fluoridate in three fractions. The major fraction was redistilled, b.p. 74–76° (1.5 mm.), $n^{25}D$ 1.3994.

Anal. Calcd. for $C_8H_{18}FO_3P$: P, 14.6. Found: P, 13.6.

The product was further identified by comparison of its infrared spectrum with that of an authentic sample (see below). Aniline tests[12] on the distillates were negative. The literature[13] gives b.p. 84–86° (0.8 mm.), $n^{25}D$ 1.412, $n^{20}D$ 1.4013. The residue from this distillation was a mobile black oil, 77.0 g., which showed no unsaturation in the infrared.

Anal. Found: P, 7.4; Cl, 10.4.

Distillation of the combined trap contents from all of these operations gave butyl chloride, b.p. 78–80°, $n^{24}D$ 1.3998, in 50% yield. No butyl fluoride was detected.

A series of experiments in which the ratio of phosphorus to chlorine was reduced from 1:1 to 1:10 gave products with higher chlorine content and lower phosphorus content, but none of them showed unsaturation in the infrared. No reaction was observed between Fluorolube S and tributyl phosphite or trimethyl phosphite in refluxing benzene (80°).

B. 2-Chlorononafluorobutane.—Tributyl phosphite (25.0 g., 0.1 mole) and 2-chlorononafluorobutane (25.5 g., 0.1 mole) were found to be immiscible at room temperature. After 2 hr. stirring the mixture was distilled, 90% of the 2-chlorononafluorobutane, b.p. 29–30°, being recovered. Another experiment, in which 100 ml. of benzene was added as a solvent, gave a homogeneous solution, but again no sign of reaction was observed.

C. 2,2-Dichlorooctafluorobutane.—2,2-Dichlorooctafluorobutane (27.1 g., 0.1 mole) was added dropwise to a solution of 25.0 g. (0.1 mole) of tributyl phosphite in 100 ml. of benzene over a 20-min. period at 25–30°. The reaction was strongly exothermic and was controlled by external cooling. When the addition was ended the solution was stirred at room temperature for 45 min. and then tested with 0.1 *N* iodine in benzene for unreacted phosphite. The test was negative. Distillation through a 3-in. column packed with glass helices gave 19.0 g. (87%) of 2-chloroheptafluoro-2-butene, b.p. 33–38°, identified by its infrared spectrum as a mixture of *cis* and *trans* isomers in about 2:3 ratio, and 12.5 g. (59%) of dibutyl phosphorofluoridate, b.p. 85–87° (2 mm.), identified by analysis, by its infrared spectrum which showed a P–F band[14] at 11.4 μ absent in dibutyl phosphorochloridate, and by a negative aniline test.[12]

Anal. Calcd. for $C_8H_{18}FO_3P$: P, 14.6. Found: P, 14.4.

The literature gives b.p. 33–35 or 32.2° for 2-chloroheptafluoro-2-butene.[8,15]

The substitution of trimethyl phosphite for tributyl phosphite in the reaction described above gave products identified by infrared as 2-chloroheptafluoro-2-butene and dimethyl phosphorofluoridate. This reaction could also be run in the absence of a solvent. 2,2-Dichlorooctafluorobutane (27.1 g., 0.1 mole) added to 12.4 g. (0.1 mole) of trimethyl phosphite gave 10.7 g. (50%) of 2-chloroheptafluoro-2-butene, b.p. 32–34° (*cis*:*trans* mixture in about 2:3 ratio), and 9.5 g. (74%) of dimethyl phosphorofluoridate, b.p. 38–44° (10 mm.), identified by analysis, by its infrared spectrum[14] which contained a P–F band at 11.3 μ absent in dimethyl phosphorochloridate and enhanced bands at 5.2 and 5.5 μ, and by a negative aniline test.

Anal. Calcd. for $C_2H_6FO_3P$: P, 24.2. Found: P, 23.0.

The literature[16] gives b.p. 43.5° (14 mm.). The trap contents from this reaction weighed 12.5 g. (calculated for methyl chloride, 5.0 g.). Infrared analysis showed them to be a mixture of methyl chloride and 2-chloroheptafluoro-2-butene.

