19643-37-9; 1,4-diiodo-7-thiabicyclo[2.2.1]heptane 7,7-dioxide, 19643-38-0; 7-thiabicyclo[2.2.1]heptane-1-carboxylic acid 7,7-dioxide, 19643-39-1; 1-deuterio-7-thiabicyclo[2.2.1]heptane 7,7-dioxide, 19643-40-4.

Acknowledgment.—We are indebted to the National Institutes of Health and the National Science Foundation for Predoctoral Fellowships to E. Block, 1962–1967.

The Chemistry of Ylides. XIX. β-Carbonyl Sulfonium Ylides[1]

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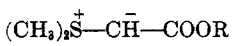
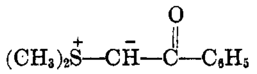
The preparation, isolation, and physical and chemical properties of dimethylphenacylidenesulfurane (II) and dimethyl(carbomethoxymethylene)sulfurane (Ia) are described. Both ylides exhibit decreased nucleophilicity and basicity as a result of the delocalization of the carbanion electrons through the carbonyl groups, the decrease being larger for II. Spectroscopic methods and chemical reactions (alkylation, acylation, and reaction with carbonyl compounds and nitrosobenzene) served to illustrate the differences. The mechanism of the thermal decomposition of sulfonium ylides to cyclopropanes appears to involve a carbenic moiety.

This paper reports the details of our work on a group of stabilized, isolable sulfonium ylides, the β-carbonyl ylides Ia and II, part of the results having been reported in a preliminary communication.[3] At the time this work was undertaken no carboalkoxy sulfonium ylides or β-keto sulfonium ylides were known. In fact, very few isolable sulfonium ylides had been prepared or studied, most of the chemistry of sulfonium ylides having been elaborated utilizing complex solutions of the ylides.[4] We feel it is important actually to isolate and characterize ylides to describe accurately their properties and behavior.



$(CH_3)_2\overset{+}{S}—\overset{-}{C}H—COOR$

Ia, $R = CH_3$
b, $R = C_2H_5$



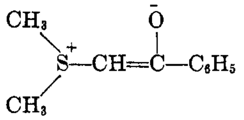
$(CH_3)_2\overset{+}{S}—\overset{-}{C}H—\overset{\overset{O}{\|}}{C}—C_6H_5$

II

Since our preliminary report on the chemistry of the phenacylide II, several groups[5,6] have reported the results of their similar studies. Nozaki, *et al.*,[7] have studied the related S-methyl-S-phenylphenacylide. Several groups[5,8–11] have reported on the chemistry of Ib while Casanova and Rutolo[12] recently reported on the properties of Ia.

Dimethylphenacylidenesulfurane (II).—The crystalline ylide II was prepared from dimethylphenacylsulfonium bromide in ethanol solution by proton abstraction with triethylamine. The anhydrous ylide, mp 67–68°, was converted into a hydrate of mp 57–58° upon standing exposed to the atmosphere or upon standing in a solvent to which a few drops of water had been added. Payne,[13] Trost,[6] and Ratts[5a] all have reported similar behavior for II. The water was detectable in the nuclear magnetic resonance (nmr) spectrum (δ 3.38) and the infrared (ir) spectrum (3260 cm^{-1}).

The ylide II could be converted into the starting sulfonium salt (ylide conjugate acid) upon treatment with hydrogen bromide. The sulfonium salt showed a pK_a of 7.68 in 95% ethanol solution.[14] Nmr studies showed the methyl groups of the ylide (δ 2.92) to be more highly shielded than those of the conjugate acid (3.05). In addition, the methine proton of II (δ 4.31), as expected, appeared at higher field than the methylene protons of the ylide conjugate acid (5.74). The carbonyl group of the ylide conjugate acid absorbed at 1665 cm^{-1} in the ir while that of the ylide II absorbed at 1508 cm^{-1}, indicating considerable enolate character for the ylide (*i.e.*, considerable contribution of structure III). The stability of the phenacylide undoubtedly is largely due to the delocalization provided the carbanion by the adjacent carbonyl group. X-Ray crystallographic studies of the analogous phosphonium phenacylides have provided significant evidence to this effect.[15] The broadened methine peak at δ 4.31 indicates the contribution of the two geometric isomers of III.[6a, 16]



III

The shielding effects of various carbon and sulfur substituents for a series of sulfonium ylides are presented in Table I. Interestingly, the nmr spectra of the closely related phenacylides $(CH_3)(C_6H_5)S=CHCOC_6H_5$ and $(C_6H_5)_2S=CHCOC_6H_5$ revealed that the presence of one or two phenyl groups on sulfur had the effect of deshielding both the methine protons (δ 4.55 and 4.75, respectively) and the remaining methyl

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[1] For part XVIII in this series, see A. W. Johnson and H. L. Jones, *J. Amer. Chem. Soc.*, **90**, 5232 (1968).

[2] Author to whom inquiries should be directed at the University of North Dakota.

[3] A. W. Johnson and R. T. Amel, *Tetrahedron Lett.*, 819 (1966).

[4] A. W. Johnson, "Ylid Chemistry," Academic Press, New York, N. Y., 1966, pp 310–344.

[5] (a) K. W. Ratts and A. N. Yao, *J. Org. Chem.*, **31**, 1185 (1966); (b) *ibid.*, **31**, 1689 (1966).

[6] (a) B. M. Trost, *J. Amer. Chem. Soc.*, **88**, 1587 (1966); (b) *ibid.*, **89**, 138 (1967).

[7] (a) H. Nozaki, K. Kondo, and M. Takaku, *Tetrahedron Lett.*, 251 (1965); (b) *Tetrahedron*, **22**, 2145 (1966).

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[9] K. W. Ratts and A. N. Yao, *J. Org. Chem.*, **33**, 70 (1968).

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[11] H. Nozaki, D. Tunemoto, S. Matubara, and K. Kondo, *Tetrahedron*, **23**, 545 (1967).

[12] J. Casanova and D. A. Rutolo, *Chem. Comm.*, 1224 (1967).

[13] G. B. Payne, private communication.

[14] A. W. Johnson and R. T. Amel, *Can. J. Chem.*, **46**, 461 (1968).

[15] (a) F. S. Stephens, *J. Chem. Soc.*, 5640 (1956); (b) A. J. Speziale and K. W. Ratts, *J. Amer. Chem. Soc.*, **87**, 5603 (1965).

[16] F. J. Randall and A. W. Johnson, *Tetrahedron Lett.*, 2841 (1968).

