Preparation of Ethyl 2,3-Dimethylcyclopropanecarboxylates (Mixed Isomers) (14).—To 2.6 g (0.022 mol) of thionyl chloride was added dropwise a solution of 2.0 g (0.017 mol) of a mixture of 2,3-dimethylcyclopropanecarboxylic acids consisting of 4% **9**, 6% **10**, and 90% **11** in 5 ml of benzene. The reaction mixture was stirred at room temperature for 90 min and then heated at reflux for 90 min. After cooling to room temperature, 10 ml of absolute ethanol was added dropwise. The solution was evaporated under reduced pressure to give a liquid residue. Distillation gave 1.60 g (67%) of isomeric ethyl 2,3-dimethylcyclopropanecarboxylate (**14**): bp 53–56° (7 mm); ir (neat) 5.82 (C=O), 7.65, and 8.50 μ (COC); nmr ($CDCl_3$) δ 4.03 (m, 2, OCH_2CH_3, J = 7 Hz), 1.7–0.8 (m, 12).

Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.37; H, 9.99.

A solution containing 1.35 g of **14** and 0.015 mol of sodium ethoxide in 40 ml of absolute ethanol was heated at reflux for 43 hr. A solution of 10 g of NaOH in 15 ml of water was added dropwise, and the reflux was continued for 4 hr. The ethanol was removed under reduced pressure and the remaining aqueous solution was washed with three 15-ml portions of chloroform, acidified with 50% H_2SO_4, and washed with three additional 15-ml portions of chloroform. The latter chloroform washings were dried (Na_2SO_4) and evaporated under reduced pressure to give 1.0 g of 2,3-dimethylcyclopropanecarboxylic acids. Vpc analysis showed the presence of **9** and **11** and only a trace of **10**. No additional component was evident.

Registry No.—**2**, 38868-10-9; **8**, 1758-32-3; (±)-**9**, 20431-63-4; **9a**, 20431-72-5; **10**, 34669-52-8; **11**, 34669-51-7; **12**, 1758-33-4; **14**, 17214-87-8.

Acknowledgment.—The authors are grateful to Dr. A. T. McPhail and Mrs. P. A. Luhan for the X-ray crystallographic analysis.

Preparation and Applications of (Dialkylamino)methyloxosulfonium Methylides. Synthesis of Cyclopropanes and Oxiranes[1a]

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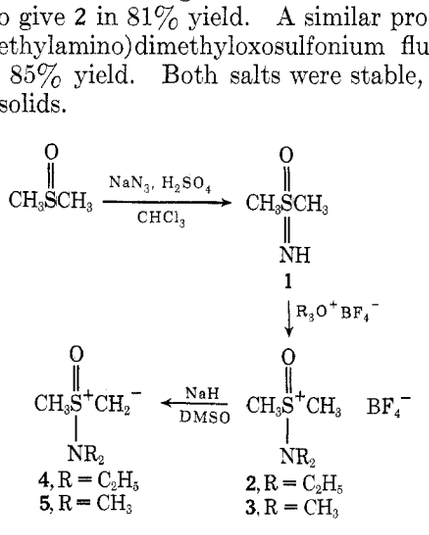
Dimethylsulfoximine, prepared from dimethyl sulfoxide, was dialkylated to give (*N*,*N*-dimethylamino)- and (*N*,*N*-diethylamino)dimethyloxosulfonium fluoroborate. Reaction of these salts with sodium hydride in a variety of aprotic solvents gave methylides. These ylides are effective as nucleophilic methylene transfer reagents; reactions with electrophilic alkenes yield cyclopropanes, while aldehydes and ketones react to give oxiranes.

In the past decade the chemistry of sulfur ylides has been an area of substantial interest.[2] The dimethylsulfonium and dimethyloxosulfonium methylides introduced by Corey and Chaykovsky are very useful synthetic reagents.[3] These ylides have been used to transfer a methylene group in a stepwise fashion across the double bond of a carbonyl or an electrophilic olefin to yield an epoxide or a cyclopropane, respectively. The transfer of more complex groups has also been achieved.[4]

The observation in this laboratory that ylides derived from (dimethylamino)alkylaryloxosulfonium fluoroborates[5] were capable of transferring alkylidene groups prompted us to undertake a study of the preparation and chemistry of an ylide derived from dimethylsulfoximine. This ylide would be accessible to the synthetic organic chemist and could serve as a model for ylides derived from other symmetrical dialkyl sulfoximines.