D. 2,2,3-Trichloroheptafluorobutane.—A solution of 25.0 g. (0.1 mole) of tributyl phosphite in 100 ml. of benzene was treated dropwise with 28.8 g. (0.1 mole) of 2,2,3-trichloroheptafluorobutane over a 20-min. period at 25–30°. The reaction was strongly exothermic. When the addition was ended the solution was stirred for 15 min. and then tested for unreacted phosphite with 0.1 *N* iodine in benzene. The test was negative. Distillation gave 13.0 g. of a fraction, b.p. 31–53°, which was redistilled through a 4-in. column packed with glass helices to give a center cut, b.p. 34–35°, identified by its infrared spectrum as 2-chloroheptafluoro-2-butene (*cis*:*trans* mixture in about 1:1 ratio). Further distillation, after removal of the benzene and presumably the butyl chloride, gave a fraction, b.p. 122° (7 mm.), $n^{25}D$ 1.4264, identified by analysis, by its infrared spectrum, and by a strongly positive aniline test[12] as dibutyl phosphorochloridate.

Anal. Calcd. for $C_8H_{18}ClO_3P$: P, 13.5. Found: P, 13.4.

The literature[17] gives b.p. 129–130° (10 mm.), $n^{20}D$ 1.4306.

Dibutyl Phosphorofluoridate.—Dibutyl phosphorochloridate, b.p. 117–122° (8 mm.), $n^{25}D$ 1.4297, was prepared in 89% yield by the chlorination of tributyl phosphite in benzene.[18] The conversion of this substance to the fluoridate proved to be unexpectedly difficult. Even after 22 hr. of refluxing with sodium fluoride in toluene a product could not be obtained which was free from chloridate. The conditions described by Bany[13b] were 10 hr. of refluxing with sodium fluoride in benzene. A stronger fluorinating agent was obviously desirable. Cobalt trifluoride was found to be too reactive, producing a blue solution which deposited blue crystals on standing. Antimony trifluoride, however, was found to be suitable. A slurry of 20.0 g. (0.11 mole) of antimony trifluoride in 150 ml. of benzene was distilled until about 50 ml. of distillate was removed, and then, while still hot, treated dropwise with 22.9 g. (0.1 mole) of dibutyl phosphorochloridate over a 20-min. period. The mixture was heated at reflux for 2 hr., cooled, filtered, treated with lead carbonate to remove any residual acidity, and again filtered. Distillation of this product gave 5.7 g. (27%) of a fraction, b.p. 76° (0.9 mm.), $n^{25}D$ 1.3990, identified by analysis, by its infrared spectrum which contained a P–F band at 11.4 μ, absent in dibutyl phosphorochloridate, and by a negative aniline test, as dibutyl phosphorofluoridate.

Anal. Calcd. for $C_8H_{18}FO_3P$: P, 14.6. Found: P, 14.9.

Comparison of the infrared spectrum of this product with the spectra of the dibutyl phosphorofluoridates obtained from Fluorolube S and 2,2-dichlorooctafluorobutane showed that the same product was obtained from each.

Acknowledgment.—We are indebted to Mr. Leon A. Zengierski for capable technical assistance, and to Dr. Russell L. K. Carr for helpful discussions during the course of this work.

(12) B. C. Saunders, "Some Aspects of the Chemistry and Toxic Action of Organic Compounds Containing Phosphorus and Fluorine," Cambridge University Press, London, 1957, p. 48. This test was found to be quite useful for detecting traces of chloridates in phosphorofluoridates.

(13) (a) H. G. Cook, B. C. Saunders, and F. E. Smith, *J. Chem. Soc.*, 635 (1949); (b) T. Bany, *Bull. intern. acad. polon. sci., Classe sci. math. nat., Ser. A*, 1 (1951); *Chem. Abstr.*, **47**, 3791 (1953); (c) S. Öksne, *Acta Chem. Scand.*, **13**, 1814 (1959).

