(chloroform) 281 mμ (ϵ 4.10 $\times$ 10^4), 630 (6.20 $\times$ 10^3); ir (KBr) 1680, 1650 ($\nu_{C=O}$), 1530 ($\nu_{C=C}$, 1110 cm^{-1}; nmr ($CDCl_3$) τ 3.17 (s, 2 H, ring), 7.00 (s, 6 H, SCH_3).

Anal. Calcd for $C_{19}H_8O_4SCl_6$: C, 41.87; H, 1.48; O, 11.74. Found: C, 42.87; H, 1.61; O, 11.23.

Registry No.—I-B, 29164-15-6; I-C, 25158-32-1; III, 33834-93-4; IV, 33830-74-9; V, 33830-75-0; VI, 33830-76-1; VII, 33830-77-2; VIII, 33830-78-3; IX, 33830-79-4; X, 33830-80-7.

Acknowledgment.—We wish to thank Messrs. T. Yato and Y. Kumada for their technical assistance.

The 1,3,2-Dioxaphospholene–Sulfenyl Chloride Condensation. Scope and Mechanism

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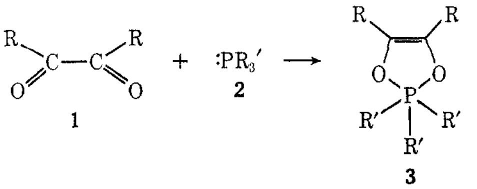
Received August 10, 1971

Sulfenyl chlorides condense exothermically with 1,3,2-dioxaphospholenes to form α-chloro-β-keto sulfides in high yield. The exact nature and number of products depend on the structure of the 1,3,2-dioxaphosphospholene. Several mechanisms were considered and the "sulfenium chloride" pathway is favored.

Trivalent phosphorus compounds are known to react with α-dicarbonyl derivatives to form 1:1 adducts which have been shown to be substituted 1,3,2-dioxaphospholenes **3**.[2,3] These adducts undergo a wide variety of reactions which are of both synthetic and mechanistic interest. For example, the reactivity of 1:1 dicarbonyl–phosphine adducts toward electrophilic centers is attested by their ready condensation with bromine,[4a] carbonyl compounds,[4b] acid chlorides,[4c] isocyanates,[4d] and ketene.[4e] We wish to report that the 1:1 dicarbonyl–phosphine adducts condense exothermically with a variety of sulfenyl chlorides.[5] The nature and the number of final products depend on the type of 1:1 adduct used. This paper describes the scope and mechanism of the condensation.



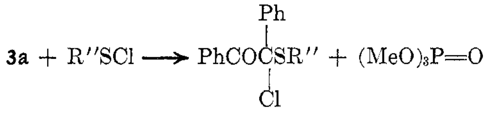
1 **2** **3**

	R		R′		R	R′
1a	C_6H_5	**2a**	CH_3O	**3a**	CH_3O	C_6H_5
1b	CH_3	**2b**	$(CH_3)_2N$	**3b**	$(CH_3)_2N$	C_6H_5
				3c	CH_3O	CH_3
				3d	$(CH_3)_2N$	CH_3

Results and Discussion

In this investigation, benzil (**1a**) and biacetyl (**1b**) were allowed to react with trivalent phosphorus compounds trimethyl phosphite (**2a**) and tris(dimethylamino)phosphine (**2b**). Of the four possible 1:1 adducts, **3a–c** were prepared according to reported procedures.[6,2d] In our hands, the preparation of the 1:1 biacetyl–tris(dimethylamino)phosphine adduct (**3d**, R′ = Me, R = NMe_2) was not successful; only a black tarry product was obtained.

Adduct **3a** reacted with a variety of sulfenyl chlorides **4** to give α-chloro-β-keto sulfides **5** and trimethyl phosphate **6** according to the following equation.[7]



$$\mathbf{3a} + R''SCl \longrightarrow PhCO\underset{Cl}{\overset{Ph}{C}}SR'' + (MeO)_3P{=}O$$

4 **5** **6**

The yields and relevant data of the α-chloro-β-keto sulfides **5** are summarized in Table I.

The progress of this condensation was monitored by nmr. As the addition of sulfenyl chloride progressed, the doublet at τ 6.35 (J = 13 Hz; OCH_3 of **3a**) diminished in intensity as the doublet at τ 6.30 increasingly appeared. Once the addition of sulfenyl chloride was over, the doublet at τ 6.35 had disappeared completely. Trimethyl phosphate was identified by gas chromatography (glpc). The formation of the products appears to be quantitative, although isolated yields are somewhat lower.

The infrared spectra of the α-chloro-β-keto sulfides **5** all show a carbonyl band at 1685 cm^{-1}. The methylene protons α to sulfur in **5d**, **5e**, and **5f** are observed to be diastereotopic[8] even though they are separated from the asymmetric center by a sulfur atom. The methylene protons of **5e** (R″ = CH_3CH_2) were a complex multiplet, thus indicating ABX_3 rather than A_2X_3 splitting. In the case of **5d** (R″ = $PhCH_2$) and **5f** (R″ = CH_2CO_2Me), AB quartets with coupling constants 12 and 16 Hz, respectively, were observed. These values indicate that the AB quartet was derived from vicinal coupling.[9]

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[1] Holder of National Research Council of Canada Scholarship, 1967–1970.

[2] (a) L. D. Quinn, G. Pfundt, and G. O. Schenk, in "1,4 Cycloaddition Reactions," J. Hamer, Ed., Academic Press, New York, N. Y., 1967, pp 83–96, 379–388. (b) F. Ramirez, *Pure Appl. Chem.*, **9**, 337 (1964), *Bull. Soc. Chim. Fr.*, 2443 (1966), *Accounts Chem. Res.*, **1**, 168 (1968). (c) F. Ramirez, S. L. Glaser, A. J. Bigler, and J. F. Pilot, *J. Amer. Chem. Soc.*, **91**, 496 (1969). (d) F. Ramirez, A. V. Patwardhan, H. J. Kugler, and C. P. Smith, *Tetrahedron Lett.*, 3053 (1966). (e) Some adducts of $(Me_2N)_3P$ with diketones exist in the phosphonium enolate form.[2d]

[3] Throughout this paper substituted 1,3,2-dioxaphospholenes will be referred to as 1:1 dicarbonylphosphine adducts.

[4] (a) F. Ramirez and N. B. Desai, *J. Amer. Chem. Soc.*, **82**, 2652 (1960); (b) F. Ramirez, A. V. Patwardhan, and C. P. Smith, *J. Org. Chem.*, **31**, 3159 (1966); (c) F. Ramirez, S. B. Bhatia, A. J. Bigler, and C. P. Smith, *ibid.*, **33**, 1192 (1968); (d) F. Ramirez, S. B. Bhatia, and C. P. Smith, *J. Amer. Chem. Soc.*, **89**, 3030 (1967); (e) *ibid.*, **89**, 3026 (1967).

[5] A preliminary account of this work has been published: D. N. Harpp and P. Mathiaparanam, *Tetrahedron Lett.*, 2089 (1970).

[6] F. Ramirez and N. B. Desai, *J. Amer. Chem. Soc.*, **85**, 3252 (1963).

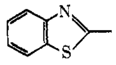
[7] Adducts such as **3a** were prepared *in situ* and dissolved in a suitable solvent (carbon tetrachloride, benzene, or methylene chloride). The color change (discharging of the red sulfenyl chloride) during the addition of sulfenyl chloride was used to follow all the reactions studied.

[8] K. Mislow in "Introduction to Stereochemistry," W. A. Benjamin, New York, N. Y., 1966, pp 93–95; M. Raban and F. B. Jones, Jr., *J. Amer. Chem. Soc.*, **93**, 2692 (1971).

[9] R. M. Silverstein and G. Bassler, "Spectrometric Identification of Organic Compounds," 2nd ed, Wiley, New York, N. Y., 1967, p 144.

