Chemistry of Resonance-Stabilized Sulfonium Ylids

K. W. RATTS AND A. N. YAO

Monsanto Company, Agricultural Division, Research Department, St. Louis, Missouri 63166

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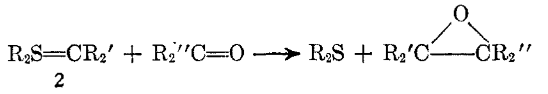
An observed difference in the reactivity of amide- or ester-stabilized and aroyl-stabilized S-ylids with aldehydes is explained by the corresponding difference in ylid nucleophilicity and a mechanism which involves reversible, aligned betaine formation, bond rotation, and elimination of dimethyl sulfide. The nucleophilic behavior of acyl-stabilized S-ylids has been demonstrated by their reaction with nitrosobenzene, alkylation, acylation, and bromination. A new class of halo S-ylids has been realized by dehydrohalogenation of the corresponding salts. Pyrolysis of the ylids leads to products which may be rationalized as trapped carbenic intermediates.

Phosphorus ylids 1 have proven to be of value in the synthesis of olefins *via* the Wittig reaction.[1] Sulfur ylids 2, however, react with carbonyl compounds to produce epoxides.[2,3] Stable sulfonium ylids, moreover, are of limited synthetic utility since nucleophilic reactivity is weak and reaction with carbonyl compounds sluggish or nonexistent.[3-5] The marked difference in the apparent reactivity of these sulfonium ylids prompted a study of their chemical properties.

$$\underset{1}{R_3P{=}CR_2'} + R_2''C{=}O \longrightarrow R_3P{=}O + R_2'C{=}CR_2''$$



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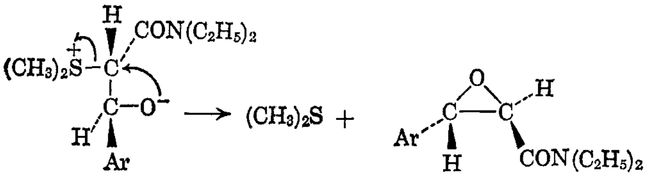
We have found that certain carbonyl-stabilized sulfonium ylids react normally with aldehydes. For example, N,N-diethyl-2-(dimethylsulfuranylidene)acetamide (3) reacts with benzaldehyde or 4-nitrobenzaldehyde to give the corresponding glycidamides. The products 5 have the *trans* configuration. The *cis*-epoxide does not isomerize to the *trans* under the reaction conditions indicating that the reaction is stereospecific. This stereospecificity has previously been observed with nonresonance-stabilized sulfur ylids.[6]

$$\underset{3}{(CH_3)_2S{=}CHCON(C_2H_5)_2} + ArCHO \rightleftarrows$$



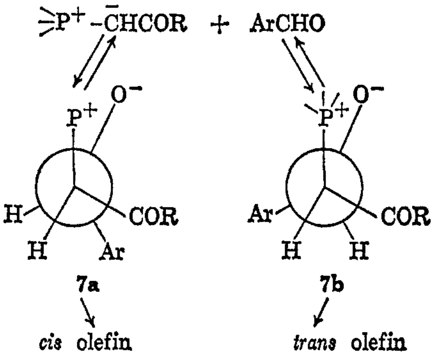
4

5a, Ar = C_6H_5
b, Ar = 4-$O_2NC_6H_4$

Amide-stabilized S-ylids have previously been shown to react with Schiff bases to produce enaminocinnamamides[7] *via* aziridine intermediates, a sequence similar to epoxide formation with aldehydes. However, 2-(dimethylsulfuranylidene)acetophenone (6) gave no reaction or isolable adduct with either benzaldehyde[8,8a] or benzalaniline. This difference in reactivity, depending upon the nature of the carbonyl group, is not observed with the P-ylids. A possible explanation of this fact is given below.

The initial nucleophilic attack of P-ylids upon aldehydes is reversible and occurs with the positive hetero atom and oxyanion aligned.[9] The favored isomer 7b leads to the more stable product, *trans* olefin (see Chart I), in the case of phosphorus ylids. With sulfur ylids the favored betaine 8b would lead to less stable *cis*-epoxide, and the more hindered betaine 8a is intermediate in formation of the lower energy *trans*-epoxide.[6] (see Chart II). Only if the S-ylid is extremely basic, as with 3,[5] is the initial equilibrium favorable so as to allow formation of the hindered betaine 8a which leads to *trans*-epoxide.

CHART I



The lack of reaction with the phenacyl sulfonium ylids cannot be explained on the basis of low nucleophilicity of the S-ylids since their basicity is greater than P-ylids which are known to react.[5] It is to be expected in these situations that basicity is proportional to nucleophilic reactivity.[10]

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[1] A. J. Speziale and K. W. Ratts, *J. Am. Chem. Soc.*, **85**, 2790 (1963).

[2] E. J. Corey and M. Chaykovsky, *ibid.*, **84**, 3782 (1962).

[3] A. W. Johnson and R. B. LaCount, *ibid.*, **83**, 417 (1961).

[4] (a) H. Nozaki, K. Kondo, and M. Takaku, *Tetrahedron Letters*, **No. 4**, 251 (1965). (b) W. J. Middleton, E. J. Buhle, J. G. McNally, Jr., and M. Zanger, *J. Org. Chem.*, **30**, 2384 (1965). (c) H. Beringer and F. Scheidl, *Tetrahedron Letters*, **No. 22**, 1757 (1965). (d) A. Hochrainer and F. Wessely, *ibid.*, **No. 12**, 721 (1965). (e) E. G. Howard, A. Kotch, R. V. Lindsey, Jr., and R. E. Putnam, *J. Am. Chem. Soc.*, **80**, 3924 (1958).