(14) L. W. Daasch and D. C. Smith, *Anal. Chem.*, **23**, 853 (1951).

(15) A. L. Henne and T. H. Newby, *J. Am. Chem. Soc.*, **70**, 130 (1948).

(16) C. E. Redemann, S. W. Chaikin, R. B. Fearing, G. R. Rotariu, J. Savit, and D. Van Hoesen, *ibid.*, **70**, 3604 (1948).

(17) H. Tolkmith, *Ann. N. Y. Acad. Sci.*, **79**, 189 (1959); *Chem. Abstr.*, **54**, 11607 (1960).

(18) W. Gerrard, *J. Chem. Soc.*, 1464 (1940).

Preparation of Some Cyclopropanes and Stable Sulfoxonium Ylides from Dimethylsulfoxonium Methylide

CARL KAISER, BARRY M. TROST, JAMES BEESON, AND JOSEPH WEINSTOCK

Research and Development Division, Smith Kline and French Laboratories, Philadelphia, Pennsylvania

Received May 24, 1965

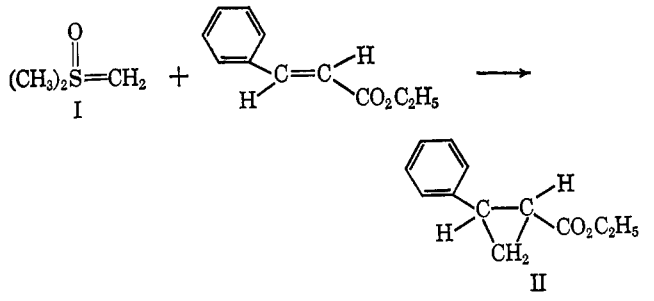
The *trans* isomer of 2-phenylcyclopropanecarboxylic acid is an intermediate for the synthesis of *trans*-2-phenylcyclopropylamine,[1] a potent inhibitor of monoamine oxidase used clinically as an antidepressant agent. In the original synthesis of this acid by the reaction of ethyl diazoacetate with styrene followed by hydrolysis of the resulting ester, a mixture of *cis* and *trans* acids is obtained[2] from which the latter isomer

(1) Tranylcypromine, Parnate®.

(2) A. Burger and W. L. Yost, *J. Am. Chem. Soc.*, **70**, 2198 (1948).

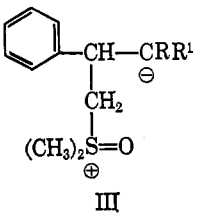
must be separated. In an attempt to find a more convenient and more stereoselective route to the *trans* acid, we investigated the reaction of dimethylsulfoxonium methylide (I)[3] with esters of cinnamic acid and related compounds. In this paper we report the results of this study and also describe the formation of a few stable sulfoxonium ylides observed in the course of exploring the reaction of I with other types of unsaturated compounds.

Reaction of I with ethyl *trans*-cinnamate[4] proceeded stereoselectively to give ethyl 2-phenylcyclopropanecarboxylate (II), consisting of 98.9% of the *trans* isomer. The yield, however, was only 31%. On the assumption that the poor yield of II might be due to a side reaction of I with the carbonyl group of ethyl



cinnamate, we also studied the reaction of I with sterically hindered esters of cinnamic acid in which this side reaction would not readily occur. Use of *t*-butyl[5] and 2-pentyl cinnamate did, in fact, result in higher yields (65–69%) of the corresponding cyclopropanecarboxylic acid esters. In these cases, also, *trans* esters were obtained. In order to determine whether some of the *cis*, as well as *trans*, ester is initially formed in these reactions and then epimerized to the *trans* isomer under the basic reaction conditions, the effect of I upon a mixture of ethyl *cis*- and *trans*-2-phenylcyclopropanecarboxylates was studied. Such an epimerization apparently does not occur as the percentage of *cis* ester was increased and that of the *trans* ester was decreased in the mixture which was recovered to the extent of only 47%. This result suggests a preferential reaction of I with the carbonyl group of the *trans* ester. Reaction of ylides with carbethoxy groups has been reported previously.[4]