TABLE I

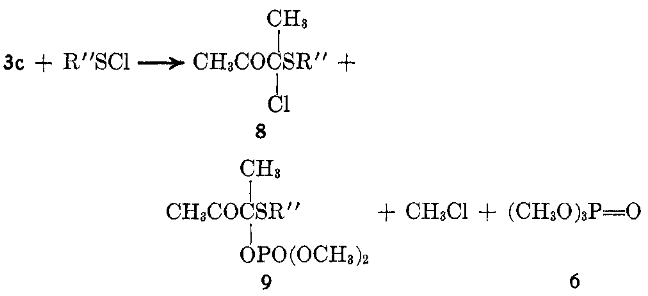
PHYSICAL, ANALYTICAL, AND SPECTROSCOPIC DATA OF α-BENZOYL-α-CHLOROBENZYL SULFIDES **5**

R″ in **5**	Mp of **5**, °C	Yield, %	Calculated, % C	Calculated, % H	Calculated, % S	Calculated, % Cl	Found, % C	Found, % H	Found, % S	Found, % Cl	Nmr data, τ
p-$CH_3C_6H_4$ (**5a**)	118–120	80	71.47	4.86	9.09	10.05	71.32	4.86	9.04	9.82	2.10–3.20 (14 H, m); 7.72 (3 H, s)
C_6H_5 (**5b**)	113–115	82	70.88	4.46	9.46	10.46	70.94	4.52	9.35	10.02	2.10–3.00 (m)
p-ClC_6H_4 (**5c**)	122–124	83	54.34	3.78	8.59	18.99	64.31	3.86	8.57	19.04	2.10–3.00 (m)
$C_6H_5CH_2$ (**5d**)	109–110	80	79.21[a]	5.70	7.55		79.19	5.76	7.53		2.00–3.00 (15 H, m); 6.15 (2 H, AB, J = 12 Hz)
CH_3CH_2 (**5e**)	Oil	60	76.12[a]	6.12	8.85		76.06	6.12	8.90		1.80–3.10 (10 H, m); 7.30–7.90 (2 H, m); 8.60–9.20 (3 H, m)
$CH_3O_2CCH_2$ (**5f**)	65–67	75	70.91[a]	5.46	7.88		70.76	5.57	7.86		1.90–2.65 (10 H, m); 6.34 (3 H, s), 6.53 (2 H, AB, J = 16 Hz)
 (**5g**)	135–136	93	63.70	3.56	16.20	8.96	63.36	3.56	16.31	9.57	1.80–2.90 (m)

[a] Analyses were performed on the corresponding benzyloxyketo sulfides.

The condensation of adduct **3b** with sulfenyl chlorides proceeds in an analogous manner to the previous reaction. For example, with p-toluenesulfenyl chloride **4a** (R″ = p-tolyl), gas chromatographic analysis of the mixture indicated the presence of hexamethylphosphoramide **7** and the α-chloro-β-keto sulfide **5a**. In addition, **5a** was isolated from the reaction mixture and was shown to be identical with an authentic sample (prepared from **3a** and **4a**).

Adduct **3c** condensed with sulfenyl chlorides to give α-chloro-β-keto sulfide **8**, trimethyl phosphate **6**, the β-keto phosphate **9**, and methyl chloride according to the following equation.



$$\mathbf{3c} + \mathrm{R''SCl} \longrightarrow \underset{\mathbf{8}}{\mathrm{CH_3CO\overset{CH_3}{\underset{Cl}{C}}SR''}} + \underset{\mathbf{9}}{\mathrm{CH_3CO\overset{CH_3}{\underset{OPO(OCH_3)_2}{C}}SR''}} + \mathrm{CH_3Cl} + \underset{\mathbf{6}}{\mathrm{(CH_3O)_3P{=}O}}$$

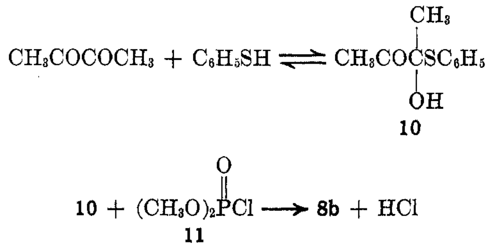
Benzene- and ethanesulfenyl chlorides were used in carbon tetrachloride as solvent. The reaction mixture was analyzed by nmr. When benzenesulfenyl chloride was used, 93% of keto sulfide **8a** was realized along with 7% of the β-keto phosphate **9a**. The ratio of products was altered somewhat in the reaction with ethanesulfenyl chloride (**8b**, 72%; **9b**, 28%).

The nmr spectra of the reaction of adduct **3c** with benzene- and ethanesulfenyl chlorides are illustrated in Figures 1 and 2. In both cases, the singlet at τ 7.00 was identified as arising from methyl chloride.[10] On evaporation of the solvent at room temperature this singlet disappeared. The doublet at τ 6.30 (J_{P-H} = 12 Hz) was due to trimethyl phosphate by comparison with an authentic sample. Also, addition of few drops of trimethyl phosphate to the reaction mixture increased the intensity of this doublet with respect to other peaks.

Considering the reaction between benzenesulfenyl chloride and adduct **3c** (e.g., Figure 1) in detail, the singlets at τ 8.32 and 7.63 can be attributed to the CH_3 and CH_3CO protons of the α-chloro-β-keto sulfide **8a** by comparison with an authentic sample.[11] The singlets at τ 7.80 and 7.67 and the doublet at τ 6.22 (J_{P-H} = 12 Hz) were assigned to the CH_3, CH_3CO, and OCH_3 protons of β-keto phosphate **8b**. All attempts toward the unequivocal synthesis of **8b** were unsuccessful. Synthetic Schemes I and II were tried.

SCHEME I

ATTEMPTED SYNTHESIS OF β-KETO PHOSPHATE **8b**

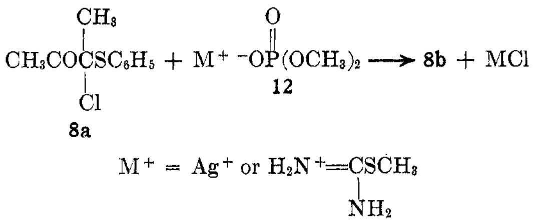


$$\mathrm{CH_3COCOCH_3 + C_6H_5SH \rightleftharpoons \underset{\mathbf{10}}{CH_3CO\overset{CH_3}{\underset{OH}{C}}SC_6H_5}}$$

$$\mathbf{10} + \underset{\mathbf{11}}{\mathrm{(CH_3O)_2\overset{O}{\overset{\|}{P}}Cl}} \longrightarrow \mathbf{8b} + \mathrm{HCl}$$

SCHEME II

ATTEMPTED SYNTHESIS OF β-KETO PHOSPHATE **8b**



$$\underset{\mathbf{8a}}{\mathrm{CH_3CO\overset{CH_3}{\underset{Cl}{C}}SC_6H_5}} + \mathrm{M^+}\ \underset{\mathbf{12}}{\mathrm{{}^-O\overset{O}{\overset{\|}{P}}(OCH_3)_2}} \longrightarrow \mathbf{8b} + \mathrm{MCl}$$

$$\mathrm{M^+ = Ag^+\ or\ H_2N^+{=}\underset{NH_2}{C}SCH_3}$$

In Scheme I biacetyl reacted exothermically with benzenethiol to form an equilibrium mixture containing 80% of the α-hydroxy-β-keto sulfide **10** (analyzed by nmr).[12] When dimethyl phosphorochloridate **11** was added to this mixture at room temperature, no reaction was observed after 2 days. On heating,

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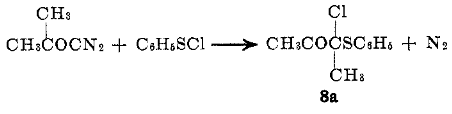
(10) One reported value is τ 6.95, ref 9, p 144.

