tain by extrapolation. The enthalpy and entropy of activation were calculated from the plot of ln $(K_h k_{-2}/T)$ *vs.* $1/T$ shown in Figure 2.[15]

The hydrogen ion and hydroxide ion catalyzed hydration of isobutyraldehyde is characterized by enthalpies of activation of 7.8 and 11.7 kcal/mol, respectively. Enthalpies of activation for dehydration of isobutyraldehyde hydrate are 13.4 kcal/mol for the acid catalysis and 17.3 kcal/mol for hydroxide ion catalysis. Calculated entropies of activation for hydration are 26 and 45 eu for hydrogen ion and hydroxide ion, respectively. Entropies of activation for the acid- and base-catalyzed dehydration of isobutyraldehyde hydrate are 46 and 65 eu, respectively.

The magnitudes of our rate constants are similar to those recently obtained by Ahrens and Maass for the acid-catalyzed hydration of 2-methylbutyraldehyde.[16] These authors apparently assumed that the extinction coefficient of their aldehyde was the same in water as in tetrahydrofuran. Because of the uncertainties arising from this approach,[2] it is probably not worthwhile to make a detailed comparison of data.

The hydration and dehydration of isobutyraldehyde has previously been reported to be subject to both general acid and general base catalysis.[4a,6,16b] In an attempt to measure the rate of carbinolamine formation through the use of dimethylamine and isobutyraldehyde, we observed on several occasions the marked acceleration of the overall rate of hydration, apparently attributable to the action of dimethylamine as a general base. Unfortunately, we have not been successful in our attempts to determine the rates of carbinolamine formation, which appears to proceed at a pace beyond the capabilities of our present instrumentation.

Registry No.—Isobutyraldehyde, 78-84-2.

(15) Values of k_{h+} were determined by the equation $k_{h+} = k_{obsd}[HClO_4]^{-1} \cdot K_h/(1 + K_h)$. A weighting factor of 7 was used and the value of k_{h+} taken from the work of Hine and Houston entered into the correlation. Values of k_{h+} and $K_h k_{-2}$ (*ca.* 728 M^{-1} sec^{-1} at 0°) taken from the work of Pocker and Dickerson were each weighted as one.

(16) M. Ahrens and G. Maass, *Angew. Chem., Int. Ed. Engl.*, **10**, 80 (1971)

Reaction of Sulfonium Ylides with Diene Esters

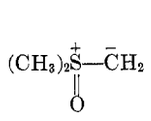
CYRIL S. F. TANG AND HENRY RAPOPORT*

Department of Chemistry, University of California, Berkeley, California 94720

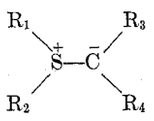
Received February 13, 1973

The reaction between diphenylsulfonium isopropylide and the diene esters, ethyl 1,3-cyclohexadienecarboxylate and methyl *trans*-2,4-hexadienoate, has been examined in dimethoxyethane, tetrahydrofuran, and tetrahydropyran. Both gave mixtures of isomeric cyclopropane products resulting from ylide addition across the α,β and γ,δ double bonds. The isomer distribution in the case of the cyclic diene ester was found to be solvent dependent, whereas the acyclic system showed preferential addition to the γ,δ double bond irrespective of solvent. The widely used method of preparing *n*-alkyldiphenylsulfonium salts by reaction between diphenyl sulfide, *n*-alkyl halide, and silver tetrafluoroborate was found to give mixtures of primary and secondary sulfonium salts. However, pure primary alkyldiphenylsulfonium salts can be prepared, although in low yield, by the reaction of diphenyl sulfide with *n*-alkyl trifluoromethanesulfonates.