[5] K. W. Ratts and A. N. Yao (in press).

[6] A. W. Johnson, V. J. Hruby, and J. L. Williams, *J. Am. Chem. Soc.*, **86**, 918 (1964).

[7] A. J. Speziale, C. C. Tung, K. W. Ratts, and A. N. Yao, *ibid.*, **87**, 3460 (1965).

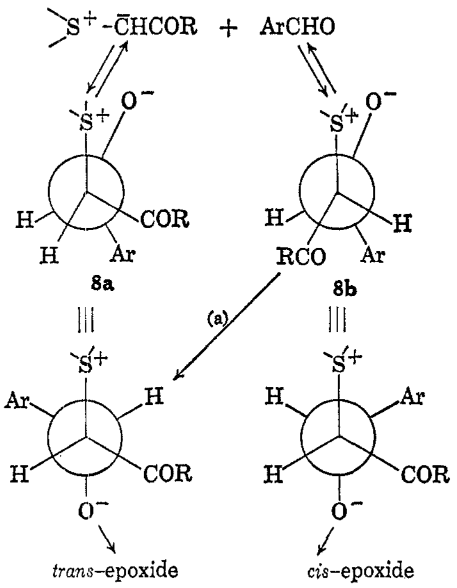
[8] During attempts to initiate reaction of 2-(dimethylsulfuranylidene)-acetophenone with 4-nitrobenzaldehyde in tetrahydrofuran a 1:1 adduct was formed, mp 109–110°. The product exhibited infrared and nmr spectra in chloroform solution which were simply those obtainable from superimposition of the spectra of the two starting compounds. A 1:1 mixture melting point showed a significant depression, mp 40–80° (ylid mp 59–60; aldehyde mp 106.5°). The infrared spectrum of the mixture as a mull indicated a strong *aldehydic* carbonyl although the adduct as a mull showed none.

[8a] NOTE ADDED IN PROOF.—A 10% yield oxirane has been recently obtained by the reaction of 6 with *p*-nitrobenzaldehyde: A. W. Johnson and R. T. Amel, *Tetrahedron Letters*, **No. 8**, 819 (1966).

[9] A. J. Speziale and D. E. Bissing, *J. Am. Chem. Soc.*, **85**, 1888, 3878 (1963).

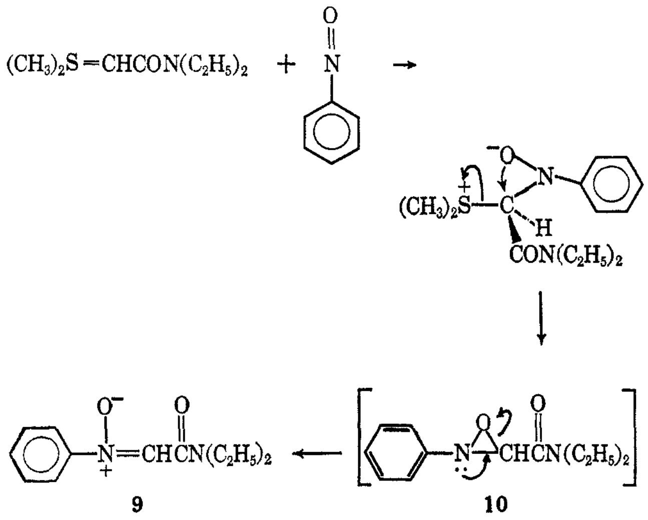
[10] S. Fliszar, R. F. Hudson, and G. Salvadori, *Helv. Chim. Acta*, **46** (5), 1580 (1963).

CHART II



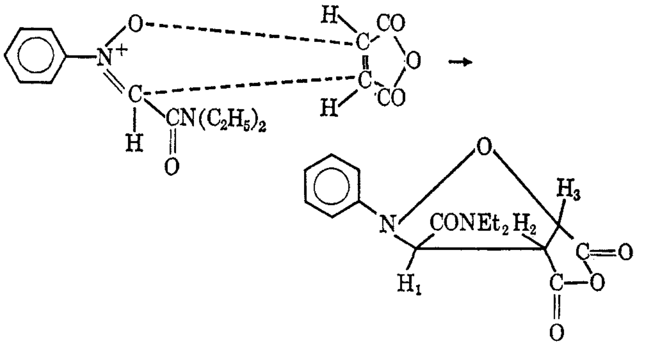
The surprising lack of reactivity of less basic S-ylids is undoubtedly due to high energy barriers to the formation of *cis*-epoxides in the second step of the reaction, which must be preceded by a C–C bond rotation of 180°, and to decreased tendency to form a betaine which is hindered. The P-ylids reactions do not involve these complicating factors since least hindered betaine can form favored *trans* olefins.

The nucleophilic character of amide-stabilized ylids is also demonstrated by their reaction with nitrosobenzene.[11] N,N-Diethyl-2-(dimethylsulfuranylidene)-acetamide reacted with nitrosobenzene to yield α-(diethylcarbamoyl)-N-phenylnitrone in 42% yield. A suggested mechanism is given below.



Reduction of the product with lithium aluminum hydride gave an 84% yield of N,N-diethyl-N′-phenylethylene diamine consistent with either an oxazirane **10** or a nitrone **9** structure. A singlet at τ 2.50 in the nmr spectrum is consistent with **9** rather than **10** (=CH– *vs.* $\overset{O}{\underset{N}{>}}$CH–) as is the ultraviolet absorption of the product: λ_{max} 268 mμ (log ϵ 5.00).

