A repeat sulfurization of 2,2′-diisocyanobiphenyl with a 6 molar excess of sulfur gave 2,2′-diisothiocyanatobiphenyl found in 67.2% yield by isolation from a silica gel column and 87.5% yield by gc (apparently there was additional reaction at 190°). The 2-isocyano-2′-isothiocyanatobiphenyl was found in 10.2% yield by isolation from a silica gel column and was not detected by gc analysis of the product mixture. There was no recovered starting material.

Registry No.—**8**, 33904-01-7; 3,4-dimethoxyformanilide, 33904-02-8; 2,4-dimethoxyphenyl isothiocyanate, 33904-03-9; 3,4-dimethoxyphenyl isothiocyanate, 33904-04-0; 2,2′-diisothiocyanatobiphenyl, 33904-05-1; 2-isocyano-2′-isothiocyanatobiphenyl, 33904-06-2.

Reactions of Dimethylsulfonium Cyclopentadienylide with Electrophiles and Dienophiles

Z. YOSHIDA,* S. YONEDA, AND M. HAZAMA

Department of Synthetic Chemistry, Kyoto University, Yoshida, Kyoto 606, Japan

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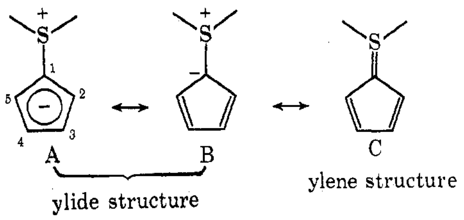
The reactions of dimethylsulfonium cyclopentadienylide (I) with electrophiles and dienophiles have been attempted. Electrophiles such as acetyl chloride, benzenesulfonic acid anhydride, Vilsmeier reagent, and triethyloxonium fluoroborate react with I to give acetyl-, benzenesulfonyl-, diformyl-, and ethyl-substituted derivatives of I, respectively. Dienophiles such as diethyl acetylenedicarboxylate, tetracyanoethylene, and chloranil react with I to afford the respective Michael addition products of I. From these reaction behaviors, an aromatic character of the five-membered ring in I has been discussed.

Dimethylsulfonium cyclopentadienylide (I) is considered to be the resonance hybrid of ylide structures A, B, and ylene structure C. Although I was first synthesized by Behringer[1] in 1965, no reactions of I have been reported so far except diazo coupling.[1] It was suggested in our previous communication[2] that the ylide structures predominantly contribute to the resonance hybrid of sulfonium and phosphonium cyclopentadienylide on the basis of theoretical consideration of their electronic spectra. In our other communications[3,4] the reaction of triphenylphosphonium cyclopentadienylide (II) with electrophiles and dienophiles were reported and it was found that electrophilic substitutions and Michael additions took place at the 2 position of the five-membered ring in II without cleavage of the C–P bond. In this paper we describe the reactions of I with electrophiles and dienophiles, and discuss which resonance structure (A, B, or C) plays an important role in the reaction.



Results and Discussion

Preparation of I.—Though I was prepared by Behringer, *et al.*,[1] in 1965, their procedure afforded I in only a few per cent yield. We used *N,N*-dimethylformamide as a solvent, and kept low temperature during the reaction. This improved procedure afforded I in considerably better yield (15–20%).

Reactions of I with Electrophiles.—The treatment of I with acetyl chloride, benzenesulfonic acid anhydride, Vilsmeier reagent, and triethyloxonium fluoroborate yielded 2-acetyl (III), 2-benzenesulfonyl (IV), 2,5-diformyl (V), and 2-ethyl (VI) derivatives of I, respectively. In the ir spectra of III and V, the carbonyl stretching vibrations were found at 1580 and 1630 cm^{-1} respectively. These shifts to lower wave numbers are attributed to the delocalization of the negative charge of the five-membered ring to the carbonyl oxygen atom. Since the delocalization of the negative charge generally stabilizes the five-membered ring, the derivatives whose substituents have electron-withdrawing nature, such as acetyl, benzenesulfonyl, and formyl, are more stable than I and the ethyl is less stable[5] than I. The position of substitution was determined by the nmr spectrum of each derivative of I. The signal for five-membered ring protons of I appears as an AA′BB′-type multiplet centered at τ 3.8 (4 H) and the exact chemical shifts and the coupling constants were obtained by simulating the spectrum.[6] The part in the lower field of the signal is assigned to the protons at 2,5 positions and the part in the higher field to the protons at 3,4 positions, as similarly in the case of II. The nmr spectrum of III exhibited three multiplets of equal area (1 H) centered at τ 3.0 (doublet of doublets, J = 3,8, 2.3 Hz), 3.5 (doublet of doublets, J = 3.8, 2.3 Hz), and 3.9 (t, J = 3.8 Hz), which are assigned to cyclopentadienyl ring protons. Among these three peaks, one is nearly in the same position as that in I and the other two peaks shift downfield from the cyclopentadienyl ring proton in I. This is well interpreted if the acetyl group is attached to the 2 position[7] of I; *i.e.*, two electron-withdrawing substituents (dimethylsulfonium and acetyl) make two