(11) Prepared from azibutanone (diazobutanone) and benzenesulfenyl chloride; see Experimental Section for details.



$$\mathrm{CH_3\overset{CH_3}{C}OCN_2 + C_6H_5SCl \longrightarrow \underset{\mathbf{8a}}{CH_3CO\overset{Cl}{\underset{CH_3}{C}}SC_6H_5}} + \mathrm{N_2}$$

(12) It has been shown that thiols react with carbonyl compounds to form an equilibrium mixture containing mainly α-hydroxy sulfides; cf. E. Campaigne in "Organo-Sulfur Compounds," Vol. 1, N. Kharasch, Ed., Pergamon Press, Elmsford, N. Y. 1961, Chapter 14. In the above synthetic scheme the reaction was extended to α diketones.

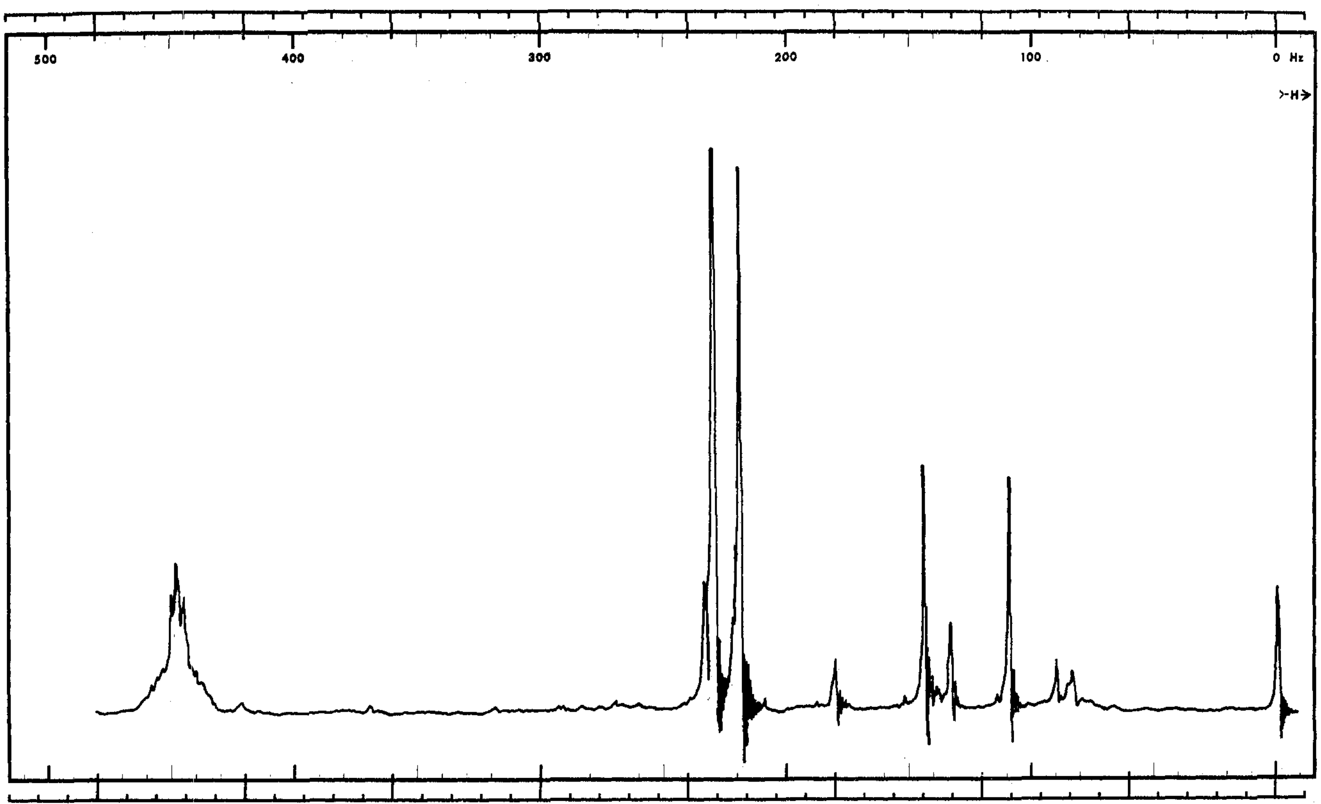


Figure 1.—Reaction of benzenesulfenyl chloride with **3c**.

extensive decomposition occurred. In another attempt, the same procedure was repeated in the presence of pyridine as hydrogen chloride scavenger. The analysis of the reaction mixture by nmr indicated the presence of biacetyl as the main product.

In Scheme II the nucleophilic displacement of the chlorine atom of **8a** with the dimethyl phosphate anion **12** was attempted in acetonitrile. The anticipated β-keto phosphate **8b** was not obtained; only a complex mixture of intractable decomposition products resulted.

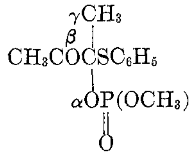
Owing to the low stability of the products from the sulfenyl chloride condensation, separation of the β-keto phosphate **8b** either by fractional distillation or by preparative glpc was not achieved. However, the mass spectrum of the reaction mixture revealed the molecular ion of **8b** at *m/e* 304 and two other ions of medium intensity at *m/e* 126 and 127. While the intensity of the molecular ion at *m/e* 304 was too weak for exact mass measurement, the exact masses were determined for ions at *m/e* 126 and 127. Details of these experiments are summarized in Table II. These ions were not present in the mass spectra of pure samples of α-chloro-β-keto sulfide **8a** and trimethyl phosphate. Thus, they appeared to be derived from the β-keto phosphate **8b**.

TABLE II

MASS SPECTRAL DATA ON IONS *m/e* 126 AND 127

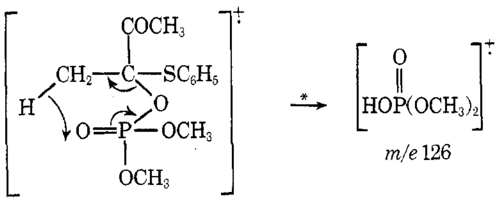
Exact mass		Chemical	
Calcd	Found	formula	Possible structure
126.0082	126.0083	$C_2H_7O_4P$	$(CH_3O)_2P(O)OH$
127.0160	127.0164	$C_2H_8O_4P$	$(CH_3O)_2P(OH)_2$

The mass spectra of several organic phosphates have been studied in some detail.[13] A distinct difference in fragmentation patterns was observed between phosphates with and without γ hydrogens to phosphorus.[14] The essential difference between trimethyl phosphate and the β-keto phosphate **8b** is that the latter has three γ hydrogens. Therefore, it is reasonable to suggest



$$CH_3CO\overset{\beta}{C}(\overset{\gamma}{C}H_3)(SC_6H_5)-\overset{\alpha}{O}P(=O)(OCH_3)_2$$

that these γ hydrogens are involved in the formation of ions at *m/e* 126 and 127 in **8b**. Fragment *m/e* 126 is probably formed by a McLafferty rearrangement of molecular ion $\mathbf{8b}^{\mp}$ as shown. The formation of ion *m/e* 127 could be rationalized as follows. Ion $\mathbf{8b}^{\mp\mp}$, formed by α-carbonyl cleavage, probably undergoes two



$\mathbf{8b}^{\mp}$

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(13) H. Budzikiewicz, C. Djerassi, and D. H. Williams in "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967, pp 647–653.

