_{gem} = 17 Hz), 2.55 (1 H, C_{13} H, br dd, J_{gem} = 17 Hz, $J_{C_{14}H}$ = 2.5 Hz), 2.72 (1 H, C_{11} H, br d, J_{gem} = 14 Hz), 3.00 (2 H, $C_{5,6}$ H, m), 6.24 (1 H, C_{14} H, d, J = 2.5 Hz); ^{13}C NMR ($CDCl_3$) δ 23.36 (q), 27.56 (q), 29.16 (t), 31.21 (s), 32.40 (q) 33.53 (t), 39.11 (t), 42.11 (t), 49.15 (s), 91.10 (s), 98.20 (s), 131.55 (d), 140.11 (s), 189.53 (s), 194.31 (s); mass spectrum, m/e (relative intensity) 316 (17), 314 (14), 288 (10), 275 (16), 273 (36), 271 (27), 255 (29), 254 (12), 253 (100), 252 (12), 251 (97), 206 (46), 205 (11), 204 (69), 197 (27), 195 (12), 189 (13), 170 (64), 161 (31), 153 (13), 145 (10), 144 (24), 143 (13), 142 (31), 141 (15), 139 (23), 133 (14), 129 (21), 128 (13), 127 (19), 93 (14), 92 (58), 91 (44), 89 (22), 98 (12), 83 (19), 79 (31), 78 (11), 77 (78); mass spectrum, CI (isobutane) m/e (relative intensity) 439 (1), 437 (2), 435 (1) (M + 1). Anal. Calcd for $C_{15}H_{18}Cl_4O_2S_2$: C, 41.50; H, 4.15. Found: C, 41.91; H, 4.28.

When the reaction of dichloroketene with **28** was carried out as described above, except that the reaction solvent was 1,2-dimethoxyethane, the yields of **29** and **30** were 42% and 27%, respectively.

Reaction of Dichloroketene with 32. The mixture obtained from reaction of dichloroketene with **32**, under the conditions as described (Table I) for allyl ethers and thioethers (reflux 24 h), was purified on silica gel with hexane/ethyl acetate (10:1) as eluent. The major product crystallized from hexane to yield 44% of 1-keto-2,5-dithia-9,9-dichloro-6,8,8-trimethylnon-6-ene (**33**): mp 84–87 °C; IR (Nujol) 1700 cm^{-1}; ^{1}H NMR ($CDCL_3$) δ 0.51 (3 H, CH_3, s), 1.67 (3 H, CH_3, s), 2.08 (3 H, CH_3, d, J = 3 Hz), 2.97 (2 H, $S(CH_2)_2S$, m), 3.32 (1 H, $S(CH_2)_2S$, m), 3.97 (1 H, $S(CH_2)_2S$, m), 5.64 (1 H, vinyl H, brs); ^{13}C NMR ($CDCl_3$) δ 24.21 (q), 25.74 (q), 28.77 (q), 32.48 (t), 38.25 (t), 49.26 (s), 97.58 (s), 137.53 (d), 137.79 (s), 194.09 (s); mass spectrum, m/e (relative intensity) 286 (9), 284 (13), 113 (100); mass spectrum, CI (isobutane) m/e (relative intensity) 287/285 (M + 1). Anal. Calcd for $C_{10}H_{14}OCl_2S_2$: C, 42.10; H, 4.91. Found: C, 42.01; H, 5.09.

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of the 400-MHz NMR spectrometer. Special acknowledgement is drawn to Dr. Alan Tracey of Simon Fraser University for design execution and interpretation of the decoupling experiment.

Registry No. **9**, 14309-15-0; **10**, 108711-49-5; **11**, 108711-50-8; **12**, 22093-99-8; **13**, 69690-89-7; **14**, 108711-51-9; **15**, 10276-04-7; **16**, 69862-37-9; **17**, 108711-52-0; **18**, 1746-13-0; **19**, 84473-44-9; **20**, 5296-64-0; **21**, 108711-53-1; **22**, 108711-54-2; **23**, 10152-76-8; **24**, 22418-49-1; **25**, 84473-43-8; **26**, 108711-55-3; **27**, 16277-67-1; **28**, 76793-94-7; **29**, 76793-95-8; **30**, 108711-56-4; **32**, 65447-92-9; **33**, 108711-57-5; dichloroketene, 4591-28-0; phenol, 108-95-2; 1-bromo-3-methylbutene, 870-63-3; 2-methyl-3-butene-2-ol, 115-18-4; thiophenol, 108-98-5; trichloroacetyl chloride, 76-02-8.