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[1] H. Behringer and F. Scheidl, *Tetrahedron Lett.*, **No. 22**, 1757 (1965).

[2] Z. Yoshida, K. Iwata, and S. Yoneda, *ibid.*, 1519 (1971); K. Iwata, S. Yoneda, and Z. Yoshida, *J. Amer. Chem. Soc.*, **93**, 6745 (1971).

[3] Z. Yoshida, S. Yoneda, H. Hashimoto, and Y. Murata, *Tetrahedron Lett.*, 1523 (1971).

[4] Z. Yoshida, S. Yoneda, Y. Murata, and H. Hashimoto, *ibid.*, 1527 (1971).

[5] VI decomposes within 2 or 3 days under nitrogen atmosphere, whereas I does not decompose for about 1 month even in the air.

[6] Z. Yoshida, S. Yoneda, and M. Hazama, *Chem. Commun.*, 716 (1971).

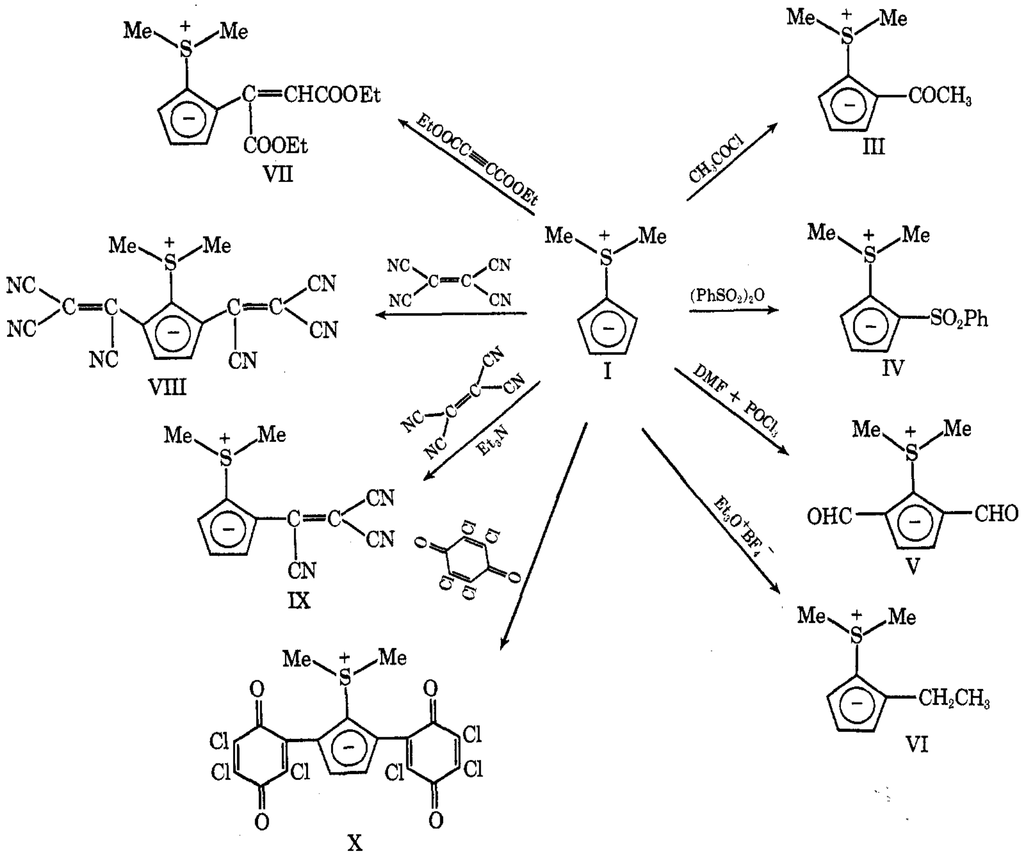
[7] Rationalization of 2 substitution was discussed in the previous publications.[3,8] Lloyd[9] also mentioned the substitution of the 2 position of the cyclopentadienyl ring of II.