(14) For example, the presence of ions at *m/e* 126 and 127 in triethyl phosphate and their absence in trimethyl phosphate could be attributed to the availability of γ hydrogens in the former.

$$(\overset{\gamma}{C}H_3\overset{\beta}{C}H_2\overset{\alpha}{O})_3P{=}O \qquad (\overset{\beta}{C}H_3\overset{\alpha}{O})_3P{=}O$$

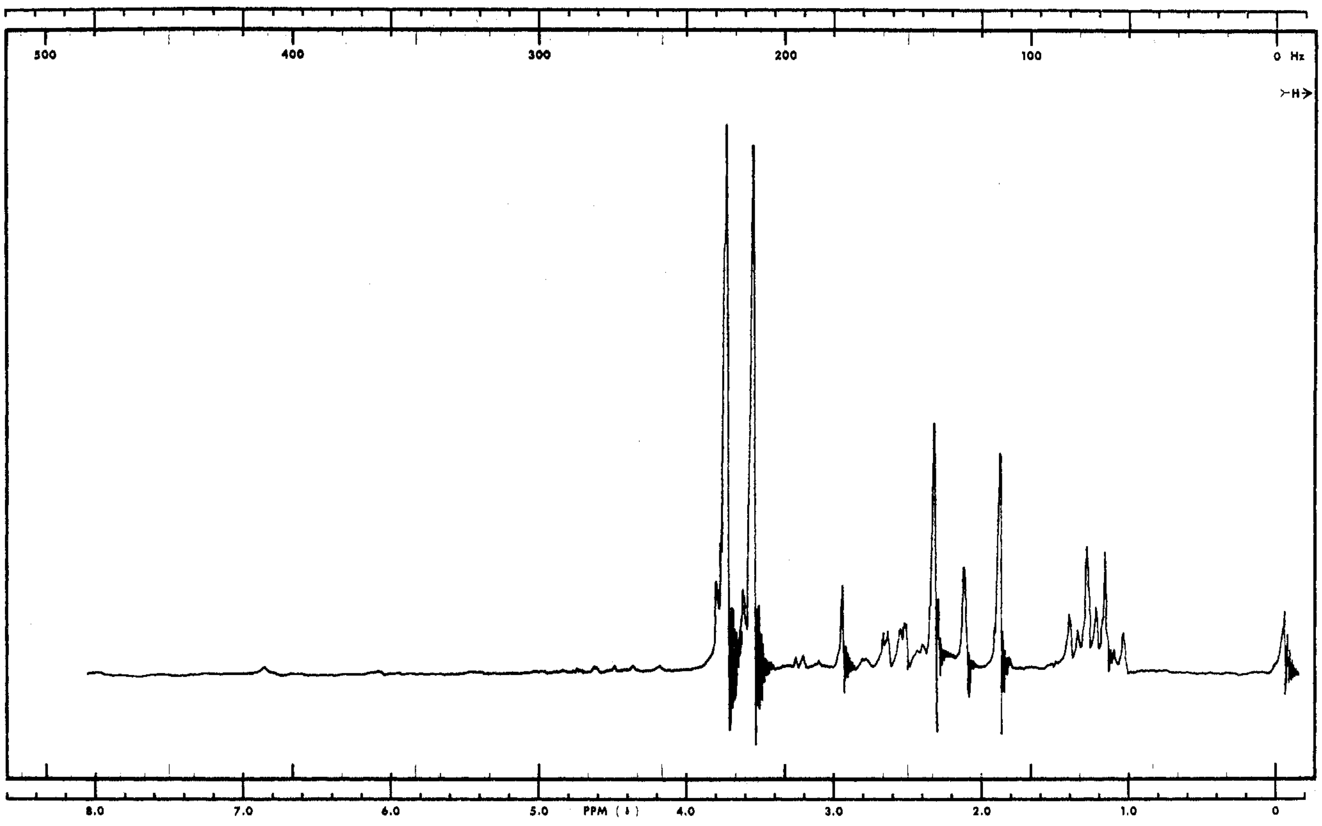
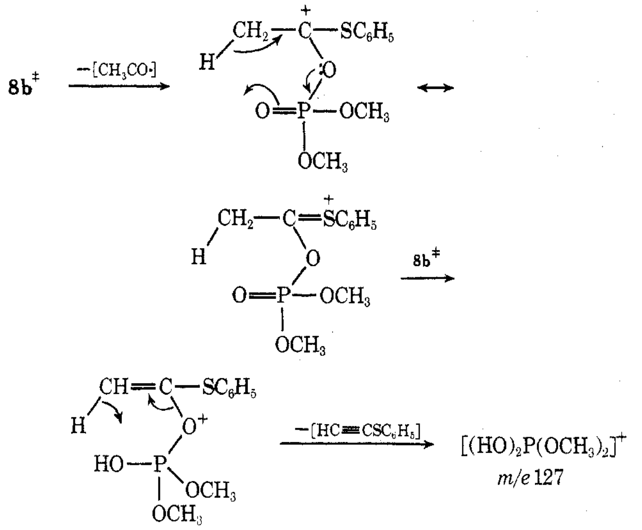
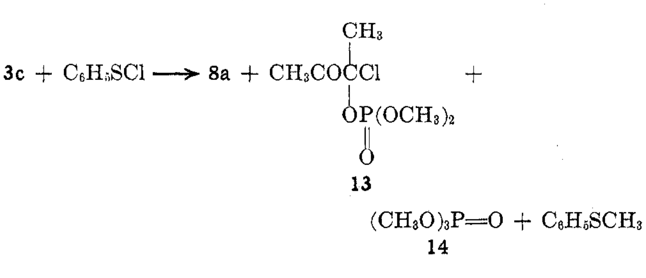


Figure 2.—Reaction of ethanesulfenyl chloride with 3c.



hydrogen shifts with the elimination of phenylthioacetylene to form ion m/e 127.

On mechanistic grounds (*vide infra*), products **13** and **14** could also be expected from the sulfenyl chloride



$$\mathbf{3c} + C_6H_5SCl \longrightarrow \mathbf{8a} + \underset{\mathbf{13}}{CH_3CO\overset{CH_3}{\underset{\underset{\overset{\|}{O}}{OP(OCH_3)_2}}{C}}Cl} + \underset{\mathbf{14}}{(CH_3O)_3P{=}O + C_6H_5SCH_3}$$

condensation. The nmr signals associated with trimethyl phosphate and α-chloro-β-keto sulfide **8a** were identified. The absence of products **13** and **14** was conclusively demonstrated by comparing the nmr spectrum of the reaction mixture with those of the authentic samples of **13** and **14**. The singlet at τ 7.73 due to the methyl protons of **14** did not correspond with any of the peaks in the nmr spectrum of the reaction mixture. Furthermore, addition of a few drops of **14** to the reaction mixture produced a new singlet at τ 7.73. Authentic α-chloro-β-keto phosphate **13** was prepared according to a reported procedure[15] by the action of chlorine on **3c**. Again, the singlets associated with the CH_3 (τ 7.93) and CH_3CO (τ 7.59) of **13** did not correspond with those of the reaction mixture. This was further checked by addition of **13** to the reaction mixture.

Mechanism.—Several mechanisms can be advanced for this condensation based on the chemistry of both 1:1 dicarbonyl–phosphine adducts and sulfenyl chlorides. A free-radical pathway has been proposed for the reaction of the adduct **3c** with bromotrichloromethane.[16] By analogy, a similar mechanism can be advanced for the sulfenyl chloride condensation. The reaction of adduct **3a** with p-toluenesulfenyl chloride (**4a**) was used to test this possibility. The condensation proceeded in the dark and in the presence of a free-radical inhibitor (1,3,5-trinitrobenzene) with no appreciable change in the rate. Furthermore, gas chromatographic analysis of the reaction mixture revealed the absence of p-tolyl disulfide, indicating the formation of the p-tolylthiyl (p-$CH_3C_6H_4S\cdot$) radical is not important. In other free-radical reactions involving thiyl radicals, disulfides are often formed as byproducts.[17] These observations make the free-radical chain mechanism unlikely.

A carbene mechanism has been suggested for the for-

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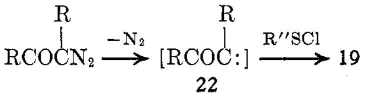
[15] F. Ramirez and N. B. Desai, *J. Amer. Chem. Soc.*, **82**, 2652 (1960).

[16] W. G. Bentrude, *ibid.*, **87**, 4026 (1965).