Since the isolation of the first sulfur ylide[1] other more reactive and less stable sulfur ylides such as **1** and **2**



1



2a, $R_1 = R_2 = CH_3$; $R_3 = R_4 = H$
2b, $R_1 = CH_3$; $R_2 = C_6H_5$; $R_3 = R_4 = H$
2c, $R_1 = R_2 = C_6H_5$; R_3, R_4 = H or alkyl
1d, $R_1 = R_2 = C_6H_5$; $R_3 = R_4 = CH_3$

have been prepared.[2] These ylides have found much use in organic syntheses, especially for the formation of epoxides and cyclopropanes. Both dimethylsulfoxonium methylide (**1**) and sulfonium alkylides **2** add to aromatic and unconjugated aldehydes and ketones to give epoxides. However, the sulfoxonium ylide **1** adds to α,β-unsaturated ketones to give cyclopropanes, while the sulfonium ylides **2** add to the same unsaturated systems to give oxiranes exclusively.[2,3] Further studies showed that, under certain circumstances, **2** also will add to an olefin conjugated to an ester.[2c,3,4]

Much less is known about the action of sulfur ylides on substrates containing extended conjugation, *viz.*, an $\alpha,\beta,\gamma,\delta$-unsaturated carbonyl. The ylide **1** in DMSO (dimethyl sulfoxide) has been shown to add to eucarvone to give the α,β-cyclopropyl ketone **3**, while **2a** in DMSO–THF (tetrahydrofuran) added exclusively at the carbonyl of eucarvone to give the oxirane **4**.[2b] Only two other examples of sulfur ylide addition to an $\alpha,\beta,\gamma,\delta$-unsaturated carbonyl system have been reported. The dicyclopropylamide **5** was obtained when 2 mol of ylide **1** in DMSO or DMF (dimethylformamide) were allowed to react with sorbic acid anilide.[5] The other example is the addition of diphenylsulfonium isopropylide (**2d**) in DME (dimethoxyethane) to methyl 5-methyl-*trans*-2,4-hexadienoate to give methyl *trans*-chrysanthemate (**6**).[6]

We now wish to report our findings on the reaction of diphenylsulfonium isopropylide **2d** with a cyclic diene ester, ethyl 1,3-cyclohexadienecarboxylate (**7**), and an acyclic diene ester, methyl *trans*-2,4-hexadienoate (**10**, methyl *trans,trans*-sorbate).

(1) C. K. Ingold and J. A. Jessop, *J. Chem. Soc.*, 713 (1930).

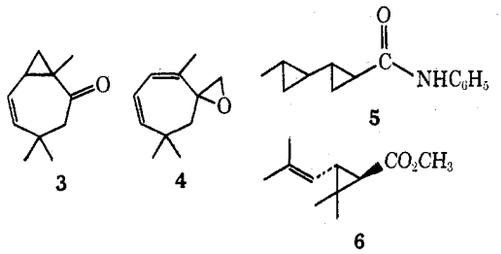
(2) (a) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **84**, 867 (1962); (b) **84**, 3782 (1962). (c) V. Franzen and H. E. Driessen, *Chem. Ber.*, **96**, 1881 (1963). (d) A. W. Johnson, V. J. Hruby, and J. L. Williams, *J. Amer. Chem. Soc.*, **86**, 918 (1964).

(3) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **87**, 1353 (1965), and references therein.

(4) E. J. Corey and M. Chaykovsky, *Tetrahedron Lett.*, 169 (1963).

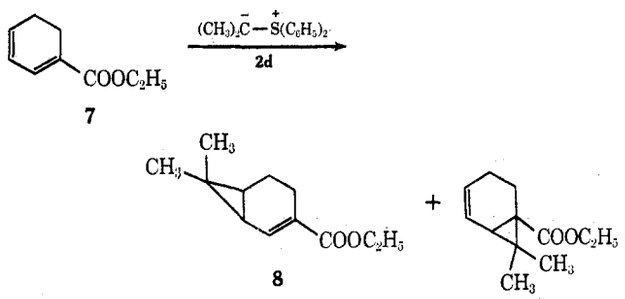
(5) H. Metzger and K. Seelert, *Angew. Chem.*, **75**, 919 (1963).