[8] Z. Yoshida, S. Yoneda, and Y. Murata, unpublished (to be submitted to *J. Org. Chem.*).

[9] D. Lloyd and M. I. C. Singer, *Chem. Ind.* (*London*), 786 (1971).

SCHEME I

REACTIONS OF I WITH ELECTROPHILES AND DIENOPHILES



protons (3 and 5 positions) shift to lower field. Moreover, the peak (H_4) resonanced in the highest field was split equally by H_3 and H_5 (J = 3.8 Hz) to a triplet, and lower peaks (H_3, H_5) was split with each other (J = 2.3 Hz) and by H_4 (J = 3.8 Hz) to a doublet of doublets. The same tendency was also found in the nmr spectra of IV. This assignment is supported by analogy to the case of phosphonium cyclopentadienylide. The proton signal for the five-membered ring of the *p*-nitrophenylazo derivative of II resembles closely those of III and IV. The substituted position of the *p*-nitrophenylazo derivative of II was experimentally confirmed by Ramirez[10] to be the 2 position.

On the other hand, the signal for the five-membered ring protons of VI exhibited a multiplet centered at τ 3.8 (3 H), in which the intensity diminished by one proton in the part of lower field. This tendency was also found in alkyl derivatives of II.[11] Since the ethyl group scarcely disturbed the electronic state of the five-membered ring, the decrease of the intensity in the lower part indicates that the 2 position was substituted by the ethyl group.

The Reactions of I with Dienophiles.—Upon treatment of I with diethyl acetylenedicarboxylate, the 1:1 adduct (VII) was obtained. The nmr spectrum of VII showed a vinyl proton at τ 4.1 (s, 1 H), five-membered ring protons centered at τ 3.6 (m, 3 H), and signals corresponding to two nonequivalent ethyl groups, methylene protons at τ 5.6 (q, 2 H) and 5.8 (q, 2 H), and methyl protons at τ 8.6 (t, 3 H) and 8.7 (t, 3 H). These nmr data indicate that VII is the Michael addition reaction product as presented in Scheme I. No evidence for Diels–Alder reaction was observed.

When I was treated with tetracyanoethylene in the absence of a base, a 1:2 Michael addition product (VIII) was obtained, while in the presence of thiethylamine only a 1:1 adduct (IX) was obtained. The difference in reaction product in the absence and in the presence of triethylamine is interpreted as follows. When no base was used, before the elimination of hydrogen cyanide from the 1:1 adduct, another molecule of tetracyanoethylene easily added to the 1:1 adduct, followed by elimination of hydrogen cyanide to give the bistricyanovinyl derivative of I. On the other hand, when triethylamine was used as a base, the elimination of hydrogen cyanide immediately would occur before another addition of tetracyanoethylene to the 1:1 adduct. Consequently, the further addition of tetracyanoethylene should be excluded, because a large electron-withdrawing nature of the tricyanovinyl group deactivates the five-membered ring.

The reaction of I with chloranil at 5° gave Michael addition reaction product X, blue crystals. Its nmr spectrum contains a singlet at τ 3.17 (2 H, cyclopentadienyl), clearly indicating that X is the 1:2 adduct of I and chloranil.

Through the reactions of I with dienophiles evidence for Diels–Alder reaction was not obtained, but the products isolated were Michael addition reaction products.

All the reactions of I with electrophiles and dienophiles are summarized in Scheme I. In the comparison of dimethylsulfonium cyclopentadienylide with

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[10] F. Ramirez and S. Levy, *J. Amer. Chem. Soc.*, **79**, 6167 (1957).