[17] N. Kharasch and Z. S. Ariyan, *Chem. Ind.* (*London*), 929 (1964).

mation of α-chloro-β-keto sulfides **19** by the action of sulfenyl chlorides on α-diazo ketones **21**.[18] Also, adduct **3c**, when irradiated in cyclohexane, gave tri-



$$\mathrm{RCO}\overset{\mathrm{R}}{\mathrm{C}}\mathrm{N_2} \xrightarrow{-\mathrm{N_2}} [\mathrm{RCO}\overset{\mathrm{R}}{\mathrm{C}}\mathrm{:}] \xrightarrow{\mathrm{R''SCl}} \mathbf{19}$$

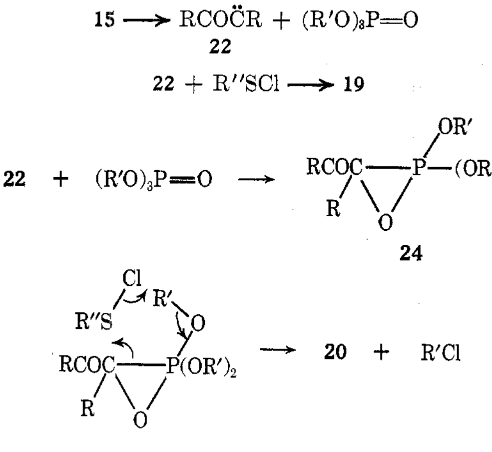
methyl phosphate, trimethyl phosphite, and biacetyl as products.[19] The formation of trimethyl phosphate indicates that a ketocarbene **23** might have been gener-

$$\mathbf{3c} \xrightarrow[?]{h\nu} \mathrm{(CH_3O)_3P{=}O} + [\mathrm{CH_3CO\ddot{C}CH_3}] \quad \mathbf{23}$$

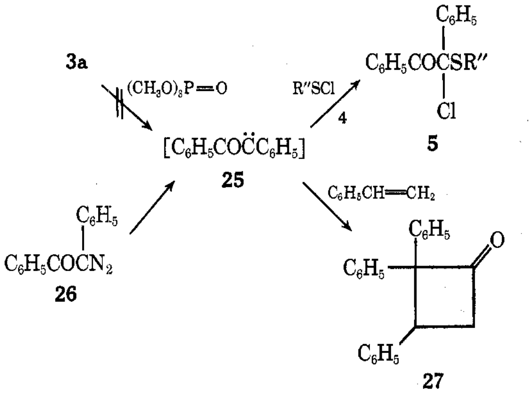
ated on photolysis.[20] Furthermore, mechanisms involving a carbene by elimination of phosphate[21] or thiophosphate[22] have been suggested for several reactions.

From these studies, it is therefore reasonable to propose a carbene mechanism (Scheme III) for the sulfenyl chloride condensation. Several experiments (Scheme IV) were designed to test the validity of this mechanism. Benzoylphenylcarbene (**25**) obtained from benzoylphenyldiazomethane (**26**) reacting with *p*-toluenesulfenyl chloride (**4a**, R″ = *p*-tolyl) to give the α-chloro-β-keto sulfide **5a** in good yield. Also, ketocarbene **25** has been shown to be intercepted by styrene to give cyclobutanone **27**.[23] However, under identical conditions, adduct **3a** did not give **27** when treated with styrene. Thus, the possibility of a carbene mechanism seems remote for the sulfenyl chloride condensation.

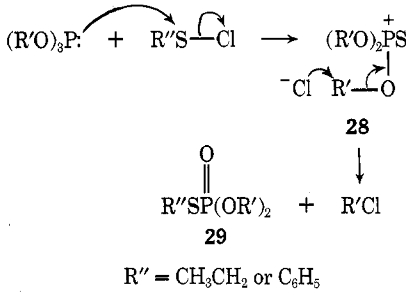
SCHEME III

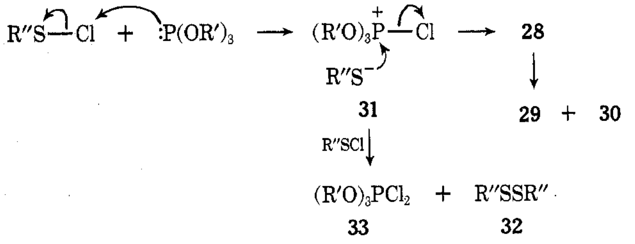


SCHEME IV



Any ionic mechanism for the sulfenyl chloride condensation should take into account the two possible modes of polarization of sulfenyl chlorides, namely, a "sulfenium chloride" mode ($R''S^{\delta+}Cl^{\delta-}$) and a "chloronium mercaptide" mode ($R''S^{\delta-}Cl^{\delta+}$). Even though the former polarization has been favored in most of the reactions of sulfenyl chlorides,[24] the latter has been shown to occur in some reactions (*e.g.*, involving *p*-nitrobenzenesulfenyl chloride). The reactions of ethane- and benzenesulfenyl chlorides with trialkyl phosphites[25] illustrate the sulfenium chloride polarization. The phosphite attacks the electrophilic sulfur to form the phosphonium intermediate **28**. The chloride ion is sufficiently nucleophilic to dealkylate the phosphonium intermediate **28** by preferential attack on an alkoxy carbon to form the energetically favored P=O bond. An alternative chloronium mercaptide mechanism would involve an initial attack of the phosphite on the chlorine similar to that observed in *tert*-butyl hypochlorite.[26] In this case, attack on chlorine seems less likely, because the mercaptide ion ($R''S^-$) would itself be strongly thiophilic and would be expected to react rapidly with remaining sulfenyl chloride to form disulfide **32** and the dichlorophosphorus compound **33**.





This chloronium mercaptide polarization of sulfenyl chlorides has been observed in the reaction of *p*-nitrobenzenesulfenyl chloride (R″ = p-$NO_2C_6H_4$) with triphenyl phosphite (R = Ph).[27] Based on these analogies, in the condensation of benzenesulfenyl chloride **4b** with the adduct **3c**, the following set of products would be expected by the two proposed

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[18] F. Weygand and H. J. Bestmann, *Z. Naturforsch. B*, **10**, 296 (1955).

[19] W. G. Bentrude, *Chem. Commun.*, 174 (1967).

[20] The mechanistic details of this reaction have not yet been reported.

[21] F. Ramirez, H. Yamanaka, and O. H. Basedow, *J. Amer. Chem. Soc.*, **83**, 173 (1961).

[22] E. J. Corey and R. A. E. Winter, *ibid.*, **85**, 2677 (1963).

[23] C. S. Marvel and M. I. Kohan, *J. Org. Chem.*, **16**, 741 (1951). In this case, the ketocarbene **5** rearranged to diphenylketene (Ph$_2$C=C=O) before addition to styrene. The assignment of structure **27** for the cyclobutanone was confirmed by ir and nmr spectra (see Experimental Section.)

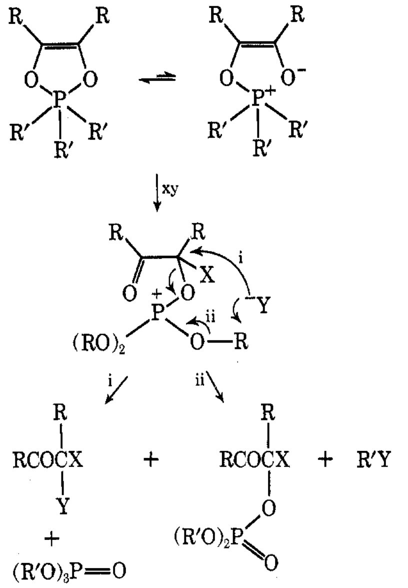
[24] W. H. Mueller, *Angew. Chem., Int. Ed. Engl.*, **8**, 482 (1969), and references cited therein.

[25] D. C. Morrison, *J. Amer. Chem. Soc.*, **77**, 181 (1955).

[26] D. B. Denney and R. R. DiLeone, *ibid.*, **84**, 4737 (1962).

[27] K. A. Petrov, G. A. Sokolskii, and B. M. Poleers, *Zh. Obshch. Khim.*, **26**, 2281 (1956); *Chem. Abstr.*, **51**, 9473 (1957). (b) *p*-Nitrophenyl disulfide and triphenoxyphosphorus dichloride were isolated in good yields.

