Dimethylsulfonium Phenacylide[1]

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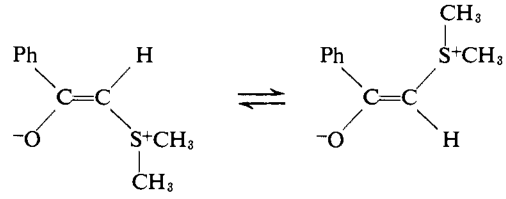
Abstract: The preparation and properties of dimethylsulfonium phenacylide, a stable sulfur ylide, are discussed. This ylide exists as an interconverting mixture of two enolate ions. The delocalization of the negative charge reduces its nucleophilicity compared to the nonstabilized sulfonium ylides. Thus, dimethylsulfonium phenacylide does not react with ketones to form epoxides, but does form cyclopropanes with suitable Michael acceptors. It condenses with acetylenic Michael acceptors to form new sulfur ylides. The thermal and photochemical behavior of this ylide is similar to diazoacetophenone—a fact that suggests both reagents decompose to the same intermediate, benzoylcarbene.

Although sulfur ylides have been known for some time,[2] it was not until the excellent work of Corey and Chaykovsky[3] that extensive activity in this area began.[4,5] In many respects, the reactions of sulfur ylides parallel those of diazo compounds. Both classes of intermediates form epoxides from aldehydes and ketones,[3,6] form cyclopropanes from olefinic compounds,[3,7,8] and undergo Wolff rearrangement upon photolysis.[9,10] In some of the reactions of diazo compounds, carbenes have been demonstrated as intermediates.[11] In order to understand more fully the similarities and differences between these two classes of reactive intermediates, we undertook the preparation and characterization of a stable sulfur ylide. In particular, we were interested in the possibility of the sulfur ylide undergoing α elimination to form carbenes.[12] The present paper describes the properties and reactions of such an ylide, dimethylsulfonium phenacylide (I),[14,15] and its conversion to benzoylcarbene.

Compound I was prepared in 79% yield by treatment of dimethylphenacylsulfonium bromide with 10% aqueous sodium hydroxide at 0–5°. The lack of any absorptions in the carbonyl region of the infrared spectrum and the presence of a strong band at 1510 cm^{-1} suggest that the ylide is best represented by the enolate structure. Two geometric isomers (Ia and b) are possible for this ylide. This equilibrium was studied by nmr spectroscopy. At 30°, a broad singlet (half-band width 9.0 cps) appears at 4.30 ppm for the methine proton. At −20°, this absorption sharpened (half-band width 1.5 cps) and appeared at δ 4.42, whereas, at 118.0°, it appeared at δ 4.24 with a half-band width of 2.0 cps. No further changes were observed upon going to lower or higher temperatures.



Ia Ib

These observations suggest that, at low temperature, only a single geometric isomer is present. As the temperature is raised, there is rotation about the carbon–carbon bond and this rotation becomes fast (on the nmr time scale) at 118°.[16] Although the present data do not allow unequivocal assignment of the most stable isomer, steric and electrostatic factors favor Ia. The fact that the methine proton shifts to lower field as the temperature is lowered also suggests that this proton is *cis* to the phenyl group in the more stable isomer.

Sulfonium ylides normally react with carbonyl groups to yield epoxides from aldehydes and ketones[3] and α-keto ylides from esters and acid halides.[9] However, when I was treated with cyclohexanone, no reaction occurred even after extended refluxing.[17] There are two steps in such reactions, (a) addition of the ylide to the carbonyl group, and (b) displacement of dimethyl sulfide by oxygen. Since the second step seems highly probable[3] (*vide infra*), we attribute the failure of the reaction to lack of carbonyl addition because of the low nucleophilicity of this ylide.

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(1) A preliminary account of a portion of this work has appeared: B. M. Trost, *J. Am. Chem. Soc.*, **88**, 1587 (1966).