[11] The alkyl derivatives of II have been recently prepared in our laboratory. The results will be published elsewhere.

triphenylphosphonium cyclopentadienylide, the former is considered likely to be more reactive than the latter, because I reacts with electrophiles and dienophiles under much more mild conditions than II. In summary from the results, it can be concluded that I has an aromatic character; that is, the structure A predominantly contributes to the resonance hybrid of I. The aromatic character of the five-membered ring in I has been also supported by the π-bond orders (P_{23} and P_{34}) estimated from the vicinal coupling constants. The π-bond orders of 0.71 and 0.56 for P_{23} and P_{34} calculated from the $J_{\text{vic}} - P_{\text{rs}}$ relation proposed by Smith, *et al.*,[12] are clearly within the aromatic range.[6]

Experimental Section

Spectra.—All ultraviolet spectra were taken on a Hitachi EPS-3T recording photometer. All infrared spectra were recorded on a Hitachi grating infrared spectrophotometer, Model 215. All nmr spectra were recorded with a JNM C-60H nmr spectrometer in deuteriochloroform with tetramethylsilane as an internal standard.

Dimethylsulfonium Cyclopentadienylide (I).—To a stirred solution of 100 g (1.5 mol) of cyclopentadiene in 300 ml of *N*,*N*-dimethylformamide (DMF) was added 240 g (1.5 mol) of bromine at −50 to −30° within 1 hr and the mixture was stirred for an additional 1 hr at this temperature. To the solution, 186 g (3 mol) of dimethyl sulfide in 200 ml of DMF was added below −30°. The orange-yellow colored solution was allowed to stand at 0° for 24 hr. The sulfonium salt precipitated was filtered and poured into 200 ml of water. After decolorization with charcoal, the mixture was made alkaline with 20% aqueous sodium hydroxide and a crude product separated was recrystallized from benzene to give 29 g (15.3%) of colorless needles: mp 134°; uv max (methylene chloride) 283 mμ (ϵ 1.15 × 10^4); ir (KBr) 3050, 2980, 2900, 1430 (s), 1420 (s), 1400 (s) 1340, 1320, 1220, 1200 (s), 1190 (s), 1040, 1030, 1020, 980 (s), 710 cm^{-1} (these infrared absorption bands are characteristic of the derivative of I); nmr ($CDCl_3$) τ 3.8 (m, AA′BB′, $J_{23} = 3.9$, $J_{34} = 2.8$, $J_{24} = 2.1$, $J_{25} = 1.9$ Hz, 4 H, ring), 7.4 (s, 6 H, SCH_3).

Dimethylsulfonium 2-Acetylcyclopentadienylide (III).—To a cooled solution of 1.26 g (0.01 mol) of I dissolved in 50 ml of methylene chloride was added 0.785 g (0.01 mol) of acetyl chloride at −10° under nitrogen atmosphere, and the mixture was stirred for 6 hr at −10°. The reaction mixture was washed with water and dried over calcium chloride, and the solvent was removed under reduced pressure. The residue was chromatographed on alumina and III was obtained as colorless needles (70 mg, 4.2% yield): mp 150°; ir (KBr) 1580 cm^{-1} ($\nu_{C=O}$); nmr ($CDCl_3$) τ 3.0 (doublet of doublets, $J = 3.8$, 2.3 Hz, 1 H, ring), 3.5 (doublet of doublets, $J = 3.8$, 2.3 Hz, 1 H, ring), 3.9 (t, 1 H, ring), 6.95 (s, 6 H, SCH_3), 7.6 (s, 3 H, $COCH_3$).

Anal. Calcd for $C_9H_{12}OS$: C, 64.23; H, 7.14; O, 9.52; S, 19.05. Found: C, 64.49; H, 7.25; O, 9.53; S, 18.92.

Dimethylsulfonium 2-Benzenesulfonylcyclopentadienylide (IV).—To a stirred solution of 1.26 g (0.01 mol) of I dissolved in 50 ml of methylene chloride was added a solution of 3 g (0.01 mol) of benzenesulfonic acid anhydride in methylene chloride at room temperature under nitrogen atmosphere. After stirring for an additional 2 hr, the reaction mixture was neutralized with 5% aqueous sodium hydroxide, extracted with methylene chloride, dried over calcium chloride, and concentrated under reduced pressure. The residual oil was chromatographed on alumina, and 150 mg (5.6%) of IV was obtained as pale yellow needles: mp 164–165°; uv max (acetonitrile) 262 mμ (ϵ 8.2 × 10^3), 292 (1.02 × 10^3); ir (KBr) 1340, 1320 (ν_{as} SO_2), 1140 cm^{-1} (ν_s SO_2); nmr ($CDCl_3$) τ 2.3 (m, 2 H, phenyl), 2.8 (m, 3 H, phenyl), 3.2 (doublet of doublets, $J = 3.8$, 2.3 Hz, 1 H, ring), 3.5 (doublet of doublets, $J = 3.8$, 2.3 Hz, 1 H, ring), 3.8 (t, $J = 3.8$ Hz, 1 H, ring), 7.1 (s, 6 H, SCH_3).