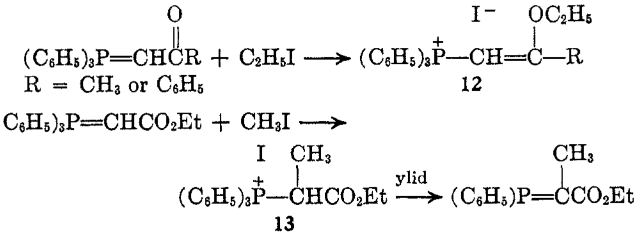
An isoxazolidine **11** was formed between maleic anhydride and the nitrone.



11

The nitrone CH at τ 2.50 in the product is absent; instead there are observed three protons, τ 4.63 singlet (1), τ 4.85 doublet (1, J = 8.0 cps), and H_2 τ 5.35 doublet (1, J = 8.0 cps). The fact that H_2 is coupled to only one of the adjacent protons suggests that H_3 is *cis* and H_1 *trans* oriented with respect to the ring. Since the 1,3-dipolar addition of the nitrone to maleic anhydride must occur in a *cis*-oriented fashion H_2 and H_3 must be on the opposite side of the ring from H_1 and the ring juncture must be *cis*. The 1,3-dipolar addition supports the nitrone rather than the oxazirane structure.

Alkylation of P-ylids has been reported to yield both O-alkylated[12] products **12** and C-alkylated products[13] **13**. Owing to the greater –I effect of R_2S^+



$$(C_6H_5)_3P{=}CH\overset{O}{\overset{\|}{C}}R + C_2H_5I \longrightarrow (C_6H_5)_3\overset{+}{P}{-}CH{=}\overset{I^-\ \ OC_2H_5}{\overset{|}{C}}{-}R$$

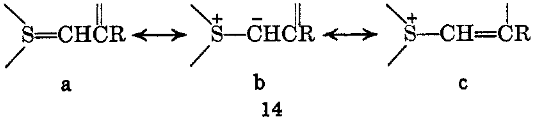
R = CH_3 or C_6H_5 **12**

$$(C_6H_5)_3P{=}CHCO_2Et + CH_3I \longrightarrow$$

$$(C_6H_5)_3\overset{+}{P}{-}\overset{I\ \ CH_3}{\overset{|}{C}}HCO_2Et \xrightarrow{\text{ylid}} (C_6H_5)P{=}\overset{CH_3}{\overset{|}{C}}CO_2Et$$

13

compared with $R_3\overset{+}{P}$– and the greater ability for π-d overlap with $R_2\overset{+}{S}$,[14] the contribution of **14a** and **14b** should be increased relative to the phosphorus hybrid.



$$>S{=}CH\overset{O}{\overset{\|}{C}}R \longleftrightarrow >\overset{+}{S}{-}\overset{-}{C}H\overset{O}{\overset{\|}{C}}R \longleftrightarrow >\overset{+}{S}{-}CH{=}\overset{O^-}{\overset{|}{C}}R$$

a b c

14

C-Alkylation might be favored in this situation if the reaction reflects the nature of the resonance hybrid at all.

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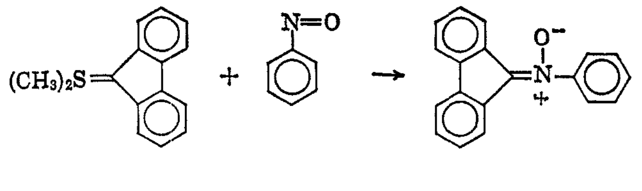
[11] The reaction of dimethylsulfonium fluorenylide with nitrosobenzene



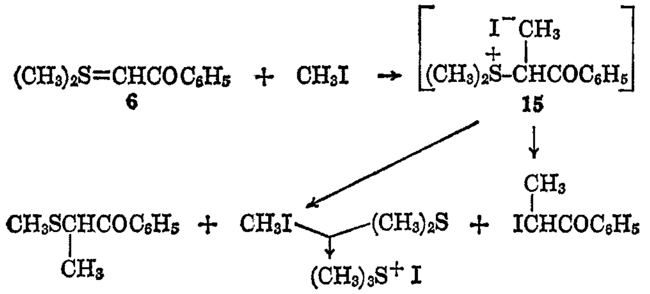
has been shown by Johnson and LaCount[8] to produce a nitrone rather than an oxazirane.

[12] F. Ramirez and S. Dershowitz, *J. Org. Chem.*, **22**, 41 (1957).

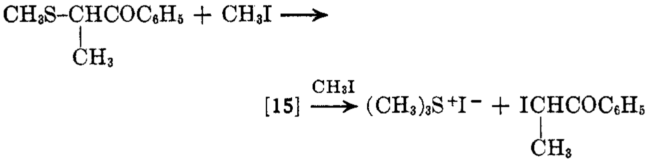
[13] (a) H. J. Bestman and H. Halberlein, *Z. Naturforsch*, **17b**, (1962). (b) H. J. Bestman and H. Schulz, *Chem. Ber.*, **95**, 2921 (1962).

[14] W. von E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.*, **77**, 521 (1955).