SCHEME V
IONIC MECHANISMS



sulfenium chloride mechanism: $X = SR''$; $Y = Cl$

chloronium mercaptide mechanism: $X = Cl$; $Y = SR''$

mechanisms (Scheme V). It has been shown earlier that the products formed in the condensation correspond to those predicted by the sulfenium chloride mechanism. Thus, it appears that the condensation in this case proceeds *via* the above mechanism. The absence of phenyl disulfide in the reaction mixture (checked by glpc) makes the chloronium mercaptide mechanism unlikely.

In the 1:1 benzil–trimethyl phosphite adduct (**3a**)–sulfenyl chloride condensation, the only products observed are the α-chloro-β-keto sulfide **5** and trimethyl phosphate. Although, these products can be accounted by both mechanisms, the sulfenium chloride pathway is preferred because there is no disulfide formation. It seems that in this case, path i is followed exclusively to path ii. This could be rationalized as follows. In path i, the tertiary carbon undergoing nucleophilic attack is not only benzylic but also α to the carbonyl group and to sulfur. All these characteristics accelerate the substitution at the carbon.[28] Moreover, additional driving force is introduced into path i by the elimination of the very stable trimethyl phosphate through energetically favored P═O bond formation. In path ii even though there are three primary carbons which can undergo nucleophilic attack, the only driving force available is P═O bond formation. In the 1:1 biacetyl–trimethyl phosphite adduct (**3c**)–sulfenyl chloride condensation ($R = R' = Me$), which lacks the benzylic group, path ii competes with path i to a significant extent.

The condensation of sulfenyl chlorides with 1:1 benzil–tris(dimethylamino)phosphine adduct **3b** can also be rationalized on the basis of sulfenium chloride mechanism. This condensation is similar to that of the adduct **3a** with sulfenyl chlorides, except that path ii is not important.

Experimental Section

Melting points were obtained on a Gallenkamp melting point apparatus and are corrected. Infared spectra were recorded on a Perkin-Elmer (Model 257 or 337) grating infrared spectrophotometer. Spectra of solids were obtained using potassium bromide pellets and a film technique was used for liquid samples. Spectra were calibrated with the 1601-cm^{-1} band of a polystyrene film reference. Nmr spectra were recorded on Varian Associates A-60 or T-60 spectrometers. All proton spectra are reported in τ units relative to tetramethylsilane (TMS). Unless otherwise stated, deuteriochloroform was used as solvent. Gas chromatographic (vpc) analyses were performed on an F & M (Model 5750) research chromatograph. Two 6 ft × $^1/_8$ in. stainless steel columns were used; 10% silicone gum rubbber UC W98 on Diatoport-S (UC-W98 column) and 10% Apiezon L on Chromosorb W/AW-MCDS (Apiezon L column). Organic microanalyses were performed by Scandanavian Microanalytical Laboratories, Herlev, Denmark, and Organic Microanalyses (Dr. C. Daessle), Montreal, Canada. Trimethyl phosphite (Aldrich Chemical Co. Ltd.) was purified by prolonged treatment with molecular sieves "Linde" Type 3A (1/16) followed by fractional distillation. Tris(dimethylamino)phosphine (Eastman Kodak Chemical Co.) was used without further purification. Carbonyl compounds (benzil, biacetyl, etc.) were freshly distilled or recrystallized from aprotic solvents.

Preparation of Aromatic Sulfenyl Chlorides.—The procedure used was a modification on the method of Emde.[29] In a 500-ml flask fitted with a dropping funnel and a reflux condenser carrying a drying tube was placed *N*-chlorosuccinimide (26.7 g, 0.2 mol). Benzene (120 ml) was added and the contents of the flask were stirred magnetically to form a slurry. A solution of the aromatic thiol (0.2 mol) in benzene (50 ml) was added dropwise with the flask being cooled by ice water. An orange-red color developed after 5 min; it deepened as the addition continued. After the addition was complete, the mixture was stirred for 24 hr at room temperature. The white solid (succinimide) was removed by filtration and the deep red filtrate was concentrated under reduced pressure. Carbon tetrachloride (30 ml) was added to the red oil to precipitate the last traces of succinimide. After filtration, the filtrate was concentrated and the residual red oil distilled under reduced pressure. The yields and boiling points are given in Table III.[30a,b]

TABLE III

RCl	Yield, %	Bp, °C (mm)	Reported bp, °C (mm)
p-$CH_3C_6H_4$ (**4a**)	70	44 (0.3)	77.5–78.5 (2.5)
C_6H_5 (**4b**)	73	58 (0.8)	73–75 (9.0)
p-ClC_6H_4 (**4c**)	86	90 (0.4)	94 (6.0)

Reaction of Aromatic Sulfenyl Chlorides with the 1:1 Benzil–Trimethyl Phosphite Adduct (3a).—To a 50-ml, three-necked, round-bottomed flask fitted with a dropping funnel, gas inlet tube, and a condenser connected to a mercury trap, was added benzil (2.10 g, 0.01 mol). The flask was flushed with dry nitrogen for 15 min. Trimethyl phosphite (1.24 g, 0.01 mol) was added; an exothermic reaction occurred immediately and the pale yellow viscous liquid was stirred for 1 hr. Benzene (10 ml) was added to dissolve the syrup. This was followed by the aromatic sulfenyl chloride (0.01 mol) in benzene (10 ml). As the addition continued, the deep red color changed to pale yellow. Once the addition was complete, the reaction mixture was stirred for 1 hr at room temperature. The solvent was removed on a flash evaporator and *n*-hexane (15 ml) was added to the residue. A white crystalline solid separated on cooling and was filtered and recrystallized from *n*-hexane–benzene. The melting points, yields, and analytical data of the aromatic chloroketo sulfides are summarized in Table I. The reaction mixture showed the presence of trimethyl phosphate when compared with an authentic sample by gas chromatography using an Apiezon L column. No aromatic disulfides were detected.

Preparation of Aliphatic Sulfenyl Chlorides.—Ethane, phenyl-

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(28) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1959, pp 280–289.

(29) H. Emde, German Patent 804,572 (1951); *Chem. Abstr.*, **46**, 529 (1952).

(30) (a) H. Lecher, F. Holschneider, K. Koberle, W. Speer, and P. Stocklin, *Ber.*, **58**, 409 (1925); (b) E. Gebauer-Fulnegg, *J. Amer. Chem. Soc.*, **49**, 2270 (1927).

TABLE IV

$$R''SSR'' + Cl_2 \longrightarrow 2R''SCl$$
(0.005 mol)

Chemical shift (τ) of α methylene protons					
Disulfide		Sulfenyl chloride		Cl_2 required, g	Temp of chlorinolysis, °C
$(CH_3CH_2S-)_2$[a]	7.30	CH_3CH_2SCl (**4e**)	6.90	0.40	−30
$(C_6H_5CH_2S-)_2$[b]	6.50	$C_6H_5CH_2SCl$ (**4d**)	5.73	0.36	0–5
$(CH_3O_2CCH_2S-)_2$[b]	6.33	$CH_3O_2CCH_2SCl$ (**4f**)	5.97	0.80	0–5

[a] Neat disulfide. [b] Carbon tetrachloride (10 ml).

methane, and carbomethoxymethanesulfenyl chlorides were generated by chlorinolysis of the corresponding disulfides. The progress of the reaction was monitored by nmr. As the sulfenyl chloride was formed a significant decrease (τ 0.4–0.5) in the chemical shifts of protons α to the sulfur atom was observed. In a typical run, chlorine was passed into the disulfide (neat or a solution in CCl_4) until the nmr signal of methylene protons α to sulfur had disappeared. The experimental procedure adopted was similar to that reported for methanesulfenyl chloride.[31] Relevant reaction data are collected in Table IV.