TABLE I

NMR SPECTRA OF SULFONIUM SALTS AND YLIDES

Compound	Solvent[a]	δ_{CH_3S}[b]	$\delta_{CH\ or\ CH_2}$
$(CH_3)_2S^+$—$CH_2COC_6H_5$ (**1**)	B	3.05	5.74
$(C_4H_9)_2S^+$—$CH_2COC_6H_5$ (**2**)	B		5.90
$(CH_3)(C_6H_5)S^+$—$CH_2COC_6H_5$ (**3**)	B	3.42	5.92
$(C_6H_5)_2S^+$—$CH_2COC_6H_5$ (**4**)	B		6.65
$(CH_3)_2S^+$—CH_2COOCH_3 (**5**)	C	3.16	4.48
$(CH_3)_2S{=}CHCOC_6H_5$ (**6**)	A	2.92	4.31
$(CH_3)(C_6H_5)S{=}CHCOC_6H_5$ (**7**)	A	3.10	4.55
$(C_6H_5)_2S{=}CHCOC_6H_5$ (**8**)	A		4.75
$(CH_3)_2S{=}C(COC_6H_5)_2$ (**9**)	A	3.07	
$(CH_3)_2S{=}CHCOOCH_3$ (**10**)	A	2.78	2.87
$(CH_3)_2S{=}C(COC_6H_5)(COOCH_3)$ (**11**)	A	2.86	

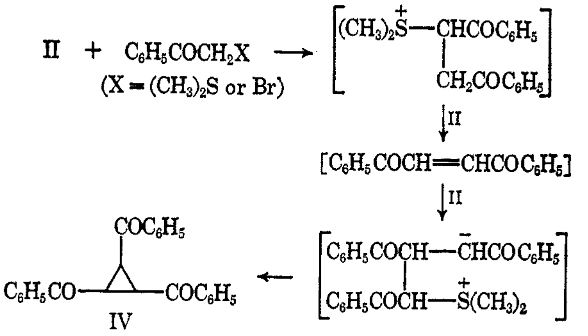
[a] A, $CDCl_3$; B, $(CD_3)_2SO$; C, trifluoroacetic acid. [b] δ, parts per million downfield from tetramethylsilane.

protons (3.10), all relative to the absorptions for II. The same effect was observed for the respective ylide conjugate acids. We interpret these observations as being due to the inductive electron withdrawal by phenyl relative to methyl. This is additional evidence for our generalization[14] that, when attached to an onium atom (sulfonium, phosphonium, arsonium), the inductive withdrawal effect more than counterbalances any conjugative donation effect of a phenyl group. It supports previous evidence based on basicity studies and our recent ^{19}F nmr evidence.[1]

Although stable in the atmosphere at room temperature, the phenacylide II was found to be subject to thermal decomposition. Heating the pure ylide in tetrahydrofuran solution afforded a 47% yield of *trans*-1,2,3-tribenzoylcyclopropane (IV). The same product could be obtained in nearly quantitative yield by treating the ylide II with either its conjugate acid (dimethylphenacylsulfonium bromide) or with phenacyl bromide. Trost[6] has reported the conversion of II into IV using ultraviolet (uv) irradiation or cupric sulfate catalyst. Much earlier, Krollpfeiffer[17] reported the conversion of the conjugate acid of II into IV by treatment with aqueous base.

The alkylation–elimination route from II to IV is proposed to proceed as shown in Scheme I. Each of the individual steps proposed has adequate analogy. The first step, the alkylation, was demonstrated in this work (see below) and is well known for phosphonium ylides. The E2 elimination of methyl sulfide also is known, although all attempts to isolate dibenzoylethylene from this reaction have failed, indicating that its consumption is more rapid than its formation. The Michael-type addition of an ylide to an α,β-unsaturated ketone has been widely explored with phosphonium ylides[18] and the specific reaction shown has been effected by Trost[6] and Nozaki, *et al.*,[7] in very high yield.

SCHEME I

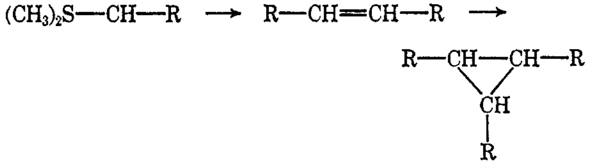


Trost[6] has proposed that photolytic decomposition of the phenacylide II proceeded *via* the generation of a carbene, the latter being trapped by the phenacylide to form dibenzoylethylene, which then was converted into IV as shown in Scheme I. The conversion of dibenzoylethylene into IV probably does not occur *via* carbene attack on the olefin owing to the reduced nucleophilicity of the latter.[19] Carrying out the reaction in cyclohexene, however, Trost was able to isolate benzoylnorcarane, presumably the result of trapping the carbene with the more nucleophilic cyclohexene.

We also were able to carry out the photochemical conversion of the phenacylide II into IV. Furthermore, we were able to trap the carbene intermediate with dimethylbenzylamine to afford, initially, an ammonium ylide (V) which underwent a Steven's rearrangement[20] to the amine (VI). An authentic sample of the ylide V was prepared from its conjugate acid (VII) and was found to afford the amine VI (Scheme II). Ratts and Yao[5b] had reported the trapping of the carbene from the analogous *p*-nitrophenacylide using triphenylphosphine, isolating the corresponding phosphonium ylide. We were unable to trap the benzoylcarbene with triphenylphosphine.

We proposed[3] that the thermal decomposition of the phenacylide II reported herein proceeds by way of a carbenoid pathway shown in Scheme III. Our observation does appear to be a bona fide thermal decomposition and not an alkylation–elimination reaction as counterproposed by Trost.[6b] Water, the presence of which might permit the formation of the conjugate acid and potential alkylating agent, dimethylphenacylsulfonium hydroxide, was demonstrated to be absent by nmr and ir spectroscopy. Furthermore, intentional addition of a small amount of water to the thermal decomposition reaction mixture had no effect on the course of the reaction. No sulfonium salt could be detected.

Previously, we had reported[21] that diphenylsulfonium benzylide thermally decomposed to stilbene. Further work[22] has shown the same decomposition to occur with dimethylsulfonium benzylide and dimethylsulfonium *p*-nitrobenzylide. A carbenoid pathway also has been proposed for these cases. Accordingly, the nature of the substituents on the ylidic carbon seems to control whether the thermal decomposition proceeds only to the olefin stage (as for the benzylides) or on to the cyclopropane stage (as for the phenacylides) (eq 1). We



(1)

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(17) F. Krollpfeiffer and H. Hartmann, *Chem. Ber.*, **83**, 90 (1950).

(18) Reference 4, pp 116–120, 336–338.

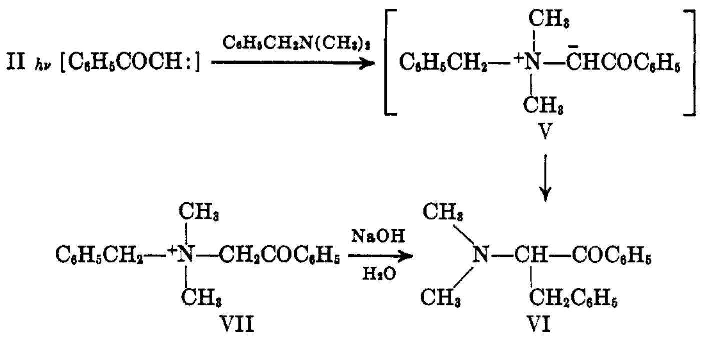
(19) F. Serratosa and J. Quintana, *Tetrahedron Lett.*, 2245 (1967).

(20) T. S. Stevens, E. M. Creighton, A. B. Gordon, and M. MacNicol, *J. Chem. Soc.*, 3193 (1928).

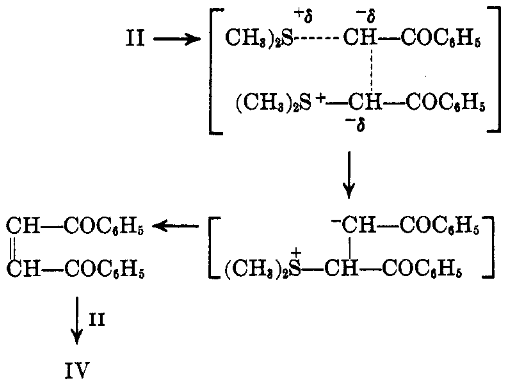
(21) A. W. Johnson, V. J. Hruby, and J. L. Williams, *J. Amer. Chem. Soc.*, **86**, 918 (1964).

(22) R. T. Amel, doctoral dissertation submitted in partial fulfillment of the degree requirements, University of Saskatchewan, Oct 1967.