(6) E. J. Corey and M. Jautelat, *J. Amer. Chem. Soc.*, **89**, 3912 (1967).



3 4 5 6

When the cyclohexadiene ester **7** was allowed to react with **2d** in DME, a 70% yield of cyclopropane products was obtained consisting of **8** and **9** in a ratio of 4:1. Compounds **8** and **9** were identified by their uv, ir, and nmr spectra. The α,β-unsaturated ester moiety of **8** was evident from its ir (1690 cm^{-1}) and uv (250 nm) absorptions, whereas the unconjugated ester **9** exhibited ir



7 8 9

and uv maxima at 1720 cm^{-1} and 205–210 nm, respectively. In their nmr spectra, the β-vinylic proton of **8** appeared at δ 7.1, integrating for one proton, whereas the vinyl protons of **9** absorbed at δ 5.66, integrating for two protons.

When the reaction was carried out in THF the cyclopropane product consisted of **8** and **9** in a 1:2 ratio. The cause of this reversal of isomer distribution could be either the change in solvent or in base, or both. We had employed dichloromethyllithium[7] as the base for generation of ylide **2d** when the solvent was DME and *tert*-butyllithium when THF was the medium, since *tert*-butyllithium reacts with DME. Therefore, sulfonium ylide **2d** also was generated by means of dichloromethyllithium in THF and was allowed to react with **7** in THF. The cyclopropane products again showed 33% addition occurring at the γ,δ position and 66% at the α,β position. Using THP (tetrahydropyran) as solvent and *tert*-butyllithium as base, we observed a similar preferential attack at the α,β position, and these results are presented in Table I.

The extent of this dramatic dependence of isomer distribution on solvent then was examined with the acylic diene ester, **10**. When **10** was allowed to react with the ylide **2d** in DME, the γ,δ- and α,β-addition products **11** and **12**, respectively, were obtained in a ratio of 4:1. Reaction of **10** with **2d** in THF and THP, however, also showed preferential attack at the γ,δ position to give predominantly **11** (Table I) in contrast to the cyclic diene ester **7**, where the isomer distribution was reversed on changing the solvent.

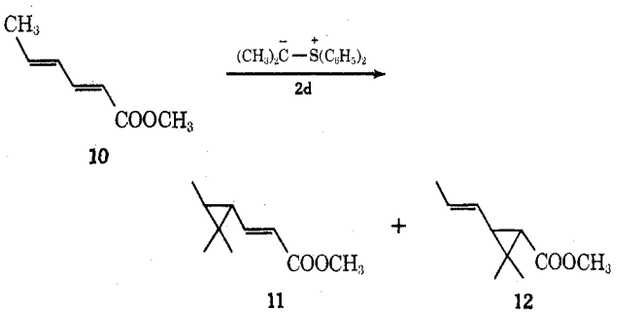
Barring solvation and steric effects, a carbanion should preferentially add to $\alpha,\beta,\gamma,\delta$-unsaturated carbonyl systems at the δ position, as in the case of Michael

(7) E. J. Corey, M. Jautelat, and W. Oppolzer, *Tetrahedron Lett.*, 2325 (1967).

TABLE I

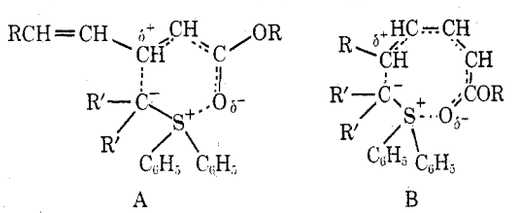
REACTION OF DIPHENYLSULFONIUM ISOPROPYLIDE (2d) WITH ETHYL 1,3-CYCLOHEXADIENECARBOXYLATE (7) AND METHYL *trans*-2,4-HEXADIENOATE (10) TO FORM CYCLOPROPANES