Reaction of Aliphatic Sulfenyl Chlorides with 3a.—Adduct **3a** was generated from benzil (2.10 g, 0.01 mol) and trimethyl phosphite (1.25 g, ∼0.01 mol) as described previously. The sulfenyl chloride (obtained by the chlorinolysis of 0.005 mol of the corresponding disulfide) was added dropwise to adduct **3a** in carbon tetrachloride (10 ml) at 0°. The red color of the sulfenyl chloride was discharged as the addition progressed. After 0.5–1 hr at room temperature, the solvent was removed under reduced pressure; last traces were removed using a vacuum pump. The resulting white chloro keto sulfide was recrystallized from *n*-hexane–benzene. The physical and spectroscopic data are summarized in Table I. Owing to the low stability of the chloroketo sulfide, it was converted to the corresponding α-benzyloxy-β-keto sulfide for elemental analysis. To the reaction mixture obtained by adding sulfenyl chloride (0.01 mol) to adduct **3a** (0.01 mol) in benzene (10 ml) were added benzyl alcohol (1.10 g, 0.01 mol) and silver carbonate (1.50 g). The mixture was stirred overnight at room temperature. Silver salts were removed by filtration and the filtrate was concentrated. The α-benzyloxy-β-keto sulfide so formed was recrystallized from methanol. The analysis data are summarized in Table I.

Reaction of 2-Benzothiazolesulfenyl Chloride (4g) with 1:1 Benzil–Trimethyl Phosphite Adduct 3a.—2-Benzothiazolesulfenyl chloride (**4g**) was prepared by the action of sulfuryl chloride on 2,2′-dithiobis(benzothiazole). To a suspension of freshly recrystallized 2,2′-dithiobis(benzothiazole) (1.65 g, 0.005 mol) in methylene chloride (20 ml) at room temperature was added sulfuryl chloride (0.68 g, 0.005 mol). As the reaction progressed, the suspended disulfide dissolved and the solution turned deep red. After 1 hr at room temperature, it was added to the adduct **3a** prepared as before from benzil (2.10 g, 0.01 mol) and trimethyl phosphite (1.25 g, 0.01 mol) in benzene (10 ml). As the addition progressed, the deep red color of 2-benzothiazolesulfenyl chloride changed to pale yellow. Once the addition was complete, the reaction mixture was stirred at room temperature for 1 hr. The solvent was removed under reduced pressure and the resulting pale yellow solid was recrystallized from methylene chloride–*n*-hexane. The α-chloro-β-keto sulfide **5g** crystallized out as white plates. See Table I for physical, analytical, and spectroscopic data.

Reaction of *p*-Toluenesulfenyl Chloride (4a) with 1:1 Benzil–Tris(dimethylamino)Phosphine Adduct 3b.—In a 50-ml, three-necked, round-bottomed flask fitted with a dropping funnel, gas inlet tube, and a condenser connected to mercury trap was placed benzil (1.05 g, 0.005 mol). Dry methylene chloride (10 ml) was added to dissolve the benzil and the solution was cooled to 5°. The reaction system was flushed with dry nitrogen for 15 min. Tris(dimethylamino)phosphine (**2b**, 0.8 g, ∼0.005 mol) was added dropwise with stirring. The yellow color of the solution turned deep red, and stirring was continued for 30 min at 5° after the addition was complete. *p*-Toluenesulfenyl chloride **4a** (0.8 g, 0.005 mol) in methylene chloride (10 ml) was added to the adduct **3b**. After 1 hr at room temperature, the solvent was removed under reduced pressure and *n*-hexane (10 ml) was added to the residue. On cooling, a yellowish white solid precipitated out, yield 0.8 g (45%). Recrystallization from *n*-hexane gave white needles melting at 117–118°. This product was shown to be identical with the α-chloro-β-keto sulfide **5a** obtained from the 1:1 benzil–trimethyl phosphite adduct (**3a**)–*p*-toluenesulfenyl chloride (**4a**) reaction by mixture melting point and ir. Chromatographic analysis of the mother liquor, using an Apiezon L column, revealed the presence of the α-chloro-β-keto sulfide **5a** and hexamethylphosphoramide **7**. No *p*-tolyl disulfide was detected.

Preparation of 1:1 Biacetyl–Trimethyl Phosphite Adduct 3c.—Adduct **3c** was prepared as previously described.[6] Biacetyl (14.8 g) was converted to adduct **3c**, 33.5 g (86%), bp 46° (0.6 mm) (lit.[6] 45–47° (0.5 mm)).

Reaction of Benzenesulfenyl Chloride (4b) with 1:1 Biacetyl–Trimethyl Phosphite Adduct 3c.—Adduct **3c** (2.10 g, 0.01 mol) was dissolved in carbon tetrachloride (10 ml) under dry nitrogen. The solution was cooled to 5°. Benzenesulfenyl chloride (**4b**, 1.45 g, 0.01 mol) in carbon tetrachloride (5 ml) was added dropwise. An exothermic reaction occurred with a disappearance of the red color of sulfenyl chloride **4b**. The nmr spectrum of the reaction mixture showed the following: τ 2.30–2.90 (5 H, m), 6.30 (3 H, d, J = 12 Hz), 6.22 (3 H, d, J = 12 Hz), 7.00 (3 H, s), 7.63 (3 H, s), 7.67 (3 H, s), 8.32 (3 H, s). Extensive decomposition occurred on distillation.

Reaction of Ethanesulfenyl Chloride (4e) with 1:1 Biacetyl–Trimethyl Phosphite Adduct 3c.—The above procedure was repeated using ethanesulfenyl chloride (**4e**, 0.01 mol) instead of benzenesulfenyl chloride (**4b**). The nmr spectrum of the reaction mixture showed the following: τ 6.24 (3 H, d, J = 12 Hz), 6.30 (3 H, d, J = 12 Hz), 7.00 (3 H, s), 7.62 (3 H, s), 7.67 (3 H, s), 7.82 (3 H, s), 8.07 (3 H, s), 7.10–7.90 (2 H, m), 8.40–8.93 (3 H, m). Extensive decomposition occurred on distillation.

Preparation of Biacetyl Monohydrazone.—The reported procedure for the preparation of biacetyl monohydrazone[32] has been modified as follows. A solution of biacetyl (10 ml) in benzene (10 ml) was cooled in an ice bath, and anhydrous hydrazine (3.87 g) was added dropwise with stirring. About 10 min after the addition was complete, a white solid precipitated and was filtered. The crude monohydrazone was dissolved in hot benzene and this layer decanted. On cooling, biacetyl monohydrazone crystallized, yield 7.5 g (65%), mp 64–65° (lit.[32] mp 67°).

Preparation of Azibutanone.—Two procedures were used to prepare azibutanone (diazobutanone) from biacetyl monohydrazone.

Procedure I. Using Silver Oxide.—Biacetyl monohydrazone (6.0 g) in methylene chloride (20 ml) was added to vigorously stirred suspension of silver oxide (20 g) and anhydrous sodium sulfate (20 g) in methylene chloride (80 ml). After the initial reaction had subsided, the mixture was stirred at room temperature for 24 hr. The inorganic salts were removed by filtration. The residue was washed with several portions of methylene chloride until the washings were devoid of yellow color. The washings were combined and concentrated in a flash evaporator. The residual red oil was distilled under reduced pressure using a water aspirator. The product boiling at 32° (7 mm) was collected: yield 3.0 g (51%); lit.[32] bp 45° (12–13 mm); ir 1650 (CO), 2070 cm^{-1} (N═N); nmr τ 7.85 (3 H, s), 8.22 (3 H, s).

Procedure II. Using Mercuric Oxide (Yellow).—Biacetyl monohydrazone (10.0 g) in methylene chloride (50 ml) was added to a vigorously stirred suspension of yellow mercuric oxide (22 g) and anhydrous sodium sulfate (30 g) in methylene chloride (150 ml) containing two drops of alcoholic sodium hydroxide. After the initial reaction had subsided, the mixture was stirred for 24 hr. Azibutanone was isolated by a similar work-up as in procedure I, yield 9.0 g (90%), bp 32° (7 mm).

Preparation of α-Acetyl-α-chloroethyl Phenyl Sulfide (8a).—

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[31] I. B. Douglass, *J. Org. Chem.*, **24**, 2004 (1959).

[32] O. Diels and K. Pflanmer, *Ber.*, **48**, 223 (1915).