Anal. Calcd for $C_{13}H_{14}S_2O_2$: C, 58.65; H, 5.26; S, 24.06; O, 12.03. Found: C, 58.71; H, 5.84; S, 23.77; O, 11.98.

Dimethylsulfonium 2,5-Diformylcyclopentadienylide (V).—The Vilsmeier reagent was prepared as follows. To 10 ml (0.13 mol) of *N*,*N*-dimethylformamide was added 1.2 ml (0.024 mol) of phosphorus oxychloride at −10 to −15° under nitrogen atmosphere, and the temperature was elevated to 5°. To this solution, 1.26 g (0.01 mol) of I was added slowly maintaining the temperature at −10 to −15°, and the mixture was stirred for 1 hr at 0°. The reddish precipitate that separated was filtered, shaken with aqueous potassium perchlorate solution, and made alkaline with 50% aqueous sodium hydroxide. The mixture was extracted with methylene chloride and the extract was dried, concentrated, and chromatographed on alumina to give 180 mg (4.4%) of V as pale brown needles: mp 159–160°; uv max (acetonitrile) 263 mμ (ϵ 1.93 × 10^4), 326 (6.85 × 10^3); ir (KBr) 1630 cm^{-1} ($\nu_{C=O}$); nmr ($CDCl_3$) τ 0.50 (s, 2 H, CHO), 2.8 (s, 2 H, ring), 6.95 (s, 6 H, SCH_3).

Anal. Calcd for $C_9H_{10}O_2S$: C, 59.31; H, 5.53; S, 17.59. Found: C, 59.49; H, 5.61; S, 17.68.

Dimethylsulfonium 2-Ethylcyclopentadienylide (VI).—To a stirred solution of 1.26 g (0.01 mol) of I in 50 ml of methylene chloride was added 2.0 g (0.0105 mol) of triethyloxonium fluoroborate at 0°, and the mixture was stirred for 1 hr at this temperature. The reaction mixture was then neutralized with 5% aqueous sodium hydroxide and extracted with methylene chloride. The extract was, after removal of the solvent, chromatographed on alumina to give 50 mg of brown precipitate (VI). Elemental analysis of VI was impossible to carry out because of its instability. This material showed ir (KBr) 3080, 3000, 2900, 2880, 2860, 2840 cm^{-1} (ν_{CH_3}, ν_{CH_2}); nmr ($CDCl_3$) τ 3.80 (m, 3 H, ring), 7.30 (s, 2 H, SCH_3), 7.30 (q, 2 H, $J = 7.5$ Hz, CH_2), 8.80 (t, 3 H, $J = 7.5$ Hz, CH_3). These spectral data clearly indicate VI to be the monoethyl derivative of I.

Dimethylsulfonium 2-(1,2-Dicarbethoxyvinyl)cyclopentadienylide (VII).—To a stirred solution of 1.0 g (7.95 mmol) of I in 30 ml of methylene chloride was added 1.45 g (7.95 mmol) of diethyl acetylenedicarboxylate at 5° under nitrogen atmosphere. After stirring for 1 hr at this temperature, the reaction mixture was concentrated under reduced pressure and chromatographed on alumina, and VII was obtained as yellow crystals (2.15 g, 88.7% yield): mp 50°; uv max 390 mμ (ϵ 1.65 × 10^4); ir (KBr) 1720, 1680 ($\nu_{C=O}$), 1560 ($\nu_{C=C}$), 1480, and 1140 cm^{-1}; nmr ($CDCl_3$) τ 3.60 (m, 3 H, ring), 4.10 (s, 1 H, vinyl), 5.60 (q, 2 H, $J = 7.5$ Hz, CH_2), 5.80 (q, 2 H, $J = 7.5$ Hz, CH_2), 7.27 (s, 6 H, SCH_3), 8.62 (t, 3 H, $J = 7.5$ Hz, CH_3), 8.70 (t, 3 H, $J = 7.5$ Hz, CH_3).