The treatment of 2-(dimethylsulfuranylidene)acetophenone with 1 equiv of methyl iodide gives, at room temperature, a mixture of 23% 2-iodopropiophenone, 22% 2-(methylmercapto)propiophenone, 42% tribenzoylcyclopropane, and presumably trimethylsulfonium iodide. The products appear to be derived from decomposition of the sulfonium salt[15] obtained by C-alkylation of the ylid. The cyclopropane arises from a series of displacement reactions involving the salt of the starting ylid.[4a]



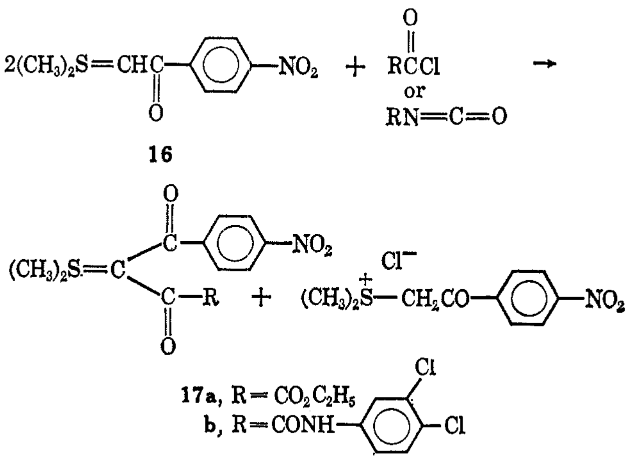
An attempt to prepare **15** by alkylation of 2-(methylmercapto)propiophenone gave only trimethylsulfonium iodide and 2-iodopropiophenone. No ylid was formed in this reaction.



$$CH_3S\text{-}\underset{CH_3}{\underset{|}{C}}HCOC_6H_5 + CH_3I \longrightarrow [15] \xrightarrow{CH_3I} (CH_3)_3S^+I^- + I\underset{CH_3}{\underset{|}{C}}HCOC_6H_5$$

The results suggest that these stable S-ylids will alkylate at carbon. However, the products appear extremely unstable even at room temperature.

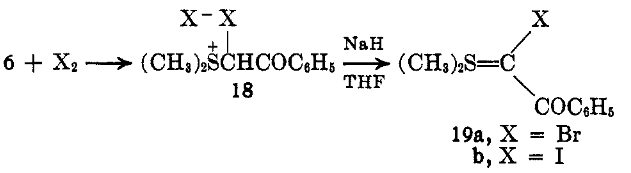
Further nucleophilic reactivity of these sulfonium ylids is demonstrated by their acylation and halogenation. 2-(Dimethylsulfuranylidene)-4′-nitroacetophenone **16** yields C-acylated products **17** upon reaction with ethoxalyl chloride and 3,4-dichlorophenyl isocyanate, respectively. The acylation of phosphorus ylids is similar although nitrogen ylids have been reported to O-acylate.[15]



16

17a, R = $CO_2C_2H_5$
b, R = CONH–

Bromine and iodine add to the ylids to yield the corresponding α-halo sulfonium salts (**18**). These salts may be dehydrohalogenated by sodium hydride in tetrahydrofuran although *aqueous* base causes their hydrolysis. The reaction of halogen with the ester or amide **3** leads to salts which are unstable so as to preclude their isolation.

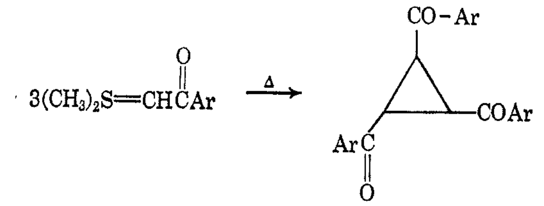


$$6 + X_2 \longrightarrow \underset{\textbf{18}}{(CH_3)_2\overset{+}{S}\overset{X}{\overset{|}{C}}HCOC_6H_5}\,X^- \xrightarrow[\text{THF}]{\text{NaH}} (CH_3)_2S{=}C(X)COC_6H_5$$

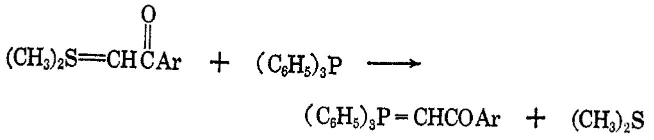
19a, X = Br
b, X = I

Upon standing the halo ylids **19** decomposed slowly to release halogen and form dark tars as opposed to the corresponding P-ylids which are stable. In general the acylation and halogenation of the S-ylids are comparable to the P-ylids except for the increased instability of the former ylids and their salts. The latter is not unexpected since the dimethyl sulfide is an excellent leaving group compared to triphenyl phosphine.

The decomposition of sulfonium ylids to carbenes has been well documented.[16] The isolation of the carbonyl-stabilized ylids provided an opportunity to generate keto carbenes. Pyrolysis of the ylids did, indeed, provide keto carbenes which were trapped *via* trimerization to yield cyclopropanes or by triphenyl phosphine to give phosphorus ylids.



20a, Ar = C_6H_5
b, Ar = $4\text{-}NO_2C_6H_4$



$$(CH_3)_2S{=}CH\overset{O}{\overset{\|}{C}}Ar + (C_6H_5)_3P \longrightarrow (C_6H_5)_3P{=}CHCOAr + (CH_3)_2S$$

Extensive precautions were taken to ensure that no water was present so as to preclude reactions of sulfonium hydroxides which would not necessarily involve carbenes. Although the yields are low the reactions indicate possible keto carbene formation.

The above studies indicate that S-ylids are nucleophilic (as are P-ylids) in their reactions. Over-all reactions are modified by the ease of dimethyl sulfide (as opposed to *t*-phosphines) elimination.

Experimental Section[17]

Reaction of Ylids and Aldehydes. N,N-Diethyl-2-(dimethylsulfuranylidene)acetamide (3). A. 4-Nitrobenzaldehyde.— The above ylid (0.05 mole) was prepared as previously described.[7] To the solution of ylid in tetrahydrofuran (250 ml, 0.055 mole) was added 4-nitrobenzaldehyde (7.6 g, 0.05 mole) in one portion. The red solution was cooled to 10°, stirred for 1 hr, then allowed to warm to room temperature, and further stirred for 30 min. The dark red solution was concentrated to give a red solid (14.3 g) mp 80–90°. Recrystallization of this solid from methylene chloride–petroleum ether (bp 30–75°) several times gave 8.4 g

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[15] F. Weygand and H. Daniel, *Chem. Ber.*, **94**, 3147 (1961).