Substrate	Base	Solvent	Ratio of α,β to γ,δ addition 9:8	12:11
7	$CHCl_2Li$	DME	1:4	
7	*t*-BuLi	THF	2:1	
7	$CHCl_2Li$	THF	2:1	
7	*t*-BuLi	THP	3:1	
10	$CHCl_2Li$	DME		1:4
10	*t*-BuLi	THF		1:4
10	*t*-BuLi	THP		1:3.5



10 11 12

additions.[8] Although the reaction of sulfur ylides with both unconjugated and conjugated carbonyl systems proceeds by similar carbanion attack at a positive center of the substrate, the sulfonium ylide reaction is complicated by the fact that the carbanion is adjacent to a positive sulfur ion. Thus the degree of interaction between the sulfur cation of the ylide and the carbonyl oxygen should consequently affect the extent of addition across the α,β or γ,δ double bonds. In the extreme case, where the interaction between these two centers is maximum, a six-membered (A) or eight-membered (B)



A B

cyclic complex is formed. One would expect predominant addition across the α,β double bond, since the six-membered cyclic intermediate is favored. In general, depending upon the degree of $^{+}S\cdots O^{\delta-}$ interaction, the amount of γ,δ addition will decrease as this interaction increases.

This picture may be used to rationalize our experimental observations. Normally, γ,δ addition will be favored, as it is for all cases with the acyclic diene ester **10**. With the cyclohexadiene ester **7**, the rigidity imposed by the cyclic system allows a stronger polar interaction, and complexing of type A leads to predominant α,β addition in THF and THP. When DME is the solvent, this polar interaction between ylide and substrate is diminished by solvation of the sulfur cation, involving coordination with the two oxygen atoms of DME. This weakening of the ylide–substrate complexing results in a return to the predominance of the normal γ,δ addition in DME.

(8) (a) E. H. Farmer and A. T. Healey, *J. Chem. Soc.*, 1060 (1927); (b) E. H. Farmer and T. N. Mehta, *ibid.*, 1610 (1930); (c) J. Bloom and C. K. Ingold, *ibid.*, 2765 (1931).

It should be noted that the reaction between **2d** and methyl 5-methyl-*trans*-2,4-hexadienoate in DME has been reported[6] to give only α,β addition, yielding **6**. This difference with our results can be attributed to the presence of the 5-methyl group in **6** which sterically hinders carbanion approach at the δ position. Such steric hindrance was also observed in the case of Michael additions to methyl 5-methyl-*trans*-2,4-hexadienoate.[9]

In the course of our work with sulfonium ylide **2d** we investigated the preparation of *n*-alkyldiphenylsulfonium salts **13**. When R = CH_3, the salt **13a** can be

$$(C_6H_5)_2\overset{+}{S}-CH_2R\ X^-$$

13a, R = CH_3; X = Br^-, I^-, BF_4^-, $CF_3SO_3^-$
b, R = CH_2CH_3
c, R = $CH_2CH_2CH_3$

prepared unambiguously by treatment of diphenyl sulfide with triethyloxonium tetrafluoroborate[7] or by reaction between diphenyl sulfide, ethyl iodide, and silver tetrafluoroborate.[10] However, for longer chain *n*-alkylsulfonium salts, *e.g.*, **13b** and **13c**, we found that the use of diphenyl sulfide, *n*-alkyl halide, and silver tetrafluoroborate gave, distinctly, a mixture of primary and secondary diphenylsulfonium salts, contrary to previous reports.[10]

Initially, we carried out salt formation by addition of silver tetrafluoroborate to a solution of diphenyl sulfide and *n*-butyl bromide in methylene chloride. The crystals which were isolated showed, in the nmr, a mixture of primary and secondary sulfonium salts in the ratio of 3:2. The protons adjacent to the positive sulfur in the primary and secondary salts were seen at δ 4.26 and 4.88, respectively.[11a] In an attempt to obtain the pure primary sulfonium salt, we repeated the reported[10] procedure in which *n*-butyl bromide was added in large excess. Once again the nmr of the crystals isolated from this procedure[11b] displayed signals at δ 4.48 and 5.1 corresponding to the methylene and methine protons adjacent to positive sulfur in the primary and secondary sulfonium salts, respectively, in the ratio of 3:2. Similarly, *n*-propyl iodide by the previous[10] method gave a mixture of primary and secondary sulfonium salts in the ratio of 2:1, respectively.[11b]