SCHEME II

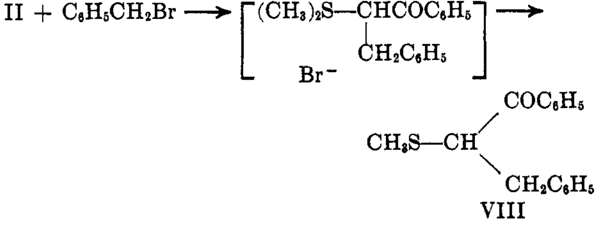


SCHEME III



have proposed that the ylide-to-olefin step involves a carbenoid mechanism where R = phenyl, *p*-nitrophenyl, or benzoyl (see Scheme III). The second step obviously must not be carbenoid but must involve nucleophilic attack of the ylide on the olefin. Such an attack (Michael addition) would be expected to proceed only where R is a group which provides significant stabilization for the carbanion intermediate (*e.g.*, a benzoyl group). Were the second step carbenoid, the cyclopropane would be expected to be obtained from stilbene (R = phenyl) but not from dibenzoylethylene (R = benzoyl) owing to the reduced nucleophilicity of the latter. The failure to obtain triphenylcyclopropane where R = phenyl implies that carbenoids are trapped by ylide before they could react with the stilbene, presumably owing to the greater nucleophilicity of the ylide.

The nucleophilicity of the phenacylide II was demonstrated by several reactions. The ylide was C alkylated with benzyl bromide although the product VIII was obtained only in 16% yield (eq 2). The sulfonium salt apparently was demethylated by the bromide ion. Ratts and Yao[6b] reported low yields in a similar methylation and also observed subsequent demethylation.

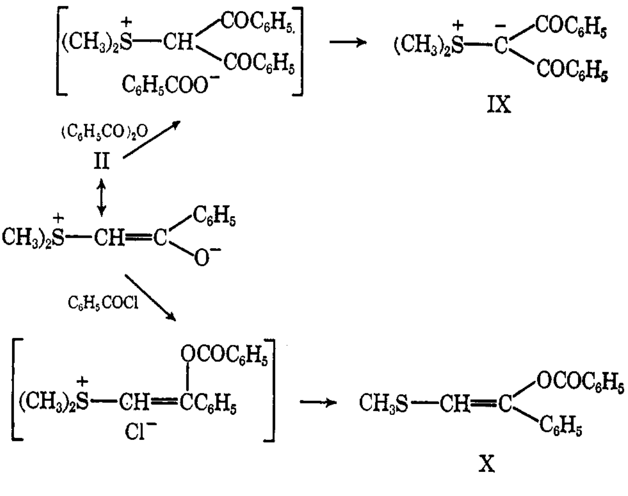


(2)

The course of the acylation of the phenacylide II varied with the nature of the acylating agent. Treatment with benzoic anhydride afforded the highly stabilized ylide, dimethyl(dibenzoylmethylene)sulfurane (IX), the result of a C acylation and proton abstraction. The new ylide (IX) was extremely nonbasic, exhibiting a pK_a of 0.79, and was hydrolyzable to dimethylphenacylsulfonium chloride and benzoic acid. Acylation of II with benzoyl chloride resulted in an O acylation, affording the enol benzoate (X) of α-methylmercaptoacetophenone. The structure was proven by its nmr spectrum (methyl singlet at δ 2.31, vinyl singlet at 6.47, and aromatic multiplet at 7.2–8.3, with an integrated area ratio of 3:1:10), its ir spectrum (ν_{CO} 1735 cm^{-1}), its elemental analysis, and an oxidative hydrolysis to methylphenacyl sulfone and benzoic acid. Nozaki, *et al.*,[7b] subsequently reported identical results.

The course of the acylation reaction is illustrated in Scheme IV. The pattern of O acylation and C acylation is identical with that reported by Chopard, *et al.*,[23] for triphenylphosphonium phenacylides and by Krohnke, *et al.*,[24] for pyridinium phenacylide. Carroll and O'Sullivan[25a] have reported that the monoanion of methylphenacyl sulfone also underwent O acylation with benzoyl chloride while Konig and Metzger[25b] found that phenacylidenedimethyloxysulfurane (prepared *in situ*) underwent C acylation with benzoyl

SCHEME IV



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[23] P. A. Chopard, R. J. G. Searle, and F. H. Devitt, *J. Org. Chem.*, **30**, 1015 (1965).

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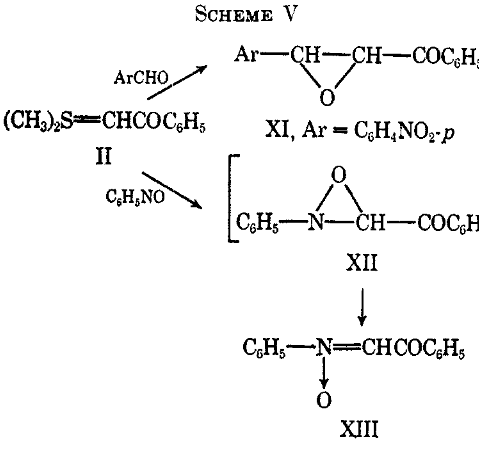
chloride. Because acylation with benzoyl chloride appears to be a kinetically controlled reaction[23] it may be argued that in the series of phenacylides shown in Chart I the extent of C or O acylation is reflective of the extent of delocalization of the carbanion by the two competing electron sinks attached, the vacant 3d orbitals of sulfur and the carbonyl group. The observations coincide with theoretical predictions,[26] the anion with the least $p\pi$–$d\pi$ stabilization having more enolate character and therefore undergoing O acylation. On this basis it could be predicted that the unknown acylation of the monoanion of methylphenacyl sulfoxide with benzoyl chloride would be an O acylation owing to the relatively insignificant $p\pi$–$d\pi$ overlap of the carbanion with sulfur.

CHART I

Phenacylides	Direction of ↓
$CH_3—SO_2C^-HCOC_6H_5$	1. increasing positive charge on sulfur
$(CH_3)_2S^+—C^-HCOC_6H_5$	2. increasing $p\pi$–$d\pi$ overlap
$(CH_3)_2S^+(O)—C^-HCOC_6H_5$	3. decreasing enolate character

One of the interests in sulfonium ylides stems from their reaction with carbonyl compounds to form epoxides, a reaction discovered by us ten years ago.[27] When the current work was undertaken only one stabilized ylide, the fluorenylide, had been found to react with carbonyls. Since then, Ratts and Yao[5b] reported the formation of a 1-carbamido-2-phenyloxirane from benzaldehyde and $(CH_3)_2S{=}CHCON(C_2H_5)_2$. We have now found that the phenacylide II reacts with *p*-nitrobenzaldehyde, although in low yield, to afford a known epoxide (XI). In addition, the phenacylide underwent a similar reaction with nitrosobenzene, presumably first forming the nonisolable oxazirane (XII)[28] which rearranged to the stable nitrone (XIII) (Scheme V). The latter gave the expected nmr spectrum (vinyl singlet at δ 8.37 and aryl multiplet at 7.2–8.0, area ratio of 1:10) and ir spectrum (ν_{CO} 1650 cm^{-1} ν_{NO} 1510 and 1310 cm^{-1}) and could be hydrolyzed with aqueous sodium hydroxide to mandelic acid.

SCHEME V



In its reactions the isolable phenacylide exhibited typical ylide characteristics although they were modified somewhat in degree and kind from the normal, mainly owing to the ambident character of the anionic portion of the ylide.