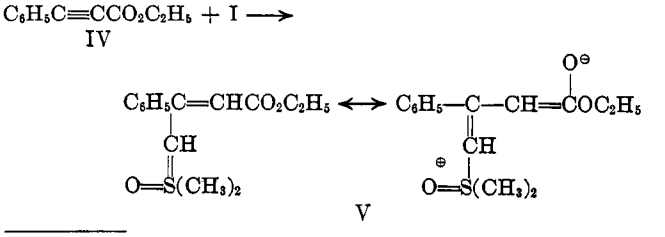
In common with the cinnamic esters, *trans*-N,N-dimethylcinnamamide reacted stereoselectively with the methylide I to yield only *trans*-N,N-dimethyl-2-phenylcyclopropanecarboxamide. In contrast, reaction of *trans*-cinnamonitrile with I gave 47% of a mixture of isomeric 2-phenylcyclopropanecarbonitriles consisting of 78% of the *trans* and 21% of the *cis* isomer.[6] Perhaps the stereochemical course of the reaction depends to a large extent upon the degree of interaction of the α substituents with the β-phenyl group in the intermediate (III) leading to cyclopropane ring formation. When the α substituent is small, *e.g.*, the cyano group, an appreciable amount of *cis*-cyclopropane derivative is formed, but when the α substituent is a bulky ester or amide group, the product is almost entirely the *trans* isomer. Consistent with this idea is the fact that no cyclopropane derivative was obtained from the reaction of ethyl α-methylcinnamate with I. Unreacted olefinic ester (12%) was the only water-insoluble material isolated in this ex-



periment. Perhaps severe steric interaction in the transition state (III, R = CH_3, R^1 = $CO_2C_2H_5$) prevented cyclization to a cyclopropane ring and allowed reversal of the ylide addition. The reaction of dimethylsulfoxonium methylide (I) with diethyl benzalmalonate, on the other hand, afforded 60% of diethyl 2-phenylcyclopropane-1,1-dicarboxylate. Apparently in this case the added stability provided to the intermediate anion (III, R = R^1 = $CO_2C_2H_5$) by the two ester groups compensated for the added bulk and permitted cyclization to a cyclopropane in preference to ylide elimination. Similarly, diethyl 3,4-dimethoxybenzalmalonate and I produced a cyclopropane derivative in 81% yield. Hydrolysis of this cyclopropane 1,1-diester followed by thermal decarboxylation, however, did not give a cyclopropanecarboxylic acid. γ-(3,4-Dimethoxyphenyl)-γ-butyrolactone was obtained almost quantitatively. Lactone formation also has been reported[7] to occur during pyrolysis of cyclopropane-1,1-dicarboxylic acid.

Attempted synthesis of 2-phenylcyclopropylpiperidine from I and styrylpiperidine was unsuccessful as the olefin was recovered quantitatively. Reaction of I with β-nitrostyrene likewise failed to produce a cyclopropane derivative. In this case an amorphous polymeric solid resulted.

The reaction of dimethylsulfoxonium methylide (I) with an acetylenic derivative, ethyl phenylpropiolate (IV), was investigated in an attempt to obtain ethyl 2-phenylcyclopropenecarboxylate. A crystalline product resulted. This material analyzed as an addition product of I and IV. The n.m.r. spectrum showed absorption at 1.27 (triplet) and 4.17 (quartet) p.p.m. (ethyl ester), a singlet at 2.96 p.p.m. (two methyl groups), single peaks at 4.78 and 6.28 p.p.m. assignable to hydrogens on a double bond, and a phenyl absorption at 7.43 p.p.m. The infrared (carbonyl at 6.0 μ) and ultraviolet [λ_{max}^{EtOH} 346, 270, and 229 mμ (ϵ 1.61 $\times$ 10^4, 6.70 $\times$ 10^3, and 7.78 $\times$ 10^3)] spectra were indicative of a highly conjugated system. On the basis of these data the resonance-stabilized ylide structure V