[16] (a) V. Franzen, H. J. Schmidt and C. Mertz, *ibid.*, **94**, 2942 (1961). (b) A. W. Johnson and V. J. Hruby, *J. Am. Chem. Soc.*, **84**, 3586 (1962). (c) C. Gardner Swain and E. R. Thornton, *ibid.*, **83**, 4033 (1961). (d) A. W. Johnson and R. B. LaCount, *ibid.*, **83**, 417 (1961). (e) F. Krollpfeiffer, H. Hartmann, and F. Schmidt, *Ann.*, **563**, 15 (1949).

[17] Melting points are uncorrected. Analyses were performed by Galbraith Laboratories.

(64%) *trans*-N,N-diethyl-3-(4-nitrophenyl)glycidamide, mp 96–97°.

Anal. Calcd for $C_{13}H_{16}N_2O_4$: C, 59.08; H, 6.10; N, 10.60. Found: C, 59.16; H, 6.75; N, 10.74.

B. Benzaldehyde.—*trans*-N,N-Diethyl-3-phenylglycidamide was prepared in the above manner in 66% yield, mp 80–84°. Recrystallization of this solid from hexane gave mp 85-87.5°, identical in all respects with authentic material.[18]

2-(Dimethylsulfuranylidene)acetophenone (6). A. 4-Nitrobenzaldehyde.—The above ylid (0.025 mole) was prepared by the method previously described.[7] To the solution of ylid in tetrahydrofuran (125 ml, 0.025 mole) was added in one portion of 4-nitrobenzaldehyde (3.18 g, 0.025 mole). The solution was stirred at room temperature for 3 hr and then concentrated to give a yellow-green solid (8.9 g), mp 108–110° dec. The infrared spectrum in chloroform and the nmr spectrum in deuterated chloroform indicated a 1:1 mixture of starting materials. An infrared spectrum in Nujol, however, showed no aldehyde carbonyl band. A 1:1 mixture of 2-(dimethylsulfuranylidene)-acetophenone (mp 59–60°) and 4-nitrobenzaldehyde (mp 106.5°) exhibited a carbonyl band in the infrared spectrum (Nujol) and melted at 40–80°. The crude product was washed repeatedly with ether to give a yellow solid (6.0 g, 72%), mp 109–111°.

Anal. Calcd for $C_7H_5NO_3 \cdot C_{10}H_{12}OS$: C, 61.61; H, 5.17; N, 4.23; S, 9.68. Found: C, 61.65; H, 5.28; N, 4.43; S, 9.54.

Several attempts to recrystallize the solid were not successful. The ether wash was concentrated to a residual red tar.

B. Benzaldehyde.—To a solution of 2-(dimethylsulfuranylidene)acetophenone (0.025 mole) in tetrahydrofuran (125 ml, 0.025 mole) was added benzaldehyde (2.65 g, 0.025 mole) in one portion. The mixture was stirred at room temperature for 5 days then concentrated to a dark oil. The oil was extracted with ether to leave 1.19 g solid, mp >200°; recrystallization of this material from methylene chloride gave 0.3 g (26%) of 1,2,3-tribenzoylcyclopropane. The ether extract was concentrated to yield 2.1 g (47%) of the starting ylid. The mother liquors were concentrated to a red oil which was characterized by infrared analysis as benzaldehyde.

α-Diethylcarbamoyl)-N-phenylnitrone (9).—N,N-Diethyl 2-(dimethylsulfuranylidene)acetamide was prepared by the sodium hydride method.[7] To the reaction mixture containing the sulfonium ylid (0.05 mole) and sodium chloride in tetrahydrofuran was added in one portion of nitrosobenzene (5.36 g, 0.05 mole). The mixture was stirred overnight at room temperature and filtered to remove the sodium chloride (3.7 g, >100%). The filtrate was concentrated and the residue crystallized by trituration with ether and petroleum ether with cooling. Fine yellow needles crystallized and were filtered to give the product (4.7 g, 0.021 mole 42%), mp 82–84.5°. Recrystallization of the nitrone from ether gave an analytical sample: mp 85-86.5°; infrared spectrum ($CHCl_3$), $\nu_{C=O}$ 1620 cm^{-1}; nmr spectrum ($CDCl_3$), ArH at τ 2.59 multiplet (5), –CH– at τ 2.50 singlet (1), $-CH_2-$ at τ 6.63 multiplet (4), $-CH_3-$ τ 8.81 triplet (6); ultraviolet spectrum, λ_{max}^{EtOH} 268 mμ (log ε 5.00).

Anal. Calcd for $C_{12}H_{16}N_2O_2$ (220.27): C, 65.43; H, 7.32; N, 12.72. Found: C, 65.70; H, 7.50; N, 12.49.