The first goal of this work was to prepare an ylide from dimethyl sulfoxide (DMSO) in as few steps as possible. Dimethylsulfoximine (**1**) could be prepared in 85% yield from DMSO using 1.1 equiv of hydrazoic acid, generated in a chloroform slurry from sodium azide and sulfuric acid.[6] The *N*,*N*-diethyl salt (**2**)[7] was chosen as the model ylide precursor. The choice of the *N*,*N*-diethyl derivative was prompted by the fact that triethyloxonium fluoroborate, the alkylating agent of choice, requires one less step in its preparation than trimethyloxonium fluoroborate. The dialkylation of the crude sulfoximine was accomplished in one flask using excess sodium carbonate as a base to give **2** in 81% yield. A similar procedure gave (dimethylamino)dimethyloxosulfonium fluoroborate (**3**) in 85% yield. Both salts were stable, white, crystalline solids.



(Diethylamino)methyloxosulfonium methylide (**4**) was readily prepared by dissolving the salt **2** in DMSO

(1) (a) Part XXXIX in the series "Chemistry of Sulfoxides and Related Compounds." We gratefully acknowledge support by the National Science Foundation (GP 19623). (b) National Science Foundation Graduate Trainee, 1968–1971.

(2) A. W. Johnson, "Ylid Chemistry," Academic Press, London and New York, 1966.

(3) (a) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **84**, 867 (1962); (b) *ibid.*, 3782 (1962); (c) *ibid.*, **86**, 1640 (1964); (d) *ibid.*, **87**, 1353 (1965); (e) H. Konig, *Fortschr. Chem. Forsch.*, **9**, 487 (1968).

(4) (a) E. J. Corey and W. Oppolzer, *J. Amer. Chem. Soc.*, **86**, 1899 (1964); (b) E. J. Corey, M. Jautelat, and W. Oppolzer, *Tetrahedron Lett.*, 2325 (1967); (c) G. B. Payne, *J. Org. Chem.*, **32**, 3351 (1967); (d) *ibid.*, **33**, 1284 (1968); (e) G. B. Payne and M. R. Johnson, *ibid.*, **33**, 1285 (1968); (f) G. B. Payne, *ibid.*, **33**, 3517 (1968).

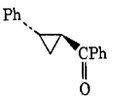
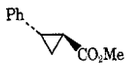
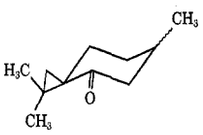
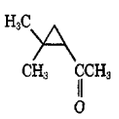
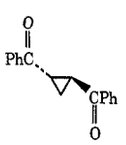
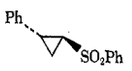
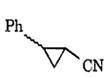
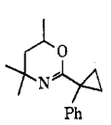
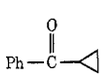
(5) (a) C. R. Johnson, E. R. Janiga, and M. Haake, *J. Amer. Chem. Soc.*, **90**, 3890 (1968); (b) C. R. Johnson, M. Haake, and C. W. Schroeck, *ibid.*, **92**, 6594 (1970).

(6) H. R. Bentley and J. K. Whitehead, *J. Chem. Soc.*, 2081 (1950).

(7) H. Schmidbaur and G. Kammel, *Chem. Ber.*, **104**, 3241 (1971), have recently described the preparation of salts **2** and **3** and the corresponding ylides **4** and **5**. Their interest was largely in the preparation and study of spectral properties.

TABLE I

CYCLOPROPANES

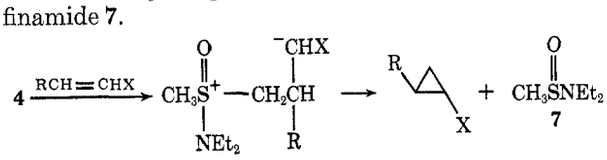
Substrate	Registry no.	Product	Registry no.	Yield, %
Benzalacetophenone	94-41-7		1145-92-2	93
Methyl cinnamate	103-26-4		5861-31-4	82
Pulegone	89-82-7		38709-59-0 (trans) 38709-60-3 (cis)	52
Mesityl oxide				62
2-Cyclohexenone	930-68-7		5771-58-4	60
trans-1,4-Diphenyl-2-butene-1,4-dione				62
Phenyl styryl sulfone	5418-11-1		21309-15-9	80
Cinnamonitrile	4360-47-8		5279-82-3 (cis) 5590-14-7 (trans)	49[a]
2-(1-Phenyl)vinyl-4,4,6-trimethyl-5,6-dihydro-1,3-oxazine	38709-86-3		38709-65-8	75
α-Bromoacetophenone	70-11-1		3481-02-5	25

[a] Composition: 21% cis and 79% trans; in addition, β-methylcinnamonitrile (9%) was produced.