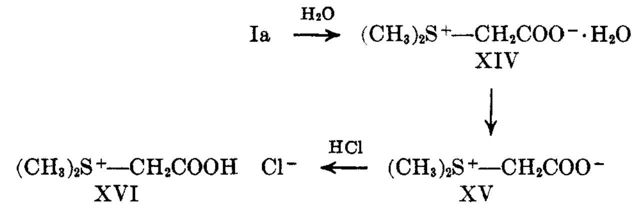
Dimethyl(carbomethoxymethylene)sulfurane (Ia).—The ester ylide (Ia) was prepared by proton abstraction with sodium hydride in tetrahydrofuran solution from dimethyl(carbomethoxymethyl)sulfonium bromide. The ylide was obtained as a clear, pale yellow viscous oil whose melting point was about 20°. Casanova and Rutolo[12] have since reported a melting point of 19–21°. The ylide was reconverted into its conjugate acid (the sulfonium salt) by treatment with aqueous acid.

The ylide showed carbonyl absorption in the ir region at 1620 cm^{-1}, typically shifted to longer wavelength compared with the absorption of the sulfonium salt (1735 cm^{-1}), owing to the adjacent carbanion. The nmr spectra of the ylide and its sulfonium salt precursor (see Table I) indicated that ylide formation led to an increased shielding of all protons α to the sulfur atom. The fact that the methine proton was more shielded than that of the phenacylide II testifies to the less extensive delocalization afforded the carbanion by the ester groups of Ia compared with the ketone group of II. The increase in shielding of the S-methyl group through conversion of the sulfonium salt to phenacylide II was 0.13 ppm while the increase in converting the sulfonium salt into the ester ylide Ia was 0.38 ppm. Apparently there is more $p\pi$–$d\pi$ overlap between a carbanion and sulfur in the ester ylide Ia than in the phenacylide II, as expected on structural grounds.

Casanova and Rutolo[12] have demonstrated and discussed the nmr evidence (two sets of parallel absorptions) for the contribution of two geometric forms of an enolate structure for the ester ylide Ia. The observations and conclusions are analogous to those made earlier for the corresponding phosphonium ylide.[29]

The ester ylide Ia decomposed slowly at room temperature either in solution or upon exposure to the atmosphere to afford dimethylthetin hydrate (XIV). The hydrate could be dehydrated to dimethylthetin (XV) and the latter could be converted into dimethylthetin chloride (XVI) (Scheme VI). These substances were identified by nmr and ir spectra and by comparison with authentic samples. The decomposition of the ylide Ia propably proceeded by conversion into the sulfonium hydroxide in the presence of water followed by hydrolysis of the ester group. This reaction interfered with many of our subsequent studies. Ratts and Yao[9] recently have reported the same decomposition.

SCHEME VI



We have been unable to obtain epoxides or any other recognizable products from the reaction of the ester ylide with *p*-nitrobenzaldehyde. Other workers also have been unable to cause ester ylides to react with

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(26) D. P. Craig and E. A. Magnusson, *J. Chem. Soc.*, 4895 (1956).

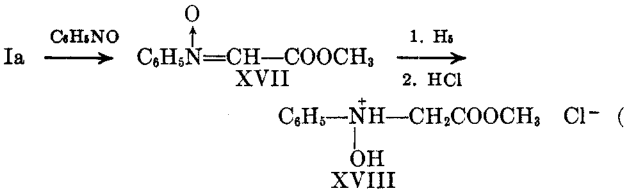
(27) A. W. Johnson and R. B. LaCount, *Chem. Ind.* (London), 1440 (1958); *J. Amer. Chem. Soc.*, **83**, 417 (1961).

(28) A. W. Johnson, *J. Org. Chem.*, **28**, 252 (1963).

(29) H. J. Bestmann, G. Joachim, I. Lengyel, S. F. M. Oth, J. Mereny, and J. Weitkamp, *Tetrahedron Lett.*, 3335 (1966).

carbonyl compounds. However, Speziale, *et al.*,[8] were able to cause Ib to react with a Schiff base, a reaction presumably proceeding *via* a three-membered ring (aziridine) intermediate and a mechanism analogous to epoxide formation. Furthermore, Ratts and Yao[5b] were able to obtain epoxides from the reaction of an amido ylide, $(CH_3)_2S{=}CHCON(C_2H_5)_2$, with aldehydes. The failure to observe an analogous reaction using the ester ylide Ia is difficult to explain, especially in view of its supposed increased nucleophilicity relative to the phenacylide II.

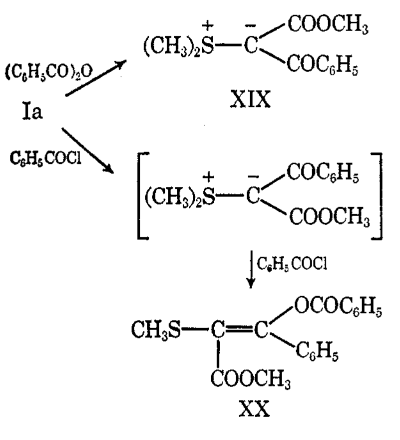
An attempt to obtain a nitrone from the reaction of Ia with nitrosobenzene led to somewhat inconclusive results. The expected nitrone (XVII) apparently was obtained but as a noncrystalline oil. Accordingly, the substance was hydrogenated over palladium on charcoal and a hydrochloride of mp 165–167°, presumably XVIII, was thereby obtained (eq 3). It showed ir absorption at 1750 cm^{-1} and nmr absorption at δ 3.70 (singlet), 4.11 (singlet), 6.9–7.5 (multiplet), and 9.90 (singlet) in a ratio of 3:1.9:5.2:2.5. Addition of a small amount of D_2O to the sample resulted in the disappearance of the δ 9.90 peak, indicating it was due to acidic protons. A comparison spectrum of N,N-dimethylhydroxylamine hydrochloride also showed absorption at very low field. However, we were unable to obtain a satisfactory elemental analysis for the presumed XVIII. Benzoylation of XVIII afforded a benzoate with nmr absorption at δ 3.75 (singlet), 4.61 (singlet), and 7.0–7.5 (multiplet) in a ratio of 2.8:2.0:10.3.



$$\mathrm{Ia} \xrightarrow{C_6H_5NO} \underset{\mathrm{XVII}}{C_6H_5\overset{\overset{O}{\uparrow}}{N}{=}CH{-}COOCH_3} \xrightarrow[2.\ HCl]{1.\ H_2} \underset{\mathrm{XVIII}}{C_6H_5{-}\underset{OH}{\overset{+}{N}}H{-}CH_2COOCH_3\ Cl^-} \quad (3)$$

The nucleophilicity of the ester ylide Ia was demonstrated by other reactions. Treatment with benzoic anhydride led to C acylation and the formation of a new ylide (XIX). The nmr spectrum [(δ 2.86 (singlet), 3.38 (singlet), and 7.0–7.4 (multiplet) in the ratio 5.9:3.0:5.1], ir spectrum (ν_{CO} 1675 and 1545 cm^{-1}), pK_a determination (1.06), and elemental analysis confirmed the assignment of structure. Acylation of Ia with a half-equivalent quantity of benzoyl chloride also afforded XIX but use of a full equivalent of benzoyl chloride produced the enol ester (XX) (Scheme VII). The nmr spectrum [δ 2.28 (singlet), 3.66 (singlet), and 7.2–8.3 (multiplet) in the ratio of 3:3:10.1], ir spectrum (ν_{CO} 1740 and 1720 cm^{-1}), and elemental analysis confirmed the assigned structure. In a separate experiment XIX was O acylated with benzoyl chloride to form XX. These observations provide striking evidence of the difference in the extent of delocalization of the carbanion electrons through the two α carbonyl groups. The complete absence of O acylation of the ester ylide Ia or any of its derivatives is consistent with the supposed larger carbon nucleophilicity and basicity, the larger amount of pπ–dπ overlap, and the larger shielding of protons on the S-methyl and ylide carbon groups, all for the ester ylide Ia when compared with the phenacylide II.