Reaction α-(Diethylcarbamoyl)-N-phenylnitrone with Maleic Anhydride. Formation of 3-(Diethylcarbamoyl)-2-phenyl-4,5-isoxazolidinedicarboxylic Acid and 3-Diethylcarbamoyl-2-phenyl-4,5-isoxazolidinedicarboxylic Anhydride (11).—To a solution of the nitrone (7.3 g, 0.0105 mole) in benzene (20 ml was added maleic anhydride (1.03 g, 0.0105 mole) in one portion. The mixture was refluxed for 2.5 hr and kept at 50° for 16.5 hr. The solution became very dark after the first 1–1.5 hr of refluxing. The benzene solvent was removed *in vacuo* leaving a black, tarry material (3.9 g). The tar was suspended in ether and methanol was added dropwise to precipitate a brown solid (0.1 g), mp 107–127°. The mother liquor was evaporated and the residue was extracted repeatedly with hexane. The hexane extract was concentrated to give a very small amount of yellow crystals, mp 100–160°. The filtrate was concentrated and the residue dissolved in methylene chloride. Petroleum ether was added to precipitate a light brown solid (0.7 g), mp 138–141°, and a second crop of 0.6 g, mp 135–140°, giving a total of 1.3 g (40%). Repeated recrystallization of this 1.3 g from methylene chloride–petroleum ether gave an analytical sample: mp 142–143°; infrared spectrum, ν_{OH} 3300, 2500, $\nu_{C=O}$ 1740, 1640 cm^{-1} in $CHCl_3$; nmr spectrum ($CDCl_3$), –COOH at τ 1.24 singlet, ArH at τ 2.95 doublet, $-CH_2-$ at τ 6.80 multiplet, $-CH_3-$ at τ 8.98 multiplet, –CH– at τ 5.74 triplet, –CH– at τ 5.01 doublet, –CH– at τ 5.28 doublet.

Anal. Calcd for $C_{16}H_{20}N_2O_6$ (336.34): C, 57.13; H, 5.99; N, 8.33. Found: C, 57.80; H, 6.15; N, 8.40.

Another run was carried out with 0.0227 mole of the nitrone and maleic anhydride. The solution was refluxed for 2 hr. The yield of anhydride was 75% using methylene chloride for the recrystallization solvent: crude mp 88–123°; 42%, mp 131–134°; infrared spectrum, $\nu_{C=O}$ 1870 (w), 1790 (s), 1640 (s) cm^{-1} in $CHCl_3$; nmr spectrum ($CDCl_3$), ArH at τ 2.78 doublet, –CH– at τ 4.63 singlet, –CH– τ 4.85 doublet (8 cps), –CH at τ 5.35 doublet (8 cps), $-CH_2-$ at τ 6.68 quadruplet, CH_3 at τ 8.84 quadruplet. There was no acid proton shown in the nmr.

Reduction of α-(Diethylcarbamoyl)-N-phenylnitrone with Lithium Aluminum Hydride. Formation of N, N-Diethyl-N′-phenylethylenediamine.—Into a four-necked round-bottomed flask, equipped with an adding funnel, reflux condenser, calcium chloride drying tube, thermometer, and mechanical stirrer, was placed lithium aluminum hydride (1.7 g) in dry ether (50 ml). To the suspension was added dropwise a solution of nitrone in dry ether (~200 ml). The mixture was stirred at room temperature for 1 hr and heated to a reflux for 14 hr. The excess lithium aluminum hydride was destroyed by addition of an ethanol–ether mixture, and finally water (50 ml) was added to precipitate the white aluminum salt. The solution was decanted and the salt was washed with more ether. The combined ether solution was dried over magnesium sulfate and evaporated to give an oil (1.75 g 84%): infrared spectrum, ν_{NH} at 3340, 1580 cm^{-1} in $CHCl_3$; nmr spectrum ($CDCl_3$), ArH at τ 3.25 multiplet (5), NH at τ 5.80 singlet (1), $-CH_2-$ at τ 7.05 triplet (2), $-CH_2-$ at τ 7.58 quadruplet (6), $-CH_3-$ at τ 9.07 triplet (6). The oil was vacuum distilled at 86–88° (0.4 mm) to give 1.25 g of pure N,N-diethyl-N′-phenylethylenediamine.

Anal. Calcd for $C_{12}H_{20}N_2$ (192.30): C, 74.94; H, 10.48; N, 14.57. Found: C, 75.07; H, 10.60; N, 14.39.

Alkylation with Methyl Iodide.—Sodium (4.6 g, 0.2 mole) was dissolved in methanol (100 ml), the solution was cooled to 10°, and methyl iodide (14.1 g, 0.1 mole) was added. With continued cooling dimethylphenacylsulfonium bromide (26.7 g, 0.1 mole) was added in small portions with stirring. The mixture was let stand 6 days, filtered, and the solid was washed with methanol (10 ml) to leave 4.9 g (42%) tribenzoylcyclopropane. Recrystallization of this product from acetonitrile gave mp 219–220°, mixture melting point with authentic material 219–220°. The filtrate and methanol washings from 4.9 g above were concentrated, benzene (150 ml) was added and the mixture was filtered to give 23.4 g of a red-brown water-soluble salt. The filtrate was concentrated to give 10.5 g of an oil which was analyzed by vpc on an SE 30, 2-ft column at 150° and shown to contain ~6 g (23%) of 2-iodopropiophenone and ~4 g (22%) of 2-methylmercaptopropiophenone.

2-(Dimethylsulfuranylidene)acetophene (6).—Sodium (0.46 g) was dissolved in methanol (10 ml) and the dimethylphenacylsulfonium bromide (2.7 g) was added. The mixture was allowed to stand at room temperature for 6 days and then concentrated to 3.4 g of solid. This residue was extracted with methylene chloride (50 ml) and the extract was concentrated to give 1.6 g (86%) of brown oil which crystallized on standing. The infrared spectrum of this product was identical with authentic ylid.[5]

Preparation of 2-(Methylmercapto)propiophenone.—The procedure followed was that of Bohme and Krause.[19] In a three-necked, round-bottomed flask, equipped with a stirrer and a drying tube, was placed methanol (30 ml). The solution was cooled and sodium (3 g) was added. The mixture was stirred until all the sodium had dissolved. The drying tube was then replaced with a gas-inlet tube and a gas-outlet tube. Methylmercaptan was bubbled into the solution until the solution no longer absorbed the gas. The gas-inlet tube was replaced with an adding funnel and 2-bromopropiophenone (25 g) was slowly added dropwise. Heat was immediately evolved and the reaction was controlled by occasional cooling with an ice bath. Addition of the ketone was completed within 0.5 hr and the mixture was heated in a water bath for 1 hr. Finally, methanol was removed *in vacuo* and water (120 ml) was added to the residual semisolid. An oil separated and was extracted with ether. The ether extract was dried and evaporated to give a crude orange oil (~20 g).