(3) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84**, 867 (1962).
(4) E. J. Corey and M. Chaykovsky, *Tetrahedron Letters*, 169 (1963).
(5) B. Abramovitch, J. C. Shivers, B. E. Hudson, and C. R. Hauser, *J. Am. Chem. Soc.*, **65**, 986 (1943).
(6) H. König and H. Metzger [*Z. Naturforsch.*, **18**, 976 (1963)] have also reported the formation of an isomeric mixture of 2-phenylcyclopropanecarbonitriles from cinnamonitrile and dimethylsulfoxonium methylide.
(7) G. H. Jeffery and A. I. Vogel, *J. Chem. Soc.*, 1804 (1948).

was assigned. Formation of dimethylsulfoxonium 3-ethoxycarbonyl-2-phenylallylide (V) may involve addition of I to the triple bond of IV followed by a proton transfer from the resulting methylene group to the anionic center concurrently formed adjacent to the ester.

As no stable, isolable sulfoxonium ylides had been reported at the time of this investigation, several other types were prepared in order to establish more firmly the structure of V and to explore further the chemistry of carbonyl conjugated sulfoxonium ylides. Reaction of I with phenyl isocyanate gave VI.[8] The structure of dimethylsulfoxonium N-phenylcarbamoylmethylide (VI) was indicated by elemental analyses, the presence

$$C_6H_5NCO + I \longrightarrow C_6H_5NHCOCH{=}\overset{\overset{O}{\|}}{S}(CH_3)_2 \xrightarrow[\Delta]{C_6H_5NHNH_2} C_6H_5NHCONHNHC_6H_5$$

VI VII

of amide absorption peaks at 6.14 and 6.28 μ in the infrared spectrum, and an ultraviolet maximum (EtOH) at 248 mμ (ϵ 3.79 $\times$ 10^4). In addition, Raney nickel desulfurization gave acetanilide, and phenylhydrazine displaced I from VI to give 1,4-diphenylsemicarbazide (VII).

Several attempts to alkylate the ylide VI apparently resulted in a similar displacement of I. Thus, the only product isolated upon treatment of VI with methyl iodide in dimethyl sulfoxide was 1,3-diphenylurea, and upon heating VI with styrene oxide only the ylide VIII was isolated. In the latter case thermal reversal

$$C_6H_5NHCOC(\overset{\overset{O}{\|}}{(CH_3)_2S}{=}O)CONHC_6H_5$$

VIII

$$(C_6H_5)_2CHC(=O)-\overset{\ominus}{C}H-\overset{\overset{O}{\|}}{S}(CH_3)_2 \oplus \longleftrightarrow (C_6H_5)_2CHC(-O^{\ominus})=CH-\overset{\oplus}{S}(CH_3)_2=O$$

IX

of the formation of VI may have produced phenyl isocyanate which reacted with another molecule of VI to give the more stable ylide VIII.

Reaction of dimethylsulfoxonium methylide (I) with diphenylketene was also investigated briefly. The product, dimethylsulfoxonium diphenylacetylmethylide (IX),[8] was identified by its elemental analysis, as well as its infrared and n.m.r. spectra. The n.m.r. spectrum showed an unsplit methyl peak at 3.42 p.p.m., single protons at 4.47 and 4.93 p.p.m., and an aromatic signal at 7.41 p.p.m. In the infrared, carbonyl absorption occurred at the abnormally high wave length of 6.45 μ which seems more consistent with the enolate-like resonance species IX than an ordinary conjugated carbonyl. Further evidence for structure IX was obtained by Raney nickel desulfurization to 1,1-diphenylacetone.