(2) The first stable sulfur ylide was isolated in 1930: C. K. Ingold and J. A. Jessop, *J. Chem. Soc.*, 713 (1930).

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

(4) A. W. Johnson, "Ylid Chemistry," Academic Press Inc., New York, N. Y., 1966, pp 304–366.

(5) N. Kharasch and B. S. Thyagarajan, *Quart. Rept. Sulfur Chem.*, **1**, 2 (1966).

(6) C. D. Gutsche, *Org. Reactions*, **8**, 364 (1954).

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

(8) F. Weygand and H. J. Bestmann, "Newer Methods of Preparative Organic Chemistry," Vol. III, Academic Press Inc., New York, N. Y., 1964, pp 451–508.

(9) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **86**, 1640 (1964).

(10) L. Horner and E. Spietschka, *Chem. Ber.*, **85**, 225 (1952).

(11) See W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964.

(12) Several reports[4,7,13] claim carbene formation from sulfur ylides. Although the results of these reports do not disagree with carbenoid intermediates, they do not necessitate this conclusion. In some of these examples, alternate explanations are more satisfactory.

(13) (a) V. Franzen, H. J. Schmidt, and C. Merz, *Chem. Ber.*, **94**, 2942 (1961); (b) C. G. Swain and E. R. Thornton, *J. Am. Chem. Soc.*, **83**, 4033 (1961).

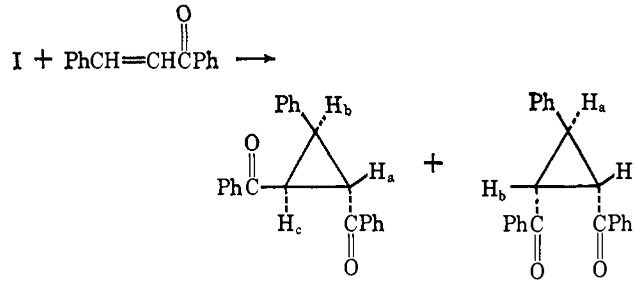
(14) Preliminary accounts of similar ylides have appeared. See (a) H. Nozaki, K. Kondo, and M. Takaku, *Tetrahedron Letters*, 251 (1965); (b) A. W. Johnson and R. T. Amel, *ibid.*, 819 (1966).

(15) Also see K. W. Ratts and A. N. Yao, *J. Org. Chem.*, **31**, 1185 (1966).

(16) (a) For similar observations in the case of diazoketones see F. Kaplan and G. K. Meloy, *J. Am. Chem. Soc.*, **88**, 950 (1966). (b) None of the second isomer could be detected at low temperature. Since this method only allows detection of greater than 5%, a minimum energy difference between Ia and b of 1.6 kcal/mole can be assigned. These data correspond to an energy barrier to rotation of about 15 kcal/mole.

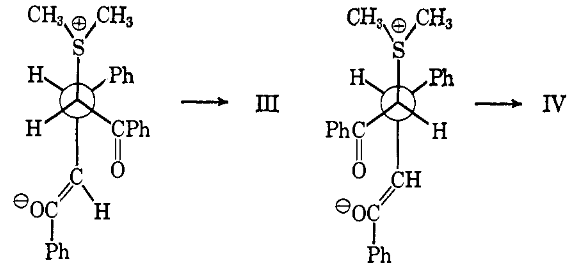
(17) Johnson and Amel[14b] report a low yield of epoxide from I and *p*-nitrobenzaldehyde. Nozaki and co-workers[14a] were unable to obtain any epoxide between methylphenylsulfonium phenacylide and this same aldehyde.

Having failed to observe addition to a carbonyl group, we next explored its potential as a Michael donor. Unlike the nonstabilized sulfonium ylides which form only epoxides with α,β-unsaturated ketones, I condenses smoothly at room temperatures with chalcone to produce a mixture of two cyclopropanes, III and IV, in the ratio of 1:2. The stereochemistry of the products is based on the nmr spectra.