In seeking a preparation of pure *n*-alkylsulfonium salts, we found that reaction between diphenyl sulfide and *n*-alkyl triflates (trifluoromethanesulfonates)[12] at temperatures between −35 and +45 in carbon tetrachloride gave unrearranged *n*-alkyldiphenylsulfonium triflates, although in poor yield. It was also observed that treatment of silver triflate with *n*-propyl iodide[13] resulted in greater than 40% isomerization to the isopropyl triflate. However, the unrearranged primary alkyl triflate could be obtained by treatment of the *n*-alkyl alcohol with trifluoromethanesulfonic acid anhydride.[12]

The dependence of isomer distribution upon solvent in the case of cyclic diene ester, **7**, provides a convenient and selective route into the carene system using the sulfonium ylides. Although the widely used method of preparing *n*-alkylsulfonium salts by means of silver tetrafluoroborate, *n*-alkyl halide, and diphenyl sulfide[2d,14] is not suitable for alkyl groups greater than ethyl, an unambiguous entree into this class of salts for alkyl groups higher than ethyl would be to alkylate diphenyl sulfide with the proper *n*-alkyl triflate. Alternatively, the alkylation of diphenylsulfonium methylide with alkyl halides might be a practical method for preparing such salts.

Experimental Section

Ethyl 1,3-cyclohexadienecarboxylate (**7**) was prepared as described.[15] Methyl *trans,trans*-sorbate was obtained by esterification of *trans-trans*-sorbic acid using the Stodola method.[16] Uv spectra were recorded on a Cary 14 spectrophotometer and are reported as $\lambda_{max}^{95\%\ EtOH}$ in nanometers; ir spectra were obtained on a Perkin-Elmer 236 spectrophotometer and are reported as $\nu_{max}^{CCl_4}$ in reciprocal centimeters. Nmr values are reported as δ values and were obtained on a Varian T-60 using CCl_4 as solvent and internal TMS (δ 0) unless otherwise stated. Mass spectra were obtained on a Varian M-66 spectrometer. Sample purity was determined by tlc and glpc using an Aerograph gas chromatograph, Model A-90-P. Analytical samples were collected at 160° from a 20-ft 10% SE-30 column. Elemental analyses were performed by the Analytical Laboratory, University of California, Berkeley.

7,7-Dimethyl-3-ethoxycarbonyl-2-norcarene (8) and 7,7-Dimethyl-6-ethoxycarbonyl-2-norcarene (9).—To a mixture of 0.54 g (0.41 ml) of CH_2Cl_2 and 50 ml of DME was added 2 g (6.35 mmol) of isopropyldiphenylsulfonium tetrafluoroborate. The mixture was cooled to −78° and a dry nitrogen atmosphere was maintained throughout. A solution of 6.95 mmol of lithium diisopropylamide in DME, prepared at −78° by the addition of 6.95 mmol of *n*-butyllithium to 6.95 mmol of diisopropylamine in 10 ml of DME, was added leading to an immediate intense orange color, and the solution was allowed to stir for 1 hr at −78°. Ethyl 1,3-cyclohexadienecarboxylate (**7**, 6.35 mmol) was injected into the ylide solution at −78°, the mixture was stirred for 45 min, the temperature of the bath was allowed to rise to −57°, and the reaction mixture was stirred for 10 hr between −57 and −40°. The mixture was then allowed to rise to room temperature overnight with stirring, 50 ml of water was added, and the aqueous phase was extracted with *n*-pentane. The pentane extracts were washed, dried, filtered, and evaporated to give 2.2 g of crude product. Glpc of this crude showed four compounds, *viz.*, **7** (30% recovery), diphenyl sulfide, and cyclopropane products (70%) of which 80% was **8** and 20% was **9**. Separation was effected on columns (a) 10 ft × 0.25 in. 10% EGA, 150° (R_T of **7**, 1.95 min; **8**, 4.0 min; **9**, 2.54 min); (b) 10 ft × 0.25 in., 5% SE-30, 135° (R_T of **7**, 1.16 min; **8**, 3.36 min; **9**, 2.15 min).