Experimental Section[9]

General Procedure. Synthesis of Cyclopropanes and Sulfoxonium Ylides from Dimethylsulfoxonium Methylide.[3]—To a stirred suspension of 0.11 mole of trimethylsulfoxonium iodide[10] in 100 ml. of dimethyl sulfoxide, which was held at 25–30° by occasional cooling, was added under nitrogen, in portions, 0.11 mole of a dispersion of sodium hydride in mineral oil. Upon completion of hydrogen evolution (*ca.* 30 min.) a solution of 0.1 mole of reagent (olefin, acetylene, isocyanate, or ketene derivative) in 50 ml. of dimethyl sulfoxide was added dropwise so that the temperature did not exceed 35°. The resulting solution (or mixture) was stirred at 25–30° for 30 min. and at 55–60° for 1 hr., then it was poured into 750 ml. of water. Stable crystalline sulfoxonium ylides (V, VI, VIII, and IX) were filtered and recrystallized. Liquid cyclopropanes were extracted into ether and the ethereal extracts were dried and concentrated. Petroleum ether (b.p. 30–60°) insoluble residues (this step was omitted for products soluble in petroleum ether) were dissolved in a small volume of acetonitrile and the mixture was extracted several times with petroleum ether to remove mineral oil. Products were isolated by concentration of the acetonitrile solution and distillation. Descriptive and analytical data for cyclopropanes and stable sulfoxonium ylides prepared by this procedure are outlined in Tables I and II.

β-Nitrostyrene, when subjected to this reaction, gave a yellow amorphous solid. The melting point and infrared spectrum of this solid were indefinite. No reaction occurred with styrylpiperidine[11] which was recovered quantitatively. With ethyl α-methylcinnamate only 12% of unreacted olefin was recovered (the water-soluble product was not isolated).

An isomeric mixture of ethyl *cis*- and *trans*-2-phenylcyclopropanecarboxylates,[2] consisting of 30.5% of *cis*- and 65.2% of *trans* isomer (v.p.c. analysis), when subjected to this general procedure, gave 47% of an ester mixture consisting of 48.6% (v.p.c. analysis) of each of the isomeric esters.

γ-(3,4-Dimethoxyphenyl)-γ-butyrolactone. From Diethyl 2-(3,4-Dimethoxyphenyl)cyclopropane-1,1-dicarboxylate.—Hydrolysis of 6.5 g. (0.02 mole) of diethyl 2-(3,4-dimethoxyphenyl)cyclopropane-1,1-dicarboxylate with excess aqueous–ethanolic potassium hydroxide gave 5.2 g. of a white crystalline acid, m.p. 94–95° dec. after recrystallization from hexane. This acid was heated at 160–180° until gas evolution was completed. Recrystallization of the residue from ethyl acetate–hexane gave 4.2 g. (95%) of colorless crystals, m.p. 117–120°. The infrared spectrum showed a carbonyl absorption at 5.6 μ (γ-lactone). A melting point of 120–121° has been reported[12] for γ-(3,4-dimethyoxyphenyl)butyrolactone.

Anal. Calcd. for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 64.80; H, 6.43.

Raney Nickel Desulfurization of VI.—A mixture of 2.1 g. (0.01 mole) of VI, 8 g. of Raney nickel, and 100 ml. of ethanol was refluxed for 5 hr. The mixture was filtered and the filtrate was concentrated to 50 ml. After dilution with water, 0.2 g. of crystals, m.p. 201–202° after recrystallization from water, probably N,N′-diphenylsuccinamide, was collected.

Anal. Calcd. for $C_{16}H_{16}N_2O_2$: C, 71.63; H, 6.01. Found: C, 72.13; H, 5.87.

Concentration of the mother liquor gave 0.95 g. (70.4%) of colorless crystals, m.p. 113–114° after recrystallization from ethanol. A mixture melting point with authentic acetanilide was not depressed.

Reaction of VI with Phenylhydrazine.—A solution of 1.05 g. (0.005 mole) of VI, 0.54 g. (0.005 mole) of phenylhydrazine, and 25 ml. of dimethylformamide was heated at 100° for 30 min. and refluxed for 10 min. Dilution with water and cooling afforded 0.65 g. (57%) of pale yellow crystals, m.p. 172–173° after recrystallization from ethanol. These crystals were identical (infrared spectrum, mixture melting point) with authentic 1,4-diphenylsemicarbazide.[13]

(8) This same product was recently reported by H. König and H. Metzger, *Tetrahedron Letters*, **No. 40**, 3003 (1964).