Anal. Calcd for $C_{15}H_{20}O_4S$: C, 60.79; H, 6.80; O, 21.59; S, 10.82. Found: C, 60.23; H, 7.08; O, 21.65; S, 10.52.

Dimethylsulfonium 2,5-Bis(tricyanovinyl)cyclopentadienylide (VIII).—To a stirred solution of 1.0 g (7.95 mmol) of I in 50 ml of tetrahydrofuran was added 1.01 g (7.95 mmol) of tetracyanoethylene in tetrahydrofuran at 5° under nitrogen atmosphere. After stirring for 3 hr at this temperature, the reaction mixture was concentrated under reduced pressure and chromatographed on alumina to afford 202 mg (7.8% yield) of red crystals (VIII): mp 220°; uv max (chloroform) 308 mμ (ϵ 1.07 × 10^4), 322 (9.85 × 10^3), 404 (3.12 × 10^4), and 524 (6.00 × 10^4); ir (KBr) 2200 (ν_{CO}), 1500 ($\nu_{C=C}$), 1300 cm^{-1}; nmr (DMSO-d_6) τ 2.20 (m, 2 H, ring), 6.70 (s, 6 H, SCH_3).

Anal. Calcd for $C_{17}H_8N_6S$: C, 62.18; H, 2.46; N, 25.59; S, 9.76. Found: C, 61.95; H, 2.53; N, 25.42; S, 970.

Dimethylsulfonium 2-Tricyanovinylcyclopentadienylide (IX).—To a stirred solution of 1.0 g (7.95 mmol) of I and 8.1 g (7.95 mmol) of triethylamine in 50 ml of tetrahydrofuran was added 1.01 g (7.95 mmol) of tetracyanoethylene in tetrahydrofuran at 5° under nitrogen atmosphere, and the mixture was allowed to stir at this temperature for 3 hr. The reaction mixture was concentrated under reduced pressure and chromatographed on alumina to yield 240 mg (13.3%) of orange crystals (IX): mp 205°; uv max (chloroform) 260 mμ (ϵ 2.18 × 10^3), 428 (2.07 × 10^4), and 458 (2.79 × 10^4); ir (KBr), 2200 (ν_{CN}), 1530 ($\nu_{C=C}$), 1380, 950 cm^{-1}; nmr (DMSO-d_6) τ 3.10 (m, 3 H, ring), 6.90 (s, 6 H, SCH_3).

Anal. Calcd for $C_{12}H_9N_3S$: C, 63.43; H, 3.99; N, 18.49; S, 14.11. Found: C, 63.33; H, 4.00; N, 18.79; S, 14.20.

Preparation of X.—To a stirred solution of 1.0 g (7.95 mmol) of I in 50 ml of methylene chloride was added 1.95 g (7.95 mmol) of chloranil at 5° under nitrogen atmosphere. After stirring at this temperature for 2 hr, the reaction mixture was concentrated under reduced pressure and chromatographed on alumina to give 145 mg (8.1% yield) of blue crystals: mp 330° dec; uv max

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[12] W. B. Smith, W. H. Watson, and S. Chiranjeevi, *J. Amer. Chem. Soc.*, **89**, 1438 (1967).

(chloroform) 281 mμ (ε 4.10 × 10^4), 630 (6.20 × 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

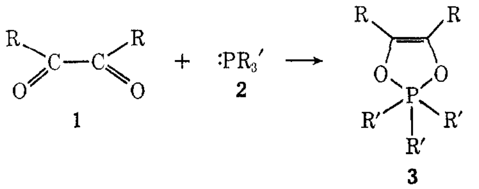
DAVID N. HARPP* AND P. MATHIAPARANAM[1]

Department of Chemistry, McGill University, Montreal, Quebec, Canada

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.



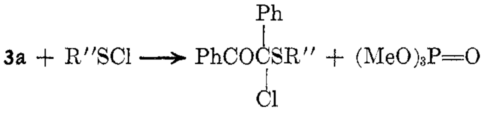
1 **2** **3**

	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]



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

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.