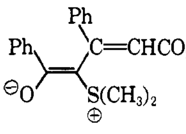
III IV

For compound III, three types of cyclopropane hydrogens should be visible in its nmr spectrum whereas compound IV should exhibit an AB_2 pattern for these hydrogens. Indeed, the minor isomer (assigned structure III) exhibited a triplet (J = 5.5 cps, 1 H) at 4.25 ppm (H_a), a quartet (J = 5.5 and 10.0 cps, 1 H) at 3.80 ppm (H_b), and a quartet (J = 5.5 and 10.0 cps, 1 H) at 3.52 ppm (H_c) for the cyclopropyl hydrogens. Analogous to other cyclopropanes,[18] the larger coupling is assigned to the *cis* couplings and the smaller to the *trans*. The cyclopropane hydrogens of the major isomer (assigned structure IV) exhibit the expected AB_2 pattern with H_a at 3.52 ppm, H_b at 3.37 ppm, and J_{AB} = 6.0 cps. Since at equilibrium only III is present[19] and since there is no interconversion of III and IV under the reaction conditions, the relative amounts of the two isomers must reflect the relative energies of rotamers Va and b. The Newman projections clearly indicate that the precursor of III possesses more unfavorable eclipsing interactions than the precursor of IV. Thus, Vb should be the preferred rotamer and IV the major product, as is observed.[20] Ylide I also undergoes smooth Michael reaction with dibenzoylethylene to give *trans*-1,2,3-tribenzoylcyclopropane in high yield.

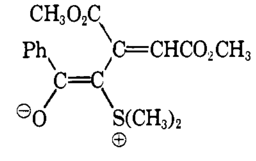


Va Vb

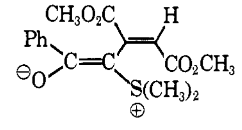
Acetylenic compounds have served as Michael acceptors for sulfur ylides.[21] In these cases, the products were new stable ylides. When a solution of I and methyl phenylpropiolate was refluxed, a 1:1 adduct (VI) was produced. Its structure was assigned on the basis of spectral data (see Experimental Section) and analogy to the previous example.[21,22] If dimethyl acetylenedicarboxylate is employed as the Michael acceptor, the reaction to produce adduct VII is extremely exothermic. The infrared spectra (see Experimental Section) support the enolate structures as the principal resonance contributor to the ground state. The nmr of adduct VII (see Experimental Section) clearly indicates that it is a mixture of two isomers. In adduct VII, the negative charge is delocalized not only through the carbonyl group of the benzoyl moiety but also through the α,β-unsaturated ester moiety. This extra delocalization would lower the π-bond order of the enolate double bond and thus lower the energy barrier to rotation. Since, at room temperature, ylide I undergoes "slow" rotation, it is thus reasonable to expect adducts VIIa and b (also VIIc and d) to be "rapidly" interconverting at room temperature. Thus, the nmr spectrum is then the averaged spectrum of VIIa and b and the averaged spectrum of VIIc and d.



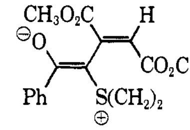
VI



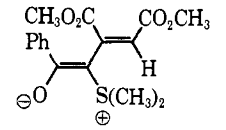
VII



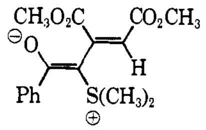
VIIa



VIIb



VIIc



VIId

The evidence clearly indicates that the stabilized ylide, in nucleophilic reactions, behaves more similarly to the sulfoxonium ylides than other sulfonium ylides. In particular, both I and the sulfoxonium ylides form cyclopropanes with chalcone whereas the more reactive sulfonium ylide forms epoxide entirely. With the more reactive ylides, the transition state should more closely resemble reactants than products[23] and reaction occurs at the most highly electron-deficient center, the carbonyl carbon atom, to form epoxide. With the more stable ylides, the converse is true (*i.e.*, the transition state should more closely resemble products than reactants) and the thermodynamically more favorable products form.