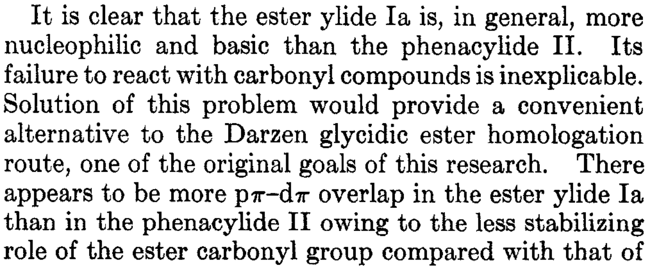
Scheme VII



The ester ylide Ia could be thermally decomposed in tetrahydrofuran solution in the presence of cupric sulfate to afford *trans*-1,2,3-tricarbomethoxycyclopropane (XXI). The same product was obtained upon photochemical decomposition but in very low yield. We were unable to trap any carbene (:CHCOOCH$_3$) that may have been formed although attempts were made using cyclohexene, triphenylphosphine, and dimethylbenzylamine. In most instances considerable dimethylthetin hydrate (XIV) was obtained along with the cyclopropane trimer (XXI).

Reaction of the ester ylide Ia with methyl bromoacetate or with the ylide conjugate acid afforded the trimer XXI. Presumably this reaction proceeded *via* an alkylation–elimination route similar to that illustrated for the phenacylide II in Scheme I. Additional evidence for this proposal was obtained by the observation that the ylide reacted with methyl maleate, probably *via* conjugate addition, to afford XXI in high yield (see Scheme VIII). This reaction more recently has been reported by Payne[10] and by Casanova and Rutolo.[12]

Scheme VIII



It is clear that the ester ylide Ia is, in general, more nucleophilic and basic than the phenacylide II. Its failure to react with carbonyl compounds is inexplicable. Solution of this problem would provide a convenient alternative to the Darzen glycidic ester homologation route, one of the original goals of this research. There appears to be more pπ–dπ overlap in the ester ylide Ia than in the phenacylide II owing to the less stabilizing role of the ester carbonyl group compared with that of the ketonic carbonyl group.

Experimental Section

General.—Melting points are uncorrected. Analyses were by Alfred Bernhardt Microanalytical Laboratory, Mülheim (Ruhr), Germany. Nmr spectra were recorded on Varian A-60 and A-60A spectrometers using tetramethylsilane (TMS) as an internal standard with chemical shifts reported as parts per million downfield from TMS. Vapor phase chromatographic analyses were carried out using an Aerograph 90-P-3 chromatograph with a column of Apiezon L on Chromosorb W. Areas were determined by planimetry. Photochemical reactions were effected using a Hanovia low pressure quartz lamp.

Phenacylidenedimethylsulfurane (II).—Stirring a mixture of 19.9 g (0.1 mol) of phenacyl bromide and 30 ml of methyl sulfide for 3 hr afforded, after washing with ether, 23.95 g (92%) of phenacyldimethylsulfonium bromide which recrystallized from ether–ethanol as colorless microcrystals, mp 139–140° (lit.[30] mp 145°), ν_{CO} 1680 cm^{-1}. The nmr spectrum in $(CD_3)_2SO$ showed a methyl singlet at δ 3.05 (area 6), a methylene singlet at 5.74 (area 2), and an aromatic multiplet at 7.6–8.2 (area 5.1). The pK_a, determined as previously described,[14] was 7.68.

Anal. Calcd for $C_{10}H_{13}OSBr$: C, 45.98; H, 5.03; S, 12.28; Br, 30.59. Found: C, 45.84; H, 4.98; S, 12.35; Br, 30.91.

To a solution of 2.61 g (10 mmol) of sulfonium salt in 50 ml of 95% ethanol stirring at 10° was added 2.8 ml (20 mmol) of triethylamine. After 2 hr the solution was quenched with water and extracted with chloroform. Evaporation of the chloroform and crystallization of the residual oil from benzene afforded ylide II of mp 57–58° in 79% yield (lit. mp 56–57,[5a] 55–57,[13] 57–59° [6a]): ν_{H_2O} 3260 cm^{-1}, ν_{CO} 1508 cm^{-1}; nmr absorption in $(CD_3)_2SO$ at δ 2.82 (methyl singlet, area 6.1), 4.43 (methinyl singlet, area 1.0), 7.2–8.0 (aromatic multiplet, area 5.0), and 3.38 (water). Extended drying in a vacuum system in the presence of P_2O_5 afforded an apparently anhydrous, but quite hygroscopic, sample of colorless ylide, mp 67–68° (lit. 78–79,[6b] 77–79° [13]), with nmr absorption in $CDCl_3$ solution at δ 2.92, 4.31, and 7.27–8.

Anal. Calcd for $C_{10}H_{12}OS$: C, 66.63; H, 6.71; S, 17.79. Found: C, 65.85; H, 6.64; S, 18.23.

Treatment of the ylide II with aqueous hydrochloric acid, evaporation of the solution to dryness, and recrystallization of the residue from ethanol–ether afforded colorless crystals of phenacyldimethylsulfonium chloride of mp 138–139° (lit.[30] mp 139°).

Thermolysis of Phenacylidenedimethylsulfurane (II).—A carefully purified sample of 0.45 g (2.5 mmol) of ylide II, shown to be free of water, phenacyl bromide, and its conjugate acid, all by nmr spectroscopy (limit of detection about 1%), was dissolved in 15 ml of THF and heated under reflux for 24 hr. Chromatography on alumina and then crystallization afforded 0.28 g of unreacted ylide and 0.05 g (47% based on ylide consumed) of *trans*-1,2,3-tribenzoylcyclopropane (IV) which crystallized from ethanol as colorless crystals, mp 218.5–219.5° (lit.[17,31] mp 215°), ν_{CO} 1665 cm^{-1}.

Anal. Calcd for $C_{24}H_{18}O_3$: C, 81.34; H, 5.12. Found: C, 81.50; H, 5.55.

Repetition of the thermolysis with the addition of an equimolar quantity of N,N-dimethylbenzylamine and anhydrous cupric sulfate afforded a 7% yield of IV and <1% dimethyl(α-benzyl)-phenacylamine (VI). The yields and identities were established using vpc, but IV also was isolated, crystallized, and shown to be identical with an authentic sample by admixture melting point and a comparison of ir spectra. Thermolysis in the presence of 0.5 equiv of water afforded a trace amount of IV.

Dimethyl(α-benzyl)phenacylamine (VI).—To a solution of 4.7 g (50 mmol) of N,N-dimethylbenzylamine in 30 ml of benzene was added 10 g (50 mmol) of phenacyl bromide. Stirring at ambient temperatures, followed by evaporation of the solvent, afforded an oil which crystallized from ether–ethanol to afford 10.15 g (61%) of N,N-dimethylbenzylphenacylammonium bromide (VII) as a colorless powder, mp 164–165° (lit.[20] mp 167–168°).

Dissolution of the ammonium salt VII in water, then addition of aqueous sodium hydroxide sufficient to raise the pH of the solution to 11, followed by heating on a steam bath for 1 hr, afforded a yellow oil which solidified. Crystallization of the oil afforded a 79% yield of the amine VI as yellow needles, mp 77–79° (lit.[20] mp 77–79°).