Where the reactions were carried out in THF with *t*-BuLi as the base and in THF with $CHCl_2Li$ as base, the conditions were as described above. When THP was used as the solvent with *t*-BuLi as base, ylide generation was accomplished at a bath temperature of −50°. After addition of diene ester **7** the reaction mixture was stirred for 2.5 hr at −50° and then allowed to reach room temperature gradually over a period of 8 hr. Isolation was as described above.

7,7-Dimethyl-3-ethoxycarbonyl-2-norcarene (8): uv λ_{max} 250 nm; ir ν_{max} 1690, 1250 cm^{-1}; nmr δ 0.93 (s, CCH_3), 1.14 (s, CCH_3), 1.25 (t, CH_2CH_3), 1.6–2.5 (m, CH_2CH_2), 4.2 (q, CH_2CH_3), 7.1 (br d, C=CH); mass spectrum *m/e* 194 (M^+).

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.2; H, 9.3. Found: C, 74.4; H, 9.6.

7,7-Dimethyl-6-ethoxycarbonyl-2-norcarene (9): uv λ_{max} 205–210 nm; ir ν_{max} 1720, 1275 cm^{-1}; nmr δ 0.98 (s, CCH_3), 1.14 (s, CCH_3), 1.28 (t, CH_2CH_3), 1.78–2.4 (m, CH_2CH_2), 4.02 (q, CH_2CH_3), 5.66 (m, HC=CH); mass spectrum *m/e* 194 (M^+).

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.2; H, 9.3. Found: C, 74.3; H, 9.2.

(9) E. B. Reid and H. W. Sause, *J. Chem. Soc.*, 516 (1954).
(10) V. Franzen, H. J. Schmidt, and C. Mertz, *Chem. Ber.*, **94**, 2942 (1961).
(11) Nmr spectra were taken in (a) CD_3OD, (b) DMSO-d_6.
(12) T. Gramstad and R. N. Haszeldine, *J. Chem. Soc.*, 4069 (1957).
(13) T. Gramstad and R. N. Haszeldine, *J. Chem. Soc.*, 173 (1956).
(14) E. J. Corey and W. Oppolzer, *J. Amer. Chem. Soc.*, **86**, 1899 (1964).
(15) C. A. Grob, M. Ohta, E. Renk, and A. Weiss, *Helv. Chim. Acta*, **41**, 1191 (1958).
(16) F. H. Stodola, *J. Org. Chem.*, **29**, 2490 (1964).

Methyl β-(2,2,3-trimethylcyclopropyl)acrylate (11) and 1-methoxycarbonyl-2,2-dimethyl-3-(1-propenyl)cyclopropane (12) were prepared from methyl *trans,trans*-sorbate (**10**) according to the procedures described above. The isomers were separated by glpc using a 20 ft × 0.25 in. column of 10% SE-30 at 160° (R_T of **10**, 7.8 min; **11**, 16.4 min; **12**, 11.8 min.

Methyl β-(2,2,3-trimethylcyclopropyl)acrylate (11): uv λ_{max} 242 nm; ir ν_{max} 1725 cm^{-1}; nmr δ 1.2 (9 H's, $C<^{CH_3}_{CH_3}$ and CH_3CH), 3.65 (s, $COOCH_3$), 5.85 (d, J = 15 Hz, $C{=}CH{-}COOCH_3$), 6.4 (m, $C{=}CHCH$); mass spectrum m/e 168 (M^+).