(9) Boiling and melting points are uncorrected. Infrared spectra were determined on a Perkin-Elmer Infracord, the n.m.r. spectra on a Varian A-60 spectrometer, and ultraviolet spectra on a Cary Model 14 spectrophotometer. Spectral analyses were performed by Dr. Walter E. Thompson and Mr. Richard J .Warren, gas phase chromatographic analyses by Mr. James W. Lockard, and microanalyses by Miss Margaret Carroll and coworkers of the Analytical and Physical Chemistry Section, Smith Kline and French Laboratories.

(10) R. Kuhn and H. Trischmann, *Ann.*, **611**, 117 (1958).

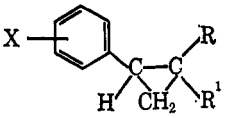
(11) C. Mannich and D. Davidsen, *Ber.*, **B69**, 2106 (1936).

(12) J. J. Trivedi and K. S. Nargund, *J. Univ. Bombay*, **10**, 99 (1941); *Chem. Abstr.*, **36**, 3801 (1942).

(13) M. Busch, *Ber.*, **42**, 4596 (1909).

TABLE I

DESCRIPTIVE AND ANALYTICAL DATA FOR CYCLOPROPANE DERIVATIVES



X	R	R^1	Yield, %	B.p., °C. (mm.)	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
H	H	$CO_2C_2H_5$	31	93–94 (0.1)[a]					
H	H	$CO_2C(CH_3)_3$	65	118–121 (0.7)[b]	$C_{14}H_{18}O_2$	77.03	76.81	8.31	8.25
H	H	$CO_2CH(CH_3)(CH_2)_2CH_3$	69	115 (0.05)[c]					
3,4-$(OCH_3)_2$	H	$CO_2C_2H_5$	29.5	143–146 (0.5)[d]	$C_{14}H_{18}O_4$	67.18	67.20	7.25	7.21
H	$CO_2C_2H_5$	$CO_2C_2H_5$	59.5	141–145 (0.7)	$C_{15}H_{18}O_4$	68.68	68.75	6.92	6.80
3,4-$(OCH_3)_2$	$CO_2C_2H_5$	$CO_2C_2H_5$	81	180–181 (0.3)	$C_{17}H_{22}O_6$	63.34	63.49	6.88	6.64
H	H	CN[e]	47.5	158–160 (30)[f]	$C_{10}H_9N$	83.88	83.81	6.34	6.40
H	H	$CON(CH_3)_2$	39	110 (0.01)[g]	$C_{12}H_{15}NO$	76.16	76.12	7.99	7.97

[a] Gas phase chromatographic analysis of this ester gave a main peak corresponding to 98.9% of the total area. On standing the liquid crystallized to give colorless needles, m.p. 35–36°. M. Julia, S. Julia, and B. Bémont [*Bull. soc. chim. France*, 304 (1960)] report m.p. 38–39°,[3] b.p. 105–106° (0.2 mm.). [b] $n^{23}D$ 1.5036; v.p.c. analysis gave a main peak corresponding to 93.4% of the total area. [c] Hydrolysis of this ester with excess aqueous–ethanolic sodium hydroxide gave 57% of an acid, m.p. 85–87°. The infared spectrum of this acid was identical with an authentic sample of *trans*-2-phenylcyclopropanecarboxylic acid.[3] V.p.c. analysis of the ester showed the presence of 5.5% of 2-pentyl cinnamate, 93.4% of the *trans* cyclopropane ester, and 0.9% of the *cis* cyclopropane ester. [d] Crystallized upon standing, m.p. 45–47° from hexane. Hydrolysis of this ester with aqueous–ethanolic potassium hydroxide gave 92% of *trans*-2-(3,4-dimethoxyphenyl)cyclopropanecarboxylic acid, m.p. 105–107°. A. Burger and G. T. Fitchett [*J. Am. Chem. Soc.*, **74**, 3415 (1952)] report m.p. 105–105.5°. [e] V.p.c. indicated two major products corresponding to 78.2 and 21.1% of the total area. Hydrolysis of this mixture with excess aqueous–ethanolic potassium hydroxide gave colorless crystals, m.p. 75–82°, which were recrystallized from water[3] to give 53% of *trans*-2-phenylcyclopropanecarboxylic acid, m.p. 92–94° (lit.[3] m.p. 93°), and 7% of the *cis* acid, m.p. 105–107° (lit.[3] m.p. 106–107°). [f] R. J. Mohrbacher and N. H. Cromwell [*J. Am. Chem. Soc.*, **79**, 401 (1957)] report b.p. 102° (1.4 mm.) for the *trans* isomer. [g] Thin layer chromatography on a silica gel G–sodium bicarbonate mixture using 85% chloroform–15% acetone as developer showed as the only product a major spot at R_f 0.75 which did fluoresce under ultraviolet light and which turned pink-orange upon treatment with a sodium dichromate in sulfuric acid spray followed by heat. An authentic sample of *trans*-N,N-dimethyl-2-phenylcyclopropanecarboxamide prepared from the acid chloride[3] and dimethylamine had the same chromatographic properties, boiling point, and infrared spectrum.