In addition to the investigation of the typical nucleophilic reactions expected for a sulfur ylide, we examined

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[18] J. D. Graham and M. T. Rogers, *J. Am. Chem. Soc.*, 84, 2249 (1962).

[19] E. P. Kohler and W. N. Jones, *ibid.*, 41, 1249 (1919). These authors did not assign stereochemistry to their products.

[20] A minimum value of 0.4 kcal/mole can be assigned to the energy difference between the two rotamers.

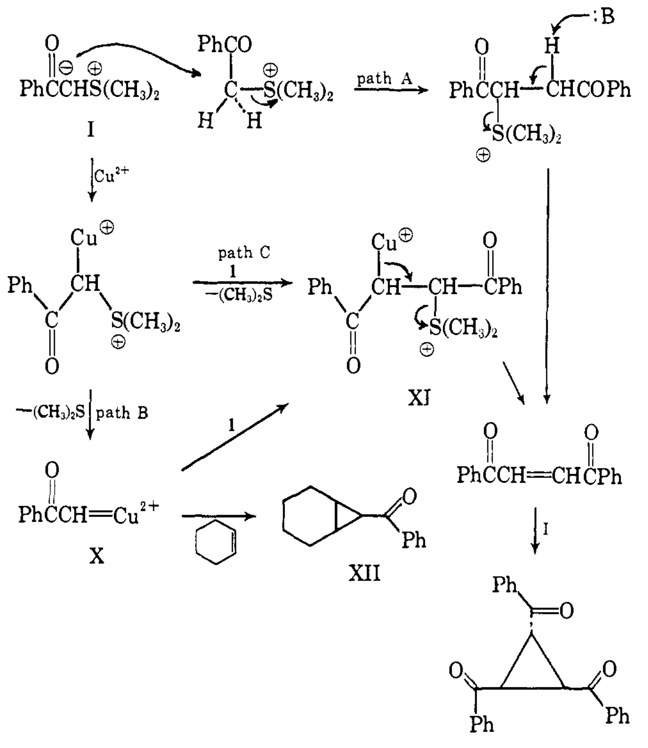
[21] C. Kaiser, B. M. Trost, J. Beeson, and J. Weinstock, *J. Org. Chem.*, 30, 3972 (1965).

[22] A similar reaction is reported for the corresponding phosphorus ylide with acetylenic esters. See J. B. Hendrickson, R. Rees, C. Hall, and J. F. Templeton, *ibid.* 30, 3312 (1965).

[23] G. S. Hammond, *J. Am. Chem. Soc.*, 77, 334 (1955).

its potentiality as a carbene precursor.[12] It had been reported that treatment of methylphenylphenacylsulfonium bromide with a hot base solution yields tribenzoylcyclopropane.[24] The authors suggested this product arose from a trimerization of an intermediate carbene. To investigate the plausibility of this pathway, we refluxed a benzene, chloroform, cyclohexene, and benzene–cyclohexanone solution of the ylide I for 6 days. There was no apparent decomposition.[25] However, refluxing a chloroform or benzene mixture of I and dimethylphenacylsulfonium bromide led to a 92% yield of tribenzoylcyclopropane (VIII). These facts refute the benzoylcarbene hypothesis, and, in conjunction with the previous observation of the facile Michael addition of I to dibenzoylethylene, support the mechanism in Scheme I (path A).[26,27]