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.4; H, 9.5. Found: C, 71.4; H, 9.7.

1-Methoxycarbonyl-2,2-dimethyl-3-(1-propenyl)cyclopropane (12): uv λ_{max} 200–210 nm; ir ν_{max} 1725 cm^{-1}; nmr δ 1.2 (6 H's, $C<^{CH_3}_{CH_3}$), 1.7 (d, J = 5 Hz, $CH_3CH{=}C$), 1.41 (d, J = 5 Hz, cyclopropane CH), 1.9 (m, cyclopropane CH), 3.65 (s, $COOCH_3$), 4.7 ($CH_3CH{=}CH$), 5.35 (m, $CH_3CH{=}CH$); mass spectrum m/e 168 (M^+).

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.4; H, 9.5. Found: C, 71.6; H, 9.4.

n-Propyldiphenylsulfonium Triflate (13b) and n-Butyldiphenylsulfonium Triflate (13c).—To a solution of 3 g (10.6 mmol) of trifluoromethanesulfonic anhydride[12] was added 10.6 mmol of the *n*-alkyl alcohol and 1.1 g (11 mmol) of triethylamine in 10 ml of CH_2Cl_2 at 0°. The mixture was stirred for 1 hr at 0°, the CH_2Cl_2 was evaporated, and the residue was chromatographed on silica eluting with *n*-pentane to give a 16% yield of the *n*-alkyl triflate.

***n*-Propyl triflate (13b)**: nmr δ 1.1 (t, CH_3CH_2), 1.83 (m, CH_3CH_2), 4.5 (t, $CH_2CH_2OSO_2CF_3$).

***n*-Butyl triflate (13c)**: nmr δ 1.0 (br d, CH_3CH_2), 1.65 (m, $CH_3CH_2CH_2CH_2$), 4.5 (t, $CH_2CH_2OSO_2CF_3$).

To a solution of 1.5 mmol of *n*-alkyl triffate was added a tenfold excess of diphenyl sulfide at −35°. With stirring, the mixture was allowed to rise to room temperature, remained at room temperature for 24 hr, and was heated to 45° for 0.5 hr. The oil that was formed was separated, washed with CCl_4, and dried *in vacuo* to give ~10% yields of sulfonium triflates **13b** and **13c**.

***n*-Propyldiphenylsulfonium triflate (13b)**: nmr (DMSO-d_6) δ 1.09 (t, CH_2CH_3), 1.85 (m, CH_2CH_3), 4.4 (t, $<S^+-CH_2CH_2$), 7.8 (m, Ar H's).

***n*-Butyldiphenylsulfonium triflate (13c)**: nmr (DMSO-d_6) δ 1.0 (br d, CH_2CH_3), 1.7 (m, $CH_2CH_2CH_2CH_3$), 4.4 (br t, $>S^+-CH_2CH_2$), 7.9 (Ar H's).

Registry No.—**2d**, 16601-43-7; **7**, 3725-40-4; **8**, 40464-16-2; **9**, 40464-17-3; **10**, 689-89-4; **11**, 40447-54-9; **12**, 40447-55-0; **13b** triflate, 40447-56-1; **13c** triflate, 40447-57-2; isopropyldiphenylsulfonium tetrafluoroborate, 40447-58-3; trifluoromethylsulfonic anhydride, 358-23-6.

Chemistry of the Sulfur–Nitrogen Bond. VI.[1] A Convenient One-Step Synthesis of Sulfenimines (*S*-Aryl Thiooximes)[2]

FRANKLIN A. DAVIS,* WILLIAM A. R. SLEGEIR, STEVEN EVANS,[3] ALAN SCHWARTZ,[3] DAVID L. GOFF,[3] AND ROBERT PALMER

Department of Chemistry, Drexel University, Philadelphia, Pennsylvania 19104

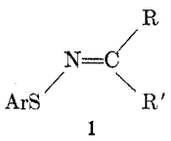
Received March 13, 1973

The scope and limitations of a convenient one-step synthesis of sulfenimines (*S*-aryl thiooximes) from aromatic disulfides, silver nitrate, ammonia, and aldehydes or ketones is described. The procedure fails with aliphatic disulfides and diaryl ketones. The structure, properties, and mechanism of formation of sulfenimines are discussed.