α-Phenylation of Ketones. Reaction of Bromo Enamines with Phenylcopper Reagents

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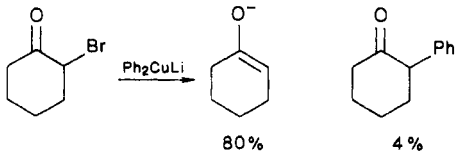
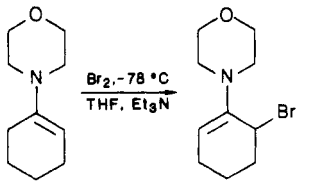
The introduction of a phenyl group α to a carbonyl is a useful step in the synthesis of a variety of biologically interesting compounds. Among the most successful phenylation procedures are the S_RN_1 reaction,[1] the reaction of arylboranes with α-bromo ketones[2] and the reaction of (*p*-tolylsulfonyl)azo olefins[3] or α,β-epoxy ketones[4] with lithium diphenylcuprate. The conceptually simple phenylation procedure based on reaction of α-halo ketones with phenylcopper reagents fails to give good yields because of a competing reduction (eq 1).[3] Our approach to



(1)

this problem is based on the observation that enamines are readily brominated at low temperature in the presence of triethylamine.[5] Although we find that solutions of the brominated products are stable for at least several hours at room temperature, concentration of the solutions results in decomposition. However, ^{1}H NMR analysis of the reaction mixture obtained from the morpholine enamine of cyclohexanone revealed a quantitative yield of the allylic bromide **1** (eq 2). We examined the reaction of a freshly prepared THF solution of **1** with a variety of organometallics (PhM) with the results shown in eq 3. Results obtained with a variety of enamines by using Ph_2CuLi are shown in Table I. The sequence appears to provide a simple method for the phenylation of symmetrical ketones in good yield. The enamine of acetophenone, which can form only a vinylic bromide, is phenylated in relatively poor yield (19%, Table I).

The regiochemistry of the phenylation reaction was briefly examined by using the equilibrium mixture of



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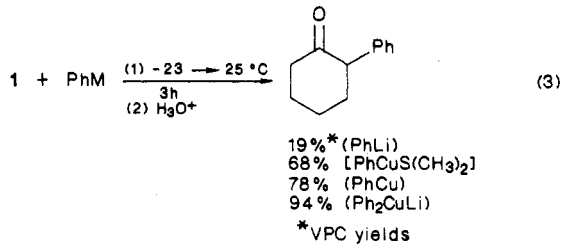
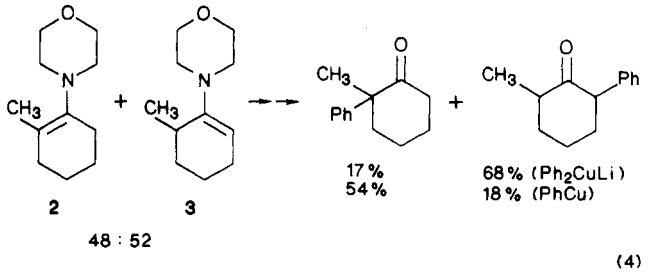


(3)

morpholine enamines of 2-methylcyclohexanone (**2** and **3**, eq 4). Interestingly, Ph_2CuLi and PhCu give a different



(4)

regioisomer major product. In neither case, however, is the ratio of products related simply to the ratio of starting enamines. Presumably this is a result of the known ability of organocuprates to react with allylic substrates both with and without allylic rearrangement.[6]

Experimental Section

All the enamines except that of acetophenone were prepared by the azeotropic method.[7] The enamine of acetophenone was prepared by using $TiCl_4$ as a water scavenger.[8] Phenyllithium and copper(I) iodide were purchased from Aldrich and were used without any purification. A typical reaction sequence is described for the preparation of 2-phenylcyclohexanone.

2-Phenylcyclohexanone. Bromine (5 mmol, 0.8 g) was added dropwise to a solution of the morpholine enamine of cyclohexanone (5 mmol, 0.84 mL) and triethylamine (5.5 mmol, 0.77 mL) in THF (5 mL) at −78 °C. After 10 min, the cold bath was removed, and the reaction mixture was stirred for 10 additional minutes. Ether (10 mL) was added to the flask, and the ammonium salt was filtered. The bromo enamine solution was injected to a flask containing 5 mmol of Ph_2CuLi in 5 mL of THF. [The organocopper reagent was prepared 5 min earlier by the addition of 5 mL of PhLi (10 mmol) to a suspension of CuI (5 mmol, 0.95 g) in THF (5 mL) at −23 °C.] The reaction mixture was stirred for 2 h at −23 °C and for 1 h at room temperature. Cold hydrochloric acid was added (10 mmol, 5 mL), and after 6 h, the organic layer was separated, the water layer was extracted twice with 10 mL of ether, the combined organic layers were dried with K_2CO_3, and the ether was evaporated. Silica gel chromatography [hexane–ether (60:40)] gave 2-phenylcyclohexanone as a white solid, mp 55–56 °C (0.76 g, 87% yield): ^{1}H NMR ($CDCl_3$) δ 1.5–2.6 (m, 8 H), 3.4–3.8 (m, 1 H), 7.2–7.4 (m, 5 H); MS, *m/e* (relative intensity) 174 (M^+, 3), 120 (25), 105 (100), 91 (8), 77 (64). In a separate experiment, solvent was removed from the bromo enamine solution and the residue (**1**) was examined: ^{1}H NMR (CD_3CN) δ 1.6–3.1 (m, 10 H), 3.7 (t, 4 H), 4.9 (m, 2 H).

With a similar procedure, the following compounds were prepared.

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