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[18] C. C. Tung, A. J. Speziale, and H. W. Frazier, *J. Org. Chem.*, **28**, 1514 (1962).

[19] H. Bohme and W. Krause, *Chem. Ber.*, **82**, 426 (1949).

The oil was vacuum distilled to give 5.5 g, 82–85° (0.4 mm), and 11.2 g, 91–97° (0.4 mm), a total yield of 16.7 g or 80%. The infrared and nmr spectra of both fractions were identical: infrared spectrum, $\nu_{C=O}$ 1670 cm^{-1} in $CHCl_3$; nmr spectrum ($CDCl_3$), ArH at τ 2.38 multiplet (5), –CH– at τ 5.67 quadruplet (1), $-CH_3-$ at τ 8.12 singlet (3), $-CH_3$ at τ 8.48 doublet (3).

Anal. Calcd for $C_{10}H_{12}OS$ (180.27): C, 66.02; H, 6.71; S, 17.79. Found: C, 66.52; H, 6.70; S, 17.49.

Attempted Alkylation of 2-(Methylmercapto)propiophenone.—2-(Methylmercapto)propiophenone (9.0 g, 0.05 mole) and methyl iodide (7.1 g, 0.05 mole) were mixed and let stand in a stoppered flask for 1 day. Benzene (25 ml) was added, the mixture was filtered, and the precipitate was washed with benzene (10 ml). The solid was dried and weighed (1.5 g). The filtrate was concentrated and let stand 3 days with methyl iodide (14.2 g, 0.1 mole). The process was repeated to give 5.0 g of solid. Methyl iodide (34.4 g, 0.24 mole) was let stand with the remainder for 21 days to yield an additional 3.8 g. The total yield was 10.3 g (100%) of trimethylsulfonium iodide, identified by nmr analysis. The remaining crude 2-iodopropiophenone (6.4 g, 50%) was chromatographed on a 2.5 × 23 cm column of Woelm neutral alumina, activity grade I, to yield 4.0 g oil which slowly darkened. The nmr spectrum was identical with that of the crude 6.4 g ($CDCl_3$): ArH τ 2.15 multiplet (5), CH τ 4.28 quartet (1, J = 6.5 cps), CH_3 τ 7.78 doublet (3, J = 6.5 cps).

Anal. Calcd for C_9H_9IO: C, 41.56; H, 3.49; I, 48.80. Found: C, 41.77; H, 3.60; I, 48.73.

Ethyl-2-dimethylsulfuranylidene-2-oxalyl 4′-nitroacetophenone (17a).—2-(Dimethylsulfuranylidene)-4′-nitroacetophenone (4.5 g, 0.02 mole) was dissolved in benzene (50 ml) and methylene chloride (10 ml) at 45–50°. Ethoxalyl chloride (1.4 g, 0.01 mole) in 10–15 ml of benzene was added dropwise with stirring over 5 min. A solid precipitated and was filtered off to give 3.8 g. The solid was washed with benzene and recrystallized from ethanol–chloroform benzene to give 1.9 g of solid, gas evolution 80–115°. One recrystallization of this solid from chloroform–ethanol gave the desired product, mp 120° with vigorous gas evolution.

Anal. Calcd for $C_{14}H_{15}NO_6S$: C, 51.68; H, 4.65; N, 4.31; S, 9.86. Found: C, 52.15; H, 4.52; N, 4.87; S, 9.99.

Hexane was added to the first filtrate to precipitate 1.0 g of solid. This 1.0 g and the mother liquors from the above recrystallization were concentrated to give 1.5 g, of dimethylphenacylsulfonium chloride, mp 163.5–164.5°.

2-Dimethylsulfuranylidene-4′-nitrobenzoyl-3,4-dichloroacetanilide (17b).—To a solution of 2-(dimethylsulfuranylidene)-4′-nitroacetophenone (4.5 g, 0.02 mole) in methylene chloride (70 ml) was added dropwise a solution of 3,4-dichlorophenyliso-cyanate (4.7 g, 0.025 mole) in methylene chloride. After 3 min the product was filtered off (6.9 g, 84%), mp 225–227°. The filtrate was concentrated to give a solid, mp 25–150°. The infrared spectrum of this solid showed a strong isocyanate band. The solid was washed with a small amount of methylene chloride to give more product (1.4 g, 16%), mp 223–229°. The solid was recrystallized from methylene chloride, mp 238–239°.

The nmr spectrum ($CDCl_3$) showed bands for ArH at τ 1.88 multiplet and τ 2.62 multiplet, $(CH_3)_2\overset{+}{S}$ τ 6.98 singlet. The infrared spectrum exhibited carbonyl bands at 1660 and 1600 cm^{-1} as well as unassigned bands at 1540 and 1360 cm^{-1} in $CHCl_3$.

Anal. Calcd for $C_{17}H_{14}Cl_2N_2O_4S$: C, 49.40; H, 3.41; Cl, 17.16; N, 6.78; S, 7.76. Found: C, 49.65; H, 3.65; Cl, 16.89; N, 6.77; S, 7.73.

Dimethyl 2-bromophenacylsulfonium Bromide (18a).—This salt was prepared from 2-(dimethylsulfuranylidene)acetophenone and bromine by a method previously described[20] in 61% yield, mp 124–125°. The infrared spectrum (Nujol) exhibits a carbonyl band at 1675 cm^{-1} and the nmr spectrum ($CDCl_3$) ArH at τ 2.08 multiplet, CH_2 at τ 6.76 singlet, and CH_3 at τ 6.80 singlet.