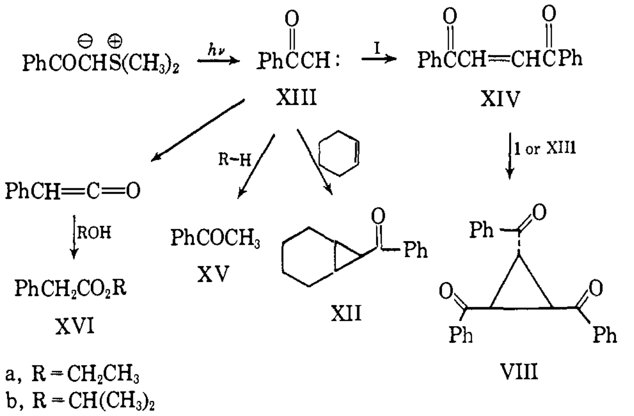
Scheme I. Thermal Decompositions of I



Since I was thermally stable, its decomposition in the presence of Lewis acids with filled or partially filled 3d shells was investigated. Copper and its salts catalyze the thermal decomposition of diazo compounds. Under these conditions, diazoacetophenone produced tribenzoylcyclopropane.[28] Copper salt catalyzed thermal decomposition of diazoacetophenone in the presence of olefins yields the cyclopropane derived from benzoylcarbene and the olefin.[29] The ylide I behaved similarly. Refluxing a benzene or chloroform solution of I with anhydrous cupric sulfate produced 90–95% yields of VIII. Two paths are conceivable. Formation of a copper–carbon σ bond leads to IX (see Scheme I). Since Cu^{2+} has nine electrons available in its 3d orbital, pπ–dπ overlap with simultaneous expulsion of dimethyl sulfide forms a copper-complexed carbene X (path B).[30] Hammond[29] suggested the same intermediate in the copper-catalyzed thermal decomposition of diazoacetophenone. This electrophilic species would be trapped by the highly nucleophilic ylide, I, to yield the adduct XI. Loss of dimethyl sulfide and the cupric ion would generate dibenzoylethylene which would react with I as discussed above. XI can also arise by the alkylation of I with IX (path C), a pathway which *a priori* cannot be excluded. However, the presence of X or a species similar in reactivity to it is indicated by the formation of benzoylnorcarane (XII) in addition to VIII by using cyclohexene as solvent. A low yield of XII was anticipated since I is a much more effective nucleophile than cyclohexene (*vide infra*). Nevertheless, we cannot exclude the possibility that both mechanisms (paths B and C) operate in the present case.

Although the results of the thermal decomposition are ambiguous, the photolytic decomposition results proved clearer. Irradiation of a solution of I in benzene or chloroform led to nearly quantitative yields of *trans*-1,2,3-tribenzoylcyclopropane (VIII; see Scheme II). In view of the thermal behavior of the ylide, its sensitivity to photolysis indicated the formation of a reactive electron-deficient species such as the carbene XIII. The cyclopropane may then arise from reaction of the carbene with a second mole of ylide to produce dibenzoylethylene (XIV) which subsequently combined with either I or XIII to produce VIII.

Scheme II: Photolysis of Ylide



Photolysis of I in alcohol and cyclohexene confirms the presence of XIII. Performing the irradiation in ethanol led to approximately a 48% yield of three volatile products and a 40–45% yield of II. The

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

(25) Nozaki and co-workers[14a] reported similar thermal stability for their ylide; however, Johnson and Amel[14b] reported a low yield of tribenzoylcyclopropane in addition to much recovered starting material upon refluxing a tetrahydrofuran solution of I. We wish to suggest that the cyclopropane arose due to the presence of moisture. Protonation of the ylide by the water would lead to sulfonium salt. Reaction of this salt with the ylide as discussed above for the reaction of I with dimethylphenacylsulfonium bromide would produce the observed product.

(26) Nozaki suggested the same mechanism but did not provide experimental evidence in support of it.

(27) Kirmse suggested a similar mechanism for the formation of tribenzoylcyclopropane from triphenylphosphonium phenacylide. See ref 11, pp 117–118.

(28) H. Strzelecka and M. Siemiatycki, *Compt. Rend.*, **252**, 3821 (1961).

(29) D. D. Cowan, M. M