Photolysis of Phenacylidenedimethylsulfurane (II).—A solution of 2.43 g (13.5 mmol) of II and 2.02 g (15 mmol) of N,N-dimethylbenzylamine in 25 ml of THF, all in a Vycor flask, was irradiated for 21 hr. Concentration to a volume of 10 ml and then vpc analysis indicated the presence of 3% amine VI and 6% cyclopropane IV. The latter subsequently was isolated and characterized.

Formation of *trans*-1,2,3-Tribenzoylcyclopropane (IV). A. From the Phenacylide II and Phenacyl Bromide.—A solution of 0.39 g (2.2 mmol) of ylide II and 0.11 g (0.54 mmol) of phenacyl bromide in 15 ml of THF was heated under reflux for 25 hr. Removal of the solvent *in vacuo* and crystallization of the residual oil from ethanol afforded 0.18 g (94%) of IV, mp 218–219°.

B. From the Phenacylide II and Phenacyldimethylsulfonium Bromide.—A solution of 0.33 g (1.8 mmol) of sulfonium salt and 0.12 g (0.45 mmol) of ylide II in 15 ml of THF was heated under reflux for 24 hr. Removal of the solvent *in vacuo* and crystallization of the residual oil from ethanol gave 0.15 g (93%) of IV, mp 219–220°.

Alkylation of the Phenacylide II with Benzyl Bromide.—A solution of 1.19 g (6.6 mmol) of ylide II in 10 ml of THF became milky upon the addition of 0.8 ml (6.6 mmol) of benzyl bromide. Stirring at room temperature for 18 hr afforded a precipitate of 0.46 g (27%) of phenacyldimethylsulfonium bromide which was removed by filtration. Evaporation of the filtrate left an oil which crystallized from hexane–chloroform to afford 0.19 g (16% based on ylide consumed) of α-methylthio-β-phenylpropiophenone (VIII) as colorless crystals, mp 62–62.5°, ν_{CO} 1670 cm^{-1}. The structure was confirmed by oxidation with hydrogen peroxide in acetic acid to afford α-methylsulfonyl-β-phenylpropiophenone as a colorless powder: mp 137–138° (lit.[25a] mp 137–138°); ν_{CO} 1670 cm^{-1}, ν_{SO_2} 1310 and 1122 cm^{-1}.

Acylation of Phenacylidenedimethylsulfurane (II). A. With Benzoic Anhydride.—A solution of 0.65 g (3.6 mmol) of ylide II and 0.82 g (3.6 mmol) of benzoic anhydride in 10 ml of THF was stirred at room temperature for 43 hr. The resultant precipitate was removed by filtration and crystallized from chloroform–hexane to afford 0.25 g (24%) of dibenzoylmethylenedimethylsulfurane (IX) as colorless crystals: mp 211–212°; ν_{CO} 1582 cm^{-1}; pK_a 0.79; nmr absorption in $CDCl_3$ at δ 3.07 (methyl singlet, area 6.0) and 6.9–7.5 (aromatic multiplet, area 10.5).

Anal. Calcd for $C_{17}H_{16}O_2S$: C, 71.84; H, 5.63; S, 11.28. Found: C, 71.17; H, 6.18; S, 11.20.

Upon concentration the filtrate from the reaction mixture afforded 0.29 g (67%) of benzoic acid, mp 121–122°.

Hydrolysis of 0.34 g of IX in 25 ml of water and 5 ml of 5 *N* hydrochloric acid afforded 0.08 g (55%) of benzoic acid, mp 121–122°, and 0.10 g (39%) of phenacyldimethylsulfonium chloride, mp 129–130°, identified by admixture melting point and comparison of ir spectra.

B. With Benzoyl Chloride.—A solution of 0.72 g (4 mmol) of ylide II in 10 ml of THF became milky upon the addition of 0.5 ml (4.3 mmol) of benzoyl chloride. After stirring at room temperature for 22 hr a small amount (0.04 g) of phenacyldimethylsulfonium chloride was removed by filtration. Removal of the solvent from the filtrate *in vacuo* left a precipitate which was recrystallized from hexane–chloroform to afford 0.82 g (76%) of the enol benzoate (X) of α-methylthioacetophenone as colorless crystals: mp 75–76°; ν_{CO} 1735 cm^{-1}; nmr absorption in $CDCl_3$ at δ 2.31 (methyl singlet, area 3), 6.47 (vinyl singlet area, 1), and 7.2–8.3 (aromatic multiplet, area 10).

Anal. Calcd for $C_{16}H_{14}O_2S$: C, 71.12; H, 5.18; S, 11.86. Found: C, 71.09; H, 5.02; S, 11.56.

Heating 0.12 g of the enol benzoate X with 0.6 ml of 50% hydrogen peroxide in 10 ml of acetic acid afforded 0.1 g (18%) of benzoic acid, mp 119–120°, and 0.3 g (30%) of methylphenacyl sulfone: mp 105–106° (lit.[32] mp 106–107°); ν_{CO} 1680 cm^{-1}, ν_{SO_2} 1302 and 1119 cm^{-1}.

Reaction of Phenacylidenedimethylsulfurane (II) with Electrophiles. A. *p*-Nitrobenzaldehyde.—A solution of 1.75 g (9.7 mmol) of ylide II and 1.5 g (10 mmol) of *p*-nitrobenzaldehyde in 50 ml of THF was heated under reflux for 27 hr. Removal of the solvent *in vacuo* and chromatography of the remaining oil on alumina afforded 0.42 g (28%) of *p*-nitrobenzyl alcohol, mp 88° (formed by reduction of the aldehyde on alumina[33]), and 0.25 g (10%) of 1-(4-nitrophenyl)-2-benzoyloxirane (XI) which crystallized from carbon tetrachloride as colorless crystals: mp 149.5–150.5° (lit.[34] mp 150°); ν_{CO} 1675 cm^{-1}; nmr absorption in $CDCl_3$ at δ 4.28 (two methinyl doublets, area 2) and 7.3–8.4 (aromatic multiplet, area 9).

B. Nitrosobenzene.—To a greenish blue solution of 0.54 g (5 mmol) of nitrosobenzene and 1.30 g (5 mmol) of phenacyldi-

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(31) G. Maier, *ibid.*, **95**, 611 (1962).

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(33) V. J. Hruby, *Proc. N. Dakota Acad. Sci.*, **16**, 12 (1962).

(34) E. Weitz and A. Scheffer, *Chem. Ber.*, **54**, 2338 (1921).

methylsulfonium bromide in 55 ml of 90% ethanol–water held at −10° was added 0.4 g (10 mmol) of sodium hydroxide dissolved in 10 ml of water. An exothermic reaction resulted and the solution became yellow. After the ice bath was removed and the solution was allowed to stand at room temperature for 25 hr, water slowly was added to the cloud point. Cooling overnight afforded a yellow precipitate which recrystallized from ethanol to afford 0.64 g (57%) of the nitrone XIII as yellow crystals: mp 108.5–110° (lit.[35] mp 109–110°); ν_{CO} 1650 cm^{-1}, ν_{NO} 1510 and 1310 cm^{-1}; nmr absorption in $CDCl_3$ at δ 8.37 (vinyl singlet, area 0.8) and 7.2–8.0 (aromatic multiplet, area 10). Hydrolysis of a sample of XIII in 8 ml of 1 *N* sodium hydroxide afforded, after extraction with ether and sublimation, 0.07 g of mandelic acid, mp 118–120° (lit.[35] mp 118–119°), ν_{CO} 1720 cm^{-1}.