Anal. Calcd for $C_{10}H_{12}Br_2OS$: C, 35.31; H, 3.56; Br, 47.00; S, 9.43. Found: C, 35.23; H, 3.38; Br, 47.05; S, 9.61.

2-Bromo-2-(dimethylsulfuranylidene)acetophenone (19a).—To a suspension of dimethyl-2-bromophenacylsulfonium bromide (17 g, 0.05 mole) in THF (250 ml) was added sodium hydride (2.3 g, 0.05 mole, 53% mineral oil dispersion) in one portion. Evolution of hydrogen started immediately and was completed within 1 hr. The mixture was filtered to give a white solid (17.5 g) which was extracted with methylene chloride. The methylene chloride extract was concentrated to give white fine crystals (12.1 g, 94%), mp 129–132°. The product was recrystallized from methylene chloride–petroleum ether to give an analytical sample, mp 129–132°. The infrared spectrum ($CHCl_3$) showed a carbonyl band at 1504 cm^{-1}. The nmr spectrum ($CDCl_3$) showed ArH at τ 2.84 (A = 5, singlet), $(CH_3)_2S-$ at τ 7.48 (6, singlet).

Anal. Calcd for $C_{10}H_{11}BrOS$ (259.17): C, 46.34; H, 4.28; Br, 30.84; S, 12.37. Found: C, 46.12; H, 4.28; Br, 30.70; S, 12.11.

Dimethyl 2-iodophenacylsulfonium Iodide (18b).—This salt was prepared from 2-(dimethylsulfuranylidene)acetophenone and iodine[20] as above in 88% yield, decomposition 88°, mp 92°. The infrared spectrum ($CHCl_3$) showed a carbonyl band at 1640 cm^{-1}. Nmr spectrum ($CDCl_3$) showed $(CH_3)_2\overset{+}{S}$ at τ 6.90 singlet.

Anal. Calcd for $C_{10}H_{12}I_2OS$: C, 27.67; H, 2.79; I, 58.47; S, 7.38. Found: C, 27.92; H, 2.72; I, 58.68; S, 7.49.

2-Iodo-2-(dimethylsulfuranylidene)acetophenone (19b).—This iodo ylid was prepared from the above salt as described for the bromo ylid in 69% yield, mp 127–129°. It rapidly decomposed and darkened. The infrared spectrum ($CHCl_3$) showed a carbonyl band at 1520 cm^{-1}. The nmr spectrum ($CDCl_3$) showed $(CH_3)_2\overset{+}{S}$ at τ 7.54 singlet.

Anal. Calcd for $C_{10}H_{11}IOS$: C, 39.23; H, 3.62; I, 41.45; S, 10.47. Found: C, 32.03; H, 3.19; I, 52.25; S, 8.47.

Pyrolysis of 2-(Dimethylsulfuranylidene)-4′-nitroacetophenone. Formation of 1,2,3-Tri(4-nitrobenzoyl)cyclopropane (20b).—A solution of 2-(dimethylsulfuranylidene)4′-nitroacetophenone (4.0 g, 0.0178 mole, recrystallized and dried over P_2O_5) was refluxed for 2 days in dioxane (80 ml). The dark solution on concentration gave a tar (5 g) which was chromatographed on neutral alumina with methylene chloride to give 0.3 g (10%) of crude 1,2,3-tribenzoylcyclopropane, mp 254–260°. The product was recrystallized from dioxane–petroleum ether; it had mp 265–266°.

Anal. Calcd for $C_{24}H_{15}N_3O_9$ (489.39): C, 58.90; H, 3.09; N, 8.59. Found: C, 59.14; H, 3.22; N, 8.27.

Pyrolysis of 2-(Dimethylsulfuranylidene)-4′-nitroacetophenone. Formation of 2-(Triphenylphosphoranylidene)-4′-nitroacetophenone.—A solution of 2-(dimethylsulfuranylidene)4′-nitroacetophenone (2.5 g, 0.0111 mole, recrystallized and dried *in vacuo* over P_2O_5) and triphenylphosphine (3.0 g, 0.114 mole) in dioxane (50 ml) was heated for 20 hr. The solution was concentrated and the residue dissolved in chloroform. [A small amount (0.2 g) of black residue was filtered off.] Hexane was added to the filtrate and a brown solid precipitated. The brown solid (0.7 g) was filtered off. The mother liquor was concentrated to a red-brown oil which was stirred with ether (50 ml) and filtered to give 1.4 g of a red-brown solid, mp 124–134°.

The red-brown solid, mp 124–134°, was recrystallized from benzene to give 0.7 g (15%) of authentic 2-(triphenylphosphoranylidene)-4′-nitroacetophenone, mp 175–178°. A mixture melting point with authentic material gave mp 178–180°. The mother liquor was again concentrated to give 2.5 g of a residual gum. Excess bromine was added to the solution of the gum in benzene (50 ml). The solution was concentrated and extracted with two 50-ml portions of water. The water extract was evaporated and taken up in methylene chloride, dried over magnesium sulfate, and concentrated. The residue was dissolved in benzene–methylene chloride and chromatographed on neutral alumina. Elution with benzene, benzene–methylene chloride, and methylene chloride gave no ylid or triphenylphosphine oxide.

2-(Triphenylphosphoranylidene)-4′-nitroacetophenone.—This compound was prepared by the dehydrohalogenation of the corresponding phosphonium salt. An 83% yield of product was obtained, mp 178.5–179.5 (lit.[10] mp 156–157°).

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[20] A. J. Speziale and K. W. Ratts, *J. Org. Chem.*, **28**, 465 (1963).