(distilled from calcium hydride) and adding it to a stirred slurry of sodium hydride in DMSO under a cover of nitrogen. After 10–15 min a clear solution of **4** was obtained. Ylide **4** was stable for extended periods at room temperature; it was found that at 52° the ylide had a half-life of approximately 40 hr. Solutions of the ylide were also prepared in dimethylformamide (DMF) and tetrahydrofuran (THF). Generation of the ylide **4** in THF required several hours owing to the heterogeneous nature of the reaction mixture. After the ylide was prepared in THF the fluoroborate salts could be filtered off and standardized solutions of **4** could be stored under nitrogen for several weeks in the refrigerator. In general, however, the ylide was prepared shortly before use. (Dimethylamino)methyloxosulfonium methylide (**5**) was prepared in the same manner as **4**.

DMSO was the solvent of choice in nearly all of the methylene transfer reactions. A qualitative kinetic study showed that the ylide reacted more rapidly in DMSO than in DMF. However, the major advantage of DMSO over other solvents lies in its greater solubility in water, allowing most of it to be easily removed by an aqueous wash. High water solubility also aided in the removal of the sulfinamide produced during the reaction. Chromatography over a short column of silica was found to be the most convenient method of product purification. Distillations were carried out when very volatile products were produced. Several methylene transfer reactions were run using both ylide **4** and ylide **5**; there was no notable difference in reactivity.

The ylide **4** was treated with a variety of α,β-unsaturated ketones, esters, sulfones, nitriles, and amides to give the corresponding cyclopropanes (Table I). These reactions are believed to occur stepwise *via* addition of the ylide to the substrate to give betaine **6** followed by ring closure with displacement of sulfinamide **7**.



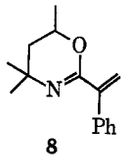
6

The rate of the ylide reactions with substrates of this nature seems to be dependent largely on the ease of betaine formation. Steric hindrance to attack by

the ylide **4** was observed to slow the rate of reaction substantially; a rapid reaction occurred with 2-cyclohexenone while pulegone and mesityl oxide reacted at much slower rates. The stability of the betaine which is formed also seemed to influence the rate of these reactions. Qualitatively, there is a good correlation between the pK_a of an aliphatic sulfone, ketone, nitrile, or ester and the rate of reaction with substrates in which these groups stabilize the betaine. Phenyl styryl sulfone and benzalacetophenone reacted rapidly, while cinnamonitrile and methyl cinnamate required longer periods of time for complete reaction. Attempts to add the ylide to methyl styryl sulfone and cinnamide were not successful even after long periods of time and use of large excesses of ylide. (In the reaction medium these substrates may exist largely as their anions.)

The reaction of the ylide with benzalacetophenone was found to give a 93% yield of *trans*-1-benzoyl-2-phenylcyclopropane. The observation of the exclusive or predominant formation of trans cyclopropanes during the course of this study points toward the existence of the proposed betaine intermediate **6**.[8] A mixture of cis and trans cyclopropanes was obtained from cinnamonitrile; this suggests that because the cyano group is smaller than some of the other groups (benzoyl, carbomethoxy, or phenyl sulfone) investigated, the ring closure of the different betaine conformers can complete effectively.

During the course of this work Meyers and coworkers[9] reported the use of 4,4,6-trimethyl-5,6-trimethyl-5,6-dihydro-1,3-oxazines as precursors to a variety of aldehydes. It was found that the ylide **4** reacted smoothly with 2-(1-phenylvinyl)-4,4,6-trimethyl-5,6-dihydro-1,3-oxazine (**8**) to give a 75% yield of the corresponding cyclopropane (Table I). The cyclopropyl compound was reduced with neutral sodium borohydride and hydrolyzed with oxalic acid to give an 81% yield of 1-phenylcyclopropanecarboxaldehyde.



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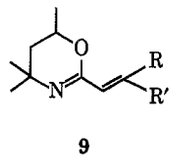


9

Several other vinyloxazines (**9**) (R = alkyl or aryl) were prepared by dehydration of the corresponding alcohols. All of these vinyloxazines failed to react with the ylide **4**. In related work it was observed that the anion of dimethyl-*N*-*p*-toluenesulfonylsulfoximine[10] and dimethyloxosulfonium methylide also failed to add across the double bond of these oxazines. These failures only serve to emphasize the importance of the betaine stability in this type of ylide reaction. The phenyl group in the betaine formed as an intermediate in the addition of the ylide **4** and **8** afforded the stabilizing effect which was needed but was not available in the other systems.

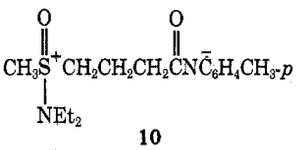
(8) C. R. Johnson and C. W. Schroeck, *J. Amer. Chem. Soc.*, **93**, 5303 (1971).

(9) (a) A. I. Meyers, A. Nabeya, H. W. Adickes, and I. R. Politzer, *ibid.*, **91**, 763 (1969); (b) A. I. Meyers, H. W. Adickes, I. R. Politzer, and W. N. Beverung, *ibid.*, **91**, 765 (1969).

(10) C. R. Johnson and G. F. Katekar, *ibid.*, **92**, 5753 (1970).

Cyclopropyl phenyl ketone was prepared by the reaction of 3.3 equiv of the ylide **4** with α-bromoacetophenone; DMF was used as a solvent owing to the known affinity of DMSO to react with α-halo ketones to give glyoxals.[11] There was only a 25% yield of isolated product, but the reaction did demonstrate the ylide's ability to introduce two methylene groups by successive reactions; phenyl vinyl ketone is presumed to be an intermediate in this reaction. Earlier examples of this type of double methylene insertion reactions with dimethyloxosulfonium methylide had been observed by Bravo and coworkers.[12]

N-*p*-Tolyl-2-pyrrolidone (**11**) was observed as the major product from the reaction of the ylide **6** with *p*-acrylotoluidide. Konig and Metzger[13] reported a similar result when the dimethyloxosulfonium methylide was treated with this substrate. A logical mechanism to explain this observation involves proton transfer from nitrogen to carbon to give intermediate **10**, which then undergoes ring closure to the pyrrolidone **11**.



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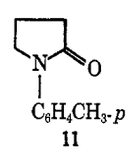

11

It was found that epoxides were formed in the reaction of the ylide with several aldehydes and ketones (Table II). As would be expected, aldehydes reacted more rapidly than ketones. In general, best results were obtained using a 30–100% excess of ylide coupled with short reaction times.

TABLE II
EPOXIDES

Substrate	Products	Yield, %
Benzaldehyde	C_6H_5-epoxide	57
p-Chlorobenzaldehyde	*p*-ClC_6H_4-epoxide	62
4-*tert*-Butylcyclohexanone		72
Heptanal	n-C_6H_{13}-epoxide	37
Cycloheptanone		42
4-Methylcyclohexanone		42

When **4** reacted with 4-*tert*-butylcyclohexanone only the *Z* epoxide was produced. Dimethyloxosulfonium methylide is reported to display a similar stereospecificity, while dimethylsulfonium methylide gave predominantly the *E* epoxide.[3d]

(11) N. Kornblum, W. J. Jones, and G. J. Anderson, *ibid.*, **81**, 4113 (1959).

(12) R. Bravo, G. Baudiano, C. Ticozzi, and A. Umani-Ronchi, *Tetrahedron Lett.*, 4481 (1968).

(13) H. Konig, H. Metzger, and K. Seelert, *Chem. Ber.*, **98**, 3712 (1965).

Experimental Section

General.—Melting points were determined with a Thomas-Hoover capillary melting-point apparatus and are uncorrected. Boiling points are also uncorrected. The microanalyses were performed by Midwest Microlabs, Inc., Indianapolis, Ind. The ir spectra were recorded on Perkin-Elmer infrared spectrophotometers, Models 137B and 621. The nmr spectra were taken on Varian spectrometers, Models A-60A and T-60, with a sweep width of 500 Hz; tetramethylsilane was used as the internal standard. Vapor phase chromatography was performed on F & M Models 5750 and 720 (thermal conductivity) chromatographs with 0.25-in. columns. The mass spectral data were obtained on either an Atlas CH4 or an AEI MS9 spectrometer mass. Many of the authentic samples used in comparisons had been previously prepared in our laboratory by ylide reactions.[5]

Dimethylsulfoximine (1).[6]—In a 2-l. flask equipped with a condenser, a mechanical stirrer, and an addition funnel, a mixture of 50 g (0.64 mol) of dimethyl sulfoxide, 46 g (0.71 mol) of sodium azide, and 570 ml of chloroform was cooled in an ice bath. Concentrated sulfuric acid (160 ml) was added to this slurry over a period of 1 hr. The mixture was slowly warmed to 42° and stirred at this temperature for 24 hr. After cooling, all the solids were dissolved in water, the chloroform layer was separated, and the aqueous layer was washed with two 150-ml portions of chloroform. The aqueous layer was made slightly alkaline using a 40% sodium hydroxide solution. The water was then removed on a rotary evaporator and the resulting salts were washed with 2 l. of warm ethanol. Removal of the ethanol and washing the ethanol-soluble salts with 500 ml of methylene chloride gave 51.5 g (87%) of the sulfoximine as a crystalline solid, nmr ($CDCl_3$) δ 3.10 (s, 6, CH_3), 2.84 (s, 1, NH).

(Diethylamino)dimethyloxosulfonium Fluoroborate (2).—In a 1-l. erlenmeyer flask fitted with a drying tube, 20.5 g (0.22 mol) of dimethylsulfoximine was dissolved in 300 ml of dry methylene chloride and cooled in a water bath. To this solution 45 g (0.24 mol) of triethyloxonium fluoroborate[14] was added as the reaction was stirred vigorously with a magnetic stirrer. After 15 min 110 g (1.04 mol) of anhydrous sodium carbonate was added and the reaction was allowed to stir for 3 hr. Then another 45 g of the triethyloxonium fluoroborate was added and the mixture was allowed to stir for 1 hr. The inorganic salts were removed and then washed with 3 l. of warm ethanol. The methylene chloride was removed and that material was added to the ethanol solution, which was reduced to about ⅔ of its original volume. At this point cooling gave 44 g of the crude sulfoximine salt. Recrystallization from ethanol gave 42 g (81%), of salt **2**: mp 107–108°; ir (Nujol) 1250, 1140–1000 cm^{-1} (BF_4^-); nmr (DMSO-d_6) δ 4.05 (s, 6, CH_3), 3.86–3.44 (q, 4, CH_2), 1.42–1.18 (t, 6, CH_3).

Anal. Calcd for $C_6H_{16}BF_4NOS$: C, 30.40; H, 6.80. Found: C, 30.55; H, 6.98.

(Dimethylamino)dimethyloxosulfonium Fluoroborate (3).—A procedure, identical with that used to prepare **4** using trimethyloxonium fluoroborate as the alkylating agent, was followed. At the conclusion the carbonate salts were washed with 2 l. of warm methanol. Recrystallization from methanol gave 39 g (85%) of the salt **3**: mp 146–147°; ir (Nujol) 1240, 1140–1020 cm^{-1} (BF_4^-); nmr (DMSO-d_6) δ 4.0 (s, 6, SMe), 3.06 (s, 6, NMe).

Anal. Calcd for $C_4H_{12}BF_4NOS$: C, 22.98; H, 6.17. Found: C, 23.25; H, 5.89.

(Diethylamino)methyloxosulfonium Methylide (4). A. Preparation in DMSO.—In a 50-ml three-necked flask equipped with a stirrer, an additional funnel, a gas inlet tube, and a serum stopper was placed 11 mmol of sodium hydride (as a 59.4% dispersion in mineral oil), and 5 ml of DMSO (distilled from calcium hydride) under a cover of nitrogen. To this, 2.60 g (11 mmol) of (diethylamino)dimethyloxosulfonium fluoroborate (**2**) in 12 ml of DMSO was added through the addition funnel over a period of 15 min with good stirring. There was a vigorous evolution of hydrogen, and the mixture was kept at room temperature with the aid of a water bath. After a few minutes a clear solution was obtained. An identical procedure can be used to prepare (dimethylamino)methyloxosulfonium methylide (**5**).

B. Preparation in THF.—The same apparatus as described above was used. The sodium hydride and the fluoroborate were placed in the flask as dry solids. The THF (distilled from sodium dispersion) was then introduced into the reaction flask all at once, and the heterogeneous mixture was stirred for several hours while being kept in room temperature with a water bath. The inorganic salts could be filtered off under nitrogen and a solution of the ylide **4** could be stored in a refrigerator for several weeks. In most cases no effort was made to remove the inorganic salts, and the ylide solution was used soon after its preparation.

Methylene Transfer Reactions.—In general, the reaction mixtures were poured into 100 ml of water and the product was extracted three times with 50-ml portions of ether. The ether solution was dried over magnesium sulfate and evaporated at reduced pressure. Chromatography over an 18 × 0.5 in. column of silica gel eluting first with 100 ml of pentane followed by benzene gave the desired products in a high state of purity. In several cases when the product was very volatile the crude product was purified by a short-path distillation.

***trans*-1-Benzoyl-2-phenylcyclopropane.**—To a stirring solution of ylide **4** (11 mmol) in 17 ml of DMSO was added a solution of 2.08 g (10 mmol) of benzalacetophenone in 8 ml of DMSO over a period of 10 min. The mixture was allowed to stir at room temperature for 4 hr. Work-up and chromatography yielded 2.08 g (94%) of an oil which solidified upon standing. The infrared spectrum was identical with that of a known sample: ir (film) 1670 cm^{-1} (C=O); nmr ($CDCl_3$) δ 8.27–7.1 (m, 10, aryl), 3.0–2.45 (m, 2, COH and CH), 2.0–1.2 (two m, 2, CH_2).

Methyl *trans*-2-Phenylcyclopropylcarboxylate.—Ylide **4** (12 mmol) was prepared in 17 ml of DMSO. A solution of 1.62 g (10 mmol) of methyl cinnamate in 8 ml of DMSO was added over a period of 30 min. The reaction mixture was allowed to stir for 48 hr at room temperature. Work-up and chromatography gave 1.45 g (82.5%) of the cyclopropyl ester. The product was one component by glpc analysis on a 8 ft × 0.25 in., 20% DEGS on C-W column at 180°: ir (film) 1730 cm^{-1} (C=O); nmr ($CDCl_3$) δ 7.5–6.0 (m, 5, aryl), 3.67 (s, OCH_3), 2.7–2.3 (m, 1, $CHCO_2$), 2.1–1.1 (m, 3, $CHCH_2$).

Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 74.70; H, 6.93.

Cyclopropyl Phenyl Ketone.—Ylide **4** (31 mmol) was prepared in 28 ml of DMF at 0°. α-Bromoacetophenone (1.92 g, 9.65 mmol) in 20 ml of DMF was added over a period of 30 min. The reaction was stirred in an ice bath for 12 hr and at room temperature for 6 hr. Work-up and chromatography gave 0.35 g (25%) of the cyclopropyl ketone. The infrared spectrum and glpc behavior were identical with that of an authentic sample; nmr ($CDCl_3$) δ 8.2–7.2 (2, m, 5, aryl), 2.9–2.4 (m, 1, OCCH), 1.4–8.0 (m, 4, cyclopropyl).

Reaction of the Ylide with Cinnamonitrile.—The ylide **4** (20 mmol) was prepared in 20 ml of DMSO. Cinnamonitrile (1.29 g, 10 mmol) was added and the reaction was stirred at 50° for 24 hr. The reaction mixture was poured into ice water and extracted with ether. The ether was dried with magnesium sulfate and evaporated. After work-up the crude product was chromatographed over silica gel to give 0.83 g (58%) of product. Glpc analysis (10 ft × 0.25 in., 15% DEGS on Diaport S at 210°) indicated the presence of three components, A, B, and C, with retention times of 10.5, 13.2, and 18.7 min in a ratio of 16:66:18. These three components could be separated by tedious chromatography on silica gel or by preparative glpc using a 6 ft × 0.75 in., 20% DEGS on Chromosorb W column.

Component A had ir (film) 2225, 1610, 1570, 790, 755 cm^{-1}; nmr ($CDCl_3$) δ 8.35 (s, 5, aryl), 5.54 (q, 1, J = 1.1 Hz, CH), 2.4 (d, 3, J = 1.1 Hz, CH_3). On the basis of the spectral evidence component A was assumed to be β-methylcinnamonitrile. A (200 mg) was stirred in 10 ml of 2 N sodium hydroxide in an oil bath at 100° for 24 hr. After cooling the mixture to room temperature it was diluted with 15 ml of water and washed with ether. The water layer was acidified and extracted with ether. The ether was dried and evaporated to give 194 mg of a solid, mp 96–97°. This compares well with mp 98° for β-methylcinnamic acid.[15]

Component B could be obtained as a crystalline solid: mp 51–52° from ether–pentane; ir (film) 2250, 1610, 1500, 1460, 1400, 750, 690 cm^{-1}; nmr ($CDCl_3$) δ 7.5–6.9 (m, 5, aryl), 2.8–2.4 (m, 1, CHCN), 1.7–1.4 (m, 3). Hydrolysis of B in 2 N NaOH gave *trans*-2-phenylcyclopropanecarboxylic acid, indicating that B is the corresponding nitrile.

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(15) L. Kh. Vinograd and N. S. Vul'fson, *J. Gen. Chem. USSR*, **29**, 2656 (1959).

Component C could be obtained as a crystalline solid: mp 37° from ether–pentane; ir (film) 2250, 1610, 1500, 1460, 760, 730, 690 cm^{-1}; nmr ($CDCl_3$) δ 7.3 (s, 5, aryl), 3.3–2.8 (m, 1, CHCN), 2.0–1.1 (m, 3). Basic hydrolysis of C in 2 *N* NaOH at reflux for 48 hr gave *cis*-2-phenylcyclopropanecarboxylic acid. These data indicate that C is *cis*-2-phenylcyclopropanecarbonitrile.

Reaction of Ylide 4 with *p*-Acrylotoluidide.—The ylide 4 was prepared by stirring 4.40 g (186 mmol) of 2 and 0.446 g (186 mmol) of sodium hydride in 16 ml of DMSO. A solution of 2.0 g (124 mmol) of *p*-acrylotoluidide in 8 ml of DMSO was added and the reaction mixture was allowed to stir for 24 hr at room temperature. After work-up the product was chromatographed over alumina and eluted with benzene to give 1.07 g (50%) of *N*-*p*-tolyl-2-pyrrolidone (11) and 190 mg (9%) of a material assigned the structure 3-(3′-*N*-*p*-tolyl-2-pyrrolidone)-*N*-*p*-tolylpropionamide. Both compounds were crystalline solids, mp 86–87° (lit.[16] mp 88–89°) and 190–191°, respectively. *N*-*p*-Tolyl-2-pyrrolidone had ir ($CHCl_3$) 1680, 1505, 1390, 1300 cm^{-1}; nmr ($CDCl_3$) δ 7.4–6.9 (2 d, 4, aryl), 3.86–3.50 (t, 2, OCH_2), 2.77–1.67 (m, 4, ring), 2.36 (s, 3, CH_3). 3-(3′-*N*-*p*-Tolyl-2-pyrrolidone)-*N*-*p*-tolylpropionamide had ir ($CHCl_3$) 3430, 1660, 1520 cm^{-1}; nmr ($CDCl_3$) δ 7.6–6.9 (m, 8, aryl), 4.5–4.1 (t, 2, $COCH_2$), 2.8–1.7 (m, 13).

Reaction of the Ylide 4 with Pulegone.—Ylide 4 (11.5 mmol) was prepared in 15 ml of DMSO. A solution of 1.52 g (10 mmol) of pulegone in 10 ml of DMSO was added and the reaction mixture was stirred at room temperature for 48 hr. Following work-up, chromatography of the crude product over silica gel gave 0.87 g (52%) of a 60:40 mixture of the diastereomeric cyclopropanes, ir (film) 1710 cm^{-1}.

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.28; H, 10.99.

2-(1-Phenyl)cyclopropyl-4,4,6-trimethyl-5,6-dihydro-1,3-oxazine.—The ylide 4 (15 mmol) was prepared in 15 ml of DMSO. A solution of 2.17 g (9.45 mmol) of 2-(1-phenyl)vinyl-4,4,6-trimethyl-5,6-dihydro-1,3-oxazine[17] in 10 ml of DMSO was added and the reaction was allowed to stir at 50° for 60 hr. Work-up gave 2.3 g of crude product which was distilled (76–84°, 0.3 mm) using a short-path distillation apparatus to give 1.74 g (75% of product which solidified on standing: ir (film) 1660 cm^{-1} (C=N); nmr ($CDCl_3$) δ 7.45–7.0 (m, 5, aryl), 4.3–3.8 (m, 1, OCH), 1.9–0.8 (m, 16).

Preparation of 1-Phenylcyclopropanecarboxaldehyde.—The 2-(1-phenyl)cyclopropyloxazine (1.72 g, 7.1 mmol) was dissolved in 20 ml of 50:50 THF–ethanol and cooled in an acetonitrile–Dry Ice bath at −45°, and 300 mg (7.95 mmol) of sodium borohydride in 1.5 ml of basic water was added slowly with periodic checks to maintain the pH as close to 7 as possible using 9 *N* HCl. After the addition of the sodium borohydride the reaction was allowed to stir for an additional 1 hr before the mixture was poured into water. The water was made basic with 40% NaOH and extracted with ether. The ether was washed with saturated NaCl, dried over potassium carbonate, and evaporated to give 2 g of crude product. Hydrated oxalic acid (11.8 g) was dissolved in 30 ml of water, which was heated to a boil in a small distillation apparatus equipped with an additional funnel. The crude tetrahydrooxazine was dissolved in ether and added slowly. The water was allowed to distil over until it was no longer cloudy. The distillate was dissolved in pentane, the solution was dried, and the pentane was evaporated to give 0.86 g (81%) of the desired aldehyde, ir (film) 1705 cm^{-1} (C=O).

***trans*-1-(Phenylsulfonyl)-2-phenylcyclopropane.**—To a solution of ylide 4 (6 mmol) in 15 ml of DMSO was added over a period of 30 min a solution of 1.22 g (5 mmol) of phenyl styryl sulfone in 10 ml of DMSO. The reaction was allowed to stir for 24 hr. Work-up and chromatography yielded 1.06 g (82%) of a crystalline solid: mp 93–94° (lit.[18] mp 95–96°); ir (film) 1300, 1150 cm^{-1}; nmr ($CDCl_3$) δ 8.1–6.9 (m, 10, aryl), 3.1–2.4 (m, 2), 2.05–1.2 (m, 2).

3-Norcaranone.—Ylide 4 (11 mmol) was prepared in 18 ml of DMSO. To this solution was added 0.96 g (10 mmol) of 2-cyclohexenone in 7 ml of DMSO and the reaction was allowed to stir for 3 hr at room temperature. Isolation of the crude product in the standard manner followed by chromatography over a short column of silica gel, eluting with pentane, followed by 50:50 methylene chloride–benzene, gave 0.63 g (57%) of 3-norcaranone: ir (film) 1690 cm^{-1}; nmr ($CDCl_3$) δ 2.7–1.45 (m, 8, cyclohexyl), 1.4–0.8 (m, 2, cyclopropyl).

Anal. Calcd for $C_7H_{10}O$: C, 76.33; H, 9.15. Found: C, 76.39. H, 9.25.

1-Methylene-4-methylcyclohexane Oxide.—Ylide 4 (13 mmol) was prepared in 17 ml of DMSO. To this solution was added 1.12 g (10 mmol) of 4-methylcyclohexanone in 5 ml of DMSO. The reaction was stirred at 50° for 8 hr. Standard work-up and chromatography gave 0.52 g (42%) of the epoxide: ir (film) 920, 840, 770 cm^{-1}; nmr ($CDCl_3$) δ 2.81 (s, 2, OCH_2), 2.2–0.8 (m, 12).

Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.8. Found, C, 76.21; H, 11.12.

1-Octene Oxide.—The ylide 4 (15 mmol) was prepared in 25 ml of DMSO. The ylide solution was warmed to 50° and 1.14 g (10 mmol) of heptanal in 20 ml of DMSO was added over a period of 90 min. The reaction was allowed to stir for an additional 2 hr at 50°. Following work-up, the crude product was chromatographed over silica gel eluting first with pentane and then pentane–ether. Bulb-to-bulb distillation gave 0.462 g (36.5%) of the epoxide. The infrared spectrum was identical with that of an authentic sample: nmr ($CDCl_3$) δ 3.2–2.4 (m, 3, $CHCH_2$), 1.8–0.7 (m, 15, alkyl).

Styrene Oxide.—Ylide 4 (13 mmol) was prepared in 17 ml of DMSO. A solution of 1.06 g (10 mmol) of benzaldehyde in 8 ml of DMSO was added over a period of 30 min. The reaction was allowed to stir for 1 hr at room temperature and 2 hr at 50°. The reaction mixture was poured into ice water and extracted with ether. The ether was dried over magnesium sulfate and evaporated; the residue was distilled at 80° (5 mm) to give 0.684 g (57%) of colorless styrene oxide, whose infrared spectrum was identical with that of an authentic sample.

***p*-Chlorostyrene Oxide.**—Following a similar procedure to that used for styrene oxide, *p*-chlorostyrene oxide was produced in 62% yield from *p*-chlorobenzaldehyde. Work-up and chromatography yielded 0.96 g (62%) of *p*-chlorostyrene oxide. The infrared spectrum of the product was identical with that of an authentic sample.

(*Z*)-1-Methylene-4-*tert*-butylcyclohexane Oxide.—A solution of ylide 4 (13 mmol in 17 ml of DMSO) was warmed to 50° and 1.54 g (0.010 mol) of 4-*tert*-butylcyclohexanone in 8 ml of DMSO was added over a period of 30 min. The reaction was stirred at this temperature for 4 hr. The crude product was chromatographed over silica gel to give 1.24 g (72%) of the *Z* epoxide, whose infrared spectrum was identical with that of an authentic sample: ir (neat) 920, 855, and 800 cm^{-1}; nmr ($CDCl_3$) δ 2.61 (s, 2, CH_2), 2.0–1.8 (m, 9, ring), 0.88 (s, 9, *t*-Bu).

Methylenecycloheptane Oxide.—Ylide 4 (26 mmol in 20 ml of DMSO) was warmed to 50° and 1.46 g (0.013 mol) of cycloheptanone in 10 ml of DMSO was added over a period of 20 min. The reaction mixture was stirred overnight at 50°. Chromatography of the crude product over silica gel gave 0.69 g (42%) of the oxirane. An infrared spectrum was identical with that of an authentic sample; nmr ($CDCl_3$) δ 2.58 (s, 2, OCH_2), 1.67 (s, 12, ring).

Registry No.—**1,** 1520-31-6; **2,** 36501-44-7; **3,** 36501-42-5; **4,** 38421-38-4; **11,** 3063-79-4; dimethyl sulfoxide, 67-68-5; sodium azide, 26628-22-8; triethyloxonium tetrafluoroborate, 368-39-8; trimethyloxonium tetrafluoroborate, 420-37-1; β-methylcinnamonitrile, 14368-40-2; *p*-acrylotoluidide, 7766-36-1; 3-(3′-*N*-*p*-tolyl-2-pyrrolidone)-*N*-*p*-tolylpropionamide, 38709-70-5; 1-methylene-4-methylcyclohexene oxide, 38709-71-6; 4-methylcyclohexanone, 589-92-4; 1-octene oxide, 2984-50-1; heptanal, 111-71-7; (*Z*)-1-methylene-4-*tert*-butylcyclohexane oxide, 7787-78-2; 4-*tert*-butylcyclohexanone, 98-53-3; methylenecycloheptane oxide, 185-85-3; cycloheptanone, 502-42-1.

(16) P. Lipp and F. Caspers, *Ber.*, **58**, 1011 (1925).

(17) A sample of the oxazine was kindly supplied by Professor A. I. Meyers.

(18) W. E. Truce and V. R. Badiger, *J. Org. Chem.*, **29**, 3277 (1964).