Carbomethoxymethylenedimethylsulfurane (Ia).—Stirring a mixture of 10 ml (0.1 mol) of methyl bromoacetate and 10 ml of methyl sulfide for 1.5 hr produced a colorless precipitate which, after being washed with ether, afforded 21.6 g (100%) of carbomethoxymethyldimethylsulfonium bromide. Recrystallization from ether–ethanol gave a pure sample: mp 81–82°; ν_{CO} 1735 cm^{-1}; nmr absorption in trifluoroacetic acid at δ 3.21 (S-methyl singlet area 6), 4.01 (O-methyl singlet, area 3), and 4.57 (methylene singlet, area 1.95).

Anal. Calcd for $C_5H_{11}O_2SBr$: C, 27.91; H, 5.16; S, 14.91; Br, 37.15. Found: C, 27.80; H, 5.29; S, 14.70; Br, 37.08.

To 1.10 g (5 mmol) of the sulfonium bromide in 10 ml of THF was added 0.30 g (6 mmol) of 50% sodium hydride in mineral oil from which the mineral oil had been removed by washing with hexane. After stirring for 3 hr at room temperature the gray color of the sodium hydride suspension had been replaced by the yellowish suspension of sodium bromide. Removal of the precipitate and evaporation of the solvent left 0.42 g (63%) of crude, yellowish oily ylide Ia which solidified below 20° but could not be crystallized. It showed ν_{CO} 1620 cm^{-1} and nmr absorption in $CDCl_3$ at δ 2.78 (S-methyl singlet) and 2.87 (methine singlet, combined area 7), as well as at 3.55 (O-methyl singlet, area 3).

Passing gaseous hydrogen bromide through a solution of the oily ylide in ether afforded the conjugate acid bromide, mp 80–82°, identified by admixture melting point and comparison of ir spectra. A similar reaction but using gaseous hydrogen chloride afforded carbomethoxymethyldimethylsulfonium chloride: mp 107–108°; ν_{CO} 1735 cm^{-1}; nmr absorption in trifluoroacetic acid at δ 3.16 (S-methyl singlet, area 5.9), 4.00 (O-methyl singlet, area 3), and 4.48 (methylene singlet, area 2).

Anal. Calcd for $C_5H_{11}O_2SCl$: C, 35.18; H, 6.50; S, 18.79; Cl, 20.78. Found: C, 35.05; H, 6.57; S, 18.60; Cl, 20.93.

Allowing the ylide Ia, formed from 10 g (46 mmol) of sulfonium salt, to stand exposed to the atmosphere in THF solution led to the appearance of a precipitate which was recrystallized from ethanol–ether to afford 2.5 g (39%) of dimethylthetin hydrate (XIV) as colorless crystals: mp 67–69°; ν_{CO} 1625 cm^{-1}; nmr absorption in $(CD_3)_2SO$ at δ 2.80 (S-methyl singlet, area 6) and 3.91 (methylene singlet, area 2). Drying the hydrate over P_2O_5 afforded dimethylthetin (XV): mp 143.5–144.5°; ν_{CO} 1625 cm^{-1}; nmr absorption in $(CD_3)_2SO$ at δ 2.80 and 3.90.

Anal. Calcd for $C_4H_8O_2S$: C, 39.97; H, 6.72; S, 26.68. Found: C, 40.01; H, 6.30; S, 26.64.

Addition of dilute hydrochloric acid to XV or XIV produced dimethylthetin chloride (XVI) which crystallized from ethanol–ether as colorless crystals: mp 134.5–135.5°; ν_{KO} 1720 cm^{-1}; nmr absorption in $(CD_3)_2SO$ at δ 3.15 (S-methyl singlet, area 6.1), 4.90 (methylene singlet, area 1.9), and 13.75 (carboxyl proton singlet, area 1.1). This substance was identical with a sample prepared by the direct combination of methyl sulfide and chloroacetic acid, as evidenced by admixture melting point and a comparison of nmr and ir spectra. This sample was then converted into dimethylthetin and its hydrate by treatment with sodium hydride.

Reaction of Ester Ylide Ia with Nitrosobenzene.—Addition of 1.54 g (14.3 mmol) of nitrosobenzene to a solution of 14.3 mmol of ester ylide Ia in 30 ml of THF gave a yellow solution after standing for 4 hr at room temperature. Removal of the solvent, addition of water, extraction with ether, drying, and then concentrating the ethereal solution afforded a yellow oil which could not be crystallized. Accordingly, the oil was dissolved in 150 ml of methanol and hydrogenated over 1 g of 10% palladium on carbon for 11 hr. Removal of the catalyst and solvent left a noncrystallizable oil which was converted into a hydrochloride. The latter crystallized from ether–ethanol as colorless crystals which were then sublimed: mp 165–167°; ν_{CO} 1750 cm^{-1}; nmr absorption in $(CD_3)_2SO$ at δ 3.70 (methyl singlet, area 3), 4.11 (methylene singlet, area 1.9), 6.9–7.5 (aromatic multiplet, area 5.2), and 9.90 (NH and OH singlet, area 2.5). Addition of D_2O caused the δ 9.90 peak to vanish and a new peak to appear at 4.71 (HOD and HOH).

Anal. Calcd for $C_9H_{12}NO_3Cl$: C, 49.65; H, 5.57; N, 6.44; Cl, 16.29. Found: C, 53.47; H, 6.08; N, 7.14; Cl, 17.48.

Treatment of the hydrochloride with benzoyl chloride afforded a benzoate which crystallized from hexane–chloroform as colorless crystals: mp 63–65°; ν_{CO} 1750 and 1650 cm^{-1}; nmr absorption at δ 3.75 (methyl singlet, area 2.8), 4.61 (methylene singlet, area 2), and 7.0–7.5 (aromatic multiplet, area 10.3).

Acylation of the Ester Ylide Ia. A. With Benzoic Anhydride.—A solution of 35 mmol of ylide Ia and 7.90 g (35 mmol) of benzoic anhydride in 80 ml of THF was stirred at room temperature for 15 hr. The reaction was quenched with 50 ml of water and washed with ether [from which 3.95 g (95%) of benzoic acid was obtained], and the aqueous layer was concentrated to afford a yellow precipitate (6.91 g, 83%). Sublimation afforded pure carbomethoxybenzoylmethylenedimethylsulfurane (XIX) as a colorless powder: mp 129–131°; ν_{CO} 1675 and 1545 cm^{-1}; nmr absorption in $CDCl_3$ at δ 2.86 (S-methyl singlet, area 5.9), 3.38 (O-methyl singlet, area 3), and 7.0–7.4 (aromatic multiplet, area 5.1).

Anal. Calcd for $C_{12}H_{14}O_3S$: C, 60.50; H, 5.92; S, 13.43. Found: C, 60.43; H, 5.82; S, 13.52.

B. With Benzoyl Chloride.—Addition of 0.64 ml (5.5 mmol) of benzoyl chloride to a solution of 11 mmol of ester ylide Ia in 50 ml of benzene caused a precipitate to form. After stirring for 24 hr at room temperature, the precipitate [0.94 g (100%) of carbomethoxymethyldimethylsulfonium chloride] was removed by filtration. Addition of hexane to the filtrate resulted in the precipitation of 1.24 g (95%) of XIX, mp 127–128°, identified by admixture melting point and comparison of ir spectra.