The carbon–nitrogen double bond in imines ($RN{=}CR_2$) has been extensively studied[4] and is an important intermediate in organic syntheses and biological transformations. The mechanism of syn–anti isomerization or stereomutation at the C–N double bond has been the subject of considerable interest.[2,5]

Compounds that contain the sulfur–nitrogen bond are important both from practical as well as theoretical points of view. They have found applications in synthesis, as pesticides, and as accelerators in the vulcanization of rubber. Knowledge of the various types of interactions possible between adjacent sulfur and nitrogen are essential to understanding lone-pair interactions, bond polarization effects, and p–d π bonding.[6]

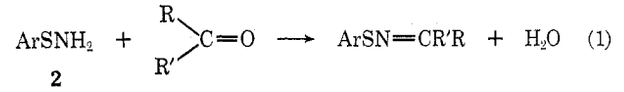
A study of sulfenimines (*S*-aryl thiooximes) **1**, which



1

contains both the imine and sulfur–nitrogen functional groups, is therefore of considerable interest. Although a few sulfenimines have been known for some time, their chemistry is relatively unexplored. Undoubtedly this is due to the lack of a convenient synthetic route to these compounds.

The method generally used for the preparation of sulfenimines is condensation of a sulfenamide, **2**, with



$$\underset{\mathbf{2}}{ArSNH_2} + \begin{matrix} R \\ \diagdown \\ \quad C{=}O \\ \diagup \\ R' \end{matrix} \longrightarrow ArSN{=}CR'R + H_2O \quad (1)$$

R′ = alkyl, aryl, H

an aldehyde or ketone (eq 1).[7–11] Quinoline sulfenimines have been prepared by oxidation of the cor-

(1) Part V: F. A. Davis, C. J. Horner, E. R. Fretz, and J. F. Stackhouse, *J. Org. Chem.*, **38**, 695 (1973).

(2) For a preliminary communication see F. A. Davis, W. A. R. Slegeir, and J. M. Kaminski, *Chem. Commun.*, 634 (1972).

(3) Undergraduate Research Participant.

(4) (a) P. Y. Sollenberger and R. B. Martin in "The Chemistry of the Amino Group," S. Patai, Ed., Interscience Publishers, New York, N. Y., 1968, Chapter 7; (b) S. Patai, Ed., "The Chemistry of the Carbon–Nitrogen Bond," Interscience Publishers, New York, N. Y., 1970; (c) R. W. Layer, *Chem. Rev.*, **63**, 489 (1963).

(5) (a) J. H. Lehn, *Fortschr. Chem. Forsch.*, **15**, 311 (1970); (b) H. Kessler *Angew. Chem., Int. Ed. Engl.*, **9**, 219 (1970); (c) M. Raban and E. Carlson, *J. Amer. Chem. Soc.*, **93**, 685 (1971); (d) W. B. Jennings and D. R. Boyd, *ibid.*, **94**, 7187 (1972).

(6) For a recent review see F. A. Davis, *Int. J. Sulfur Chem., B*, in press.

(7) T. Zincke and J. Baeumer, *Justus Liebigs Ann. Chem.*, **416**, 86 (1918).

(8) N. V. Khromov-Broisoc and M. B. Kolesova, *J. Gen. Chem. USSR*, **25**, 361 (1955).

(9) J. A. Barltrop and K. J. Morgan, *J. Chem. Soc.*, 3072 (1957).

(10) J. J. D'Amico, *J. Org. Chem.*, **26**, 3436 (1961).

(11) D. Kaminsky, J. Shavel, Jr., and R. I. Meltzer, *Tetrahedron Lett.*, 859 (1967).