Benzenesulfenyl chloride (**4b**, 1.45 g, 0.01 mol) in carbon tetrachloride (10 ml) was added dropwise to a solution of azibutanone (0.98 g, 0.01 mol) in carbon tetrachloride (10 ml) at $-10°$. As the addition continued, the deep red color of the sulfenyl chloride **4b** and the orange color of azibutanone turned lighter with vigorous evolution of nitrogen. At the end of addition, a light yellow color was obtained. The solvent was removed and the residual oil distilled under reduced pressure. The α-chloro-β-keto sulfide **8a** distilled at 126° (0.005 mm) as a pale yellow oil: yield 1.7 g (80%); ir 1725 cm^{-1} (CO); nmr τ 2.20–2.70 (5 H, m), 7.62 (3 H, s), 8.21 (3 H, s). Exact mass data: calculated for $C_{10}H_{11}OSCl$, 214.0219; found, 214.0224.

Preparation of α-Acetyl-β-chloroethylethyl Sulfide 8b.—Ethyl disulfide (2.44 g, 0.02 mol) reacted at $-30°$ with chlorine (1.42 g, 0.02 mol). The deep red ethanesulfenyl chloride **4e** was added dropwise to azibutanone (3.95 g, 0.04 mol) in carbon tetrachloride (30 ml) at $-20°$. As the addition continued, the color of the reaction mixture became lighter and was accompanied by the evolution of nitrogen. After the addition was complete, the solvent was removed on a flash evaporator and the residue yellow oil was distilled under reduced pressure. The α-chloro-β-keto sulfide **8b** distilled at 44° (0.1 mm) as a pale yellow oil: yield 5.6 g (84%); ir 1730 cm^{-1} (CO); nmr τ 7.30 (2 H, AB, J = 7 Hz), 7.59 (3 H, s), 8.03 (3 H, s), 8.75 (3 H, split t, J = 7 Hz). Exact mass data: calculated for $C_6H_{11}OSCl$, 166.0219; found, 166.0204. Owing to its low stability at room temperature, the product was stored in Dry Ice.

Preparation of Dimethyl Phosphorochloridate (11).—Trimethyl phosphite (7.4 g) in benzene (15 ml) was cooled in an ice bath. Chlorine gas was bubbled through the solution until it turned pale yellow. The solvent and other volatile products were removed on a flash evaporator and the residue was distilled under reduced pressure: yield 7.2 g (85%); bp 66° (10 mm) (lit.[33] bp 75–80° (20–25 mm)).

Preparation of *S*-Methylisothiuronium Dimethyl Phosphate.—This compound was prepared by a modification of the reported procedure.[34] In a 150-ml flask, fitted with a reflux condenser carrying a drying tube, were placed trimethyl phosphate (14.0 g), thiourea (7.6 g), and acetonitrile (35 ml). The reaction mixture was stirred and refluxed. The thiourea dissolved on warming and after 1.5 hr a white solid precipitated from the clear solution; refluxing was continued for another 2 hr. The reaction mixture was cooled and white crystals of *S*-methylisothiouronium dimethyl phosphate were collected, yield 17.7 g (82%), mp 139–141° (lit.[34] mp 136°).

Reaction of *p*-Toluenesulfenyl Chloride (4a) with 1:1 Benzil–Trimethyl Phosphite Adduct 3a in the Presence of 1,3,5-Trinitrobenzene as Free-Radical Inhibitor.—The adduct **3a** was generated as described previously from benzil (2.10 g, 0.01 mol) and trimethyl phosphite (1.25 g, 0.01 mol). It was dissolved in benzene (10 ml) and 1,3,5-trinitrobenzene (0.2 g) was added. The color changed to deep red. *p*-Toluenesulfenyl chloride (**4a**, 1.58 g, 0.01 mol) in benzene (5 ml) was added dropwise. At the end of the addition, the yellow reaction mixture was stirred for an additional 10 min. Benzene was removed on a flash evaporator and the residue recrystallized from *n*-hexane–methylene chloride mixture, yield 2.8 g (80%), mp 120–122°. This product was shown to be identical with α-benzoyl-α-chlorobenzyl *p*-tolyl sulfide (**5a**) by mixture melting point and ir spectra. Gas chromatographic analysis of the mother liquor on an Apiezon L column showed the presence of trimethyl phosphate and α-chloro-β-keto sulfide **5a**.

Reaction of *p*-Toluenesulfenyl Chloride (4a) with Azibenzil (26).[35]—In a 50-ml erlenmyer flask equipped with a magnetic stirrer was placed dry monoglyme (10 ml). Azibenzil (**26**, 2.22 g, 0.01 mol) was added with stirring and the resulting orange solution was cooled in an ice bath. *p*-Toluenesulfenyl chloride **4a** (1.59 g, 0.01 mol) was added dropwise to the azibenzil solution. As the addition progressed, the orange color of the azibenzil solution became lighter with evolution of nitrogen. Once the addition was complete, the pale yellow solution was stirred for 10 min at room temperature. The solvent was removed and the residue was recrystallized from *n*-hexane–methylene chloride. The yield of white crystalline product was 3.2 g (93%), mp 120–122°. This product was shown to be identical with α-benzoyl-α-chlorobenzyl *p*-tolyl sulfide **5a** by mixture melting point and ir spectra.

Reaction of Azibenzil (26) with Styrene.—A solution of **26** (4.4 g, 0.02 mol) and styrene (2.1 g, 0.02 mol) containing few crystals of 1,3,5-trinitrobenzene (polymerization inhibitor) in ether (10 ml) was heated under reflux for 41 hr. At the end of the reflux period, the solvent was removed under reduced pressure and the residual orange viscous oil was dissolved in acetic acid and cooled. The yellow crystals were separated by filtration and recrystallized from ethanol. Pale yellow crystals (3.1 g, 52%) of 2,2,3-triphenylcyclobutanone (**27**), mp 136–138°, were obtained. This product on further recrystallization from *n*-hexane–methylene chloride yielded white crystals melting at 137–138° (lit.[23] mp 132–136°); ir 1775 cm^{-1} (CO); nmr τ 2.20–3.20 (15 H, m), 5.47 (2 H, split t, J = 9 Hz), 6.50 (2 H, d, J = 9 Hz).

Attempted Reaction of 1:1 Benzil–Trimethyl Phosphite Adduct 3a with Styrene.—The adduct **3a** was generated as described previously from benzil (2.10 g, 0.01 mol) and trimethyl phosphite (1.25 g, 0.01 mol). It was dissolved in dry ether (10 ml) and styrene (1.05 g, 0.01 mol) containing a few crystals of 1,3,5-trinitrobenzene. The reaction mixture was refluxed for 41 hr and monitored by gas chromatography using Apiezon L and UCW-98 columns and by tlc on silica gel using 1:1 methylene chloride–hexane as eluent. The analysis of the reaction mixture showed the absence of 2,2,3-triphenylcyclobutanone (**27**).

Registry No.—**3a,** 4850-55-9; **3b,** 7137-83-9; **3c,** 1665-79-8; **4a,** 933-00-6; **4b,** 931-59-9; **4c,** 933-01-7; **4d,** 26826-81-3; **4e,** 1496-75-9; **4f,** 33537-30-3; **5a,** 28220-62-4; **5b,** 28194-60-7; **5c,** 28194-61-8; **5d,** 28194-62-9; **5e,** 28194-63-0; **5f,** 33537-32-5; **5g,** 28194-65-2; **8a,** 33487-46-6; **8b,** 33487-47-7; **26,** 3469-17-8; biacetyl monohydrazone, 33487-48-8; azibutanone, 14088-58-5.

Acknowledgment.—We wish to thank the Research Corporation and the Defense Research Board of Canada (Grant No. 9530-97) for financial support of this work.

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[33] G. M. Kosalapoff, "Organo Phosphorus Compounds," Wiley, New York, N. Y., 1950, p 252.

[34] J. B. Parker and T. D. Smith, *J. Chem. Soc.*, 442 (1961).

[35] Azibenzil (diazobenzil) was prepared according to the procedure of A. I. Vogel, in "A Textbook of Practical Organic Chemistry," Longmans, Green and Co. London, 1964, p 856.