Repetition of the experiment using 15.4 mmol of benzoyl chloride afforded the by-product, carbomethoxymethyldimethylsulfonium chloride, and an oil. Chromatography of the oil on alumina followed by crystallization from hexane–chloroform gave 1.7 g (34%) of the enol benzoate (XX) of α-methylthio-α-carbomethoxyacetophenone as colorless prisms: mp 74–74.5°; ν_{CO} 1740 and 1720 cm^{-1}; nmr absorption in $CDCl_3$ at δ 2.28 (S-methyl singlet, area 3), 3.66 (O-methyl singlet, area 3), and 7.2–8.3 (aromatic multiplet, area 10.1).

Anal. Calcd for $C_{18}H_{16}O_4S$: C, 65.85; H, 4.91; S, 9.74. Found: C, 65.71; H, 4.85; S, 9.92.

The benzoylcarbomethoxymethylenedimethylsulfurane (XIX). 2.23 g, 9.4 mmol) in 50 ml of benzene was converted by 1.1 ml (9.4 mmol) of benzoyl chloride into 1.46 g (48%) of XX, mp 74–75°, identified by admixture melting point and comparison of ir spectra.

Preparation of *trans*-1,2,3-Tricarbomethoxycyclopropane (XXI). A. Thermolysis of the Ester Ylide Ia.—A solution of 9.6 mmol of the ylide Ia in 20 ml of THF to which was added 0.14 g of cupric sulfate was heated under reflux for 122 hr. The solution was concentrated to 10 ml and then analyzed by vpc. A 19% yield of the cyclopropane XXI was detected.

B. Photolysis of the Ester Ylide Ia.—A solution of 7.9 mmol of the ylide Ia in 15 ml of THF was irradiated for 56 hr in a Vycor flask. Concentration of the solution and then vpc analysis indicated that a 5% yield of the cyclopropane XXI was formed. Repetition of the experiment but with the addition of an equimolar quantity of triphenylphosphine afforded a 13% yield of cyclopropane XXI and a 62% yield of dimethylthetin hydrate (XIV), mp 68–69°. A portion (42%) of the triphenylphosphine was recovered along with a 27% recovery of triphenylphosphine oxide.

C. Reaction of Ester Ylide Ia with Carbomethoxymethyldimethylsulfonium Bromide.—A solution of 4.67 mmol of ester ylide Ia and 0.42 g (1.95 mmol) of conjugate acid bromide in 13 ml of THF was heated under reflux for 24 hr. Concentration of the solution and vpc analysis indicated the formation of a 28% yield of the cyclopropane XXI.

D. Reaction of Ester Ylide Ia with Methyl Bromoacetate.—A solution of 4.67 mmol of ester ylide Ia and 0.30 g (1.95 mmol) of methyl bromoacetate was heated under reflux for 24 hr. Concentration and vpc analysis indicated the formation of a 24% yield of the cyclopropane XXI.

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(35) F. Krohnke and E. Barner, *Chem. Ber.*, **69**, 2006 (1936).

E. **Reaction of the Ester Ylide Ia with Methyl Maleate.**—A stirred solution of 9.2 mmol of ester ylide Ia and 1.32 g (9.2 mmol) of methyl maleate was heated under reflux for 17 hr. Concentration and vpc analysis indicated the formation of a 71% yield of cyclopropane XXI. The latter was isolated by evaporation of the solvent and sublimation of the residual oil to afford XXI as a colorless powder, mp 54-56° (lit.[36] mp 56-57°), ν_{CO} 1720 cm^{-1}.

Anal. Calcd for $C_9H_{12}O_6$: C, 50.00; H, 5.59. Found: C, 50.11; H, 5.73.

Registry No.—**1**, 19023-61-1; **2**, 19023-62-2; **3**, 19023-63-3; **4**, 19023-64-4; **5**, 19643-11-9; **6**, 5697-33-6; **7**, 19643-13-1; **8**, 19643-14-2; **9**, 19643-15-3; **10**, 19643-16-4; **11**, 19643-17-5; Ia, 18915-90-7; II, 5633-34-1; VIII, 14679-98-2; IX, 5633-35-2; X, 5633-68-1; XI, 5633-36-3; XIII, 5492-70-6; XIV, 19643-24-4; XV, 4727-41-7; XVI, 10132-50-0; XIX, 19643-27-7; XX, 19643-28-8; phenacyldimethylsulfonium bromide, 5667-47-0; carbomethoxymethyldimethylsulfonium bromide, 19643-31-3; carbomethoxymethyldimethylsulfonium chloride, 19643-32-4.

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Polarity Effects in the Solvolysis of Cyclohexane Derivatives. The Importance of Field Effects in Determining Relative Reactivities[1,2]

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The rates of acetolysis of 4-substituted cyclohexyl methanesulfonates are shown to be dependent upon the polarity and conformation of the substituent as well as the conformation of the leaving methanesulfonate group. Rates of solvolysis for *cis*- and *trans*-4-chlorocyclohexyl methanesulfonate and for *cis*- and *trans*-4-bromocyclohexyl methanesulfonate have been calculated using a field effect model by employing the observed ground-state conformer populations (as determined by infrared spectroscopy) and the appropriate bond dipoles. The good agreement of the kinetic data with rate constants calculated employing a purely field effect model indicates the absence, or at least the very small role, of "through-the-bond" inductive effects.

Some years ago investigations in these laboratories showed that the solvolysis of 4-methoxycyclohexyl tosylate occurs with methoxyl participation.[4,5] In developing a comprehensive interpretation of the nature of the products, one of the questions which was very difficult to answer was the expected rate in the absence of participation. We did not reach a definitive conclusion at this point in our earlier publications. One approach, in order to gain further information at this point, is to examine the rate of solvolysis of substituted cyclohexane derivatives with polar substituents, which should be expected *not* to participate in any transannular sense. Chloro and cyano substituents satisfy this criterion very well. It is therefore the purpose of the present report to examine the solvolysis of such systems. In the course of this study it became apparent that the influence of the polarity of the substituent causes a very substantial perturbation of the conformational equilibria of the starting materials, the cyclohexyl sulfonates, and that in addition field effects are particularly important in determining the relative reactivities of the pairs of isomers.

Results

The preparation of the requisite compounds was in general unexceptional. Treatment of 1,4-epoxycyclohexane with concentrated hydrochloric acid[6] afforded *trans*-4-chlorocyclohexanol (**1**) in excellent yield. The configuration of **1** is confirmed by the studies of Heine,[7] who demonstrated the formation of 1,4-epoxycyclohexane in the reaction of **1** with base. From **1**, tosylate **2** and methanesulfonate **3** were prepared. Treatment of **1** with sodium acetate in dimethylformamide afforded an authentic sample of *cis*-4-chlorocyclohexanol (**4**), from which tosylate **5** and methanesulfonate **6** were prepared. Solvolysis of **2** and of **5** in acetic acid showed that the *cis* isomer solvolyzes more slowly than the *trans* isomer. Examination of the products from each of these solvolyses showed that they were the normal products; *i.e.*, there was no evidence for any participation. This result shows that the polar influence of the chloro substituent vitiates the general rule that *trans*-4-substituted cyclohexane derivatives will generally react more slowly than *cis* isomers, for the reason that the *cis* isomer will have a higher population of that conformation with the reacting moiety in the axial position.

In order to determine the source of this inversion of relative reactivities, we have examined the conformational population of a number of derivatives of 4-chlorocyclohexanol. During the course of this study, Takeoka[8] reported that **1** is 28% in the diaxial conformation in carbon disulfide solution. It is known that both 1,4-dichlorocyclohexane and 1,4-dibromocyclohexane are predominantly in the diaxial conformation in a variety

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[2] A portion of this work has been published in a preliminary form: D. S. Noyce, B. N. Bastian, and R. S. Monson, *Tetrahedron Lett.*, 863 (1962).

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