TABLE II

DESCRIPTIVE AND ANALYTICAL DATA FOR SULFOXONIUM YLIDES

Structure	Yield, %	Recrystn. solvent	M.p., °C.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
V	71	Chloroform–hexane	131.5–132.5	$C_{14}H_{18}O_3S$	63.13	63.38	6.81	6.60
VI	68	Chloroform–hexane	180–181	$C_{10}H_{13}NO_2S$	56.85	56.64	6.20	6.30
VIII	9	Ethanol	176–177	$C_{17}H_{18}N_2OS_3$[a]	61.81	61.75	5.45	5.40
IX	13	Toluene	160–161.5	$C_{17}H_{18}O_2S$	71.30	71.53	6.34	6.33

[a] *Anal.* Calcd.: N, 8.48. Found: N, 8.54.

Attempted Reaction of VI with Methyl Iodide.—A solution of 2 g. (0.01 mole) of VI, 2.13 g. (0.015 mole) of methyl iodide, and 50 ml. of dimethyl sulfoxide was allowed to stand at 25° for 16 hr., then it was poured onto crushed ice. The precipitated solid (0.3 g., 32%) melted at 238–239° after recrystallization from ethanol. The infrared spectrum of this material was identical with that of an authentic sample of 1,3-diphenylurea.

Attempted Reaction of VI with Styrene Oxide.—A suspension of 2.0 g. (0.01 mole) of VI, 2.4 g. of styrene oxide, and 50 ml. of toluene was refluxed for 24 hr. The hot mixture was filtered. Upon cooling, the filtrate deposited 0.14 g. of VI. Concentration of the filtrate gave an oil which crystallized slowly. Trituration with ether followed by recrystallization from ethanol gave 0.15 g. of VIII, whose properties are recorded in Table II.

Raney Nickel Desulfurization of IX.—Treatment of 0.3 g. of IX with Raney nickel in refluxing ethanol for 4 hr. gave 0.2 g. (91%) of colorless crystals with an infrared spectrum identical with that of an authentic sample of 1,1-diphenylacetone.

Acknowledgment.—We wish to thank Dr. Charles L. Zirkle of these laboratories for his kind interest and helpful suggestions concerning this work.

The Mechanism of the Alkaline Hydrolysis of *p*-Nitrophenyl N-Methylcarbamate[1]

MYRON L. BENDER AND R. B. HOMER

Department of Chemistry, Northwestern University, Evanston, Illinois 60201

Received June 8, 1965

The usual mechanism of the alkaline hydrolysis of an ester involving acyl–oxygen fission is a two-step process involving the addition of hydroxide ion to the carbonyl group of the ester to form a tetrahedral intermediate, followed by the decomposition of this intermediate to give products.[2] This mechanism can be and has been distinguished from a direct displace-

(1) This research was supported by a grant from the National Science Foundation.

(2) M. L. Bender, *Chem. Rev.*, **60**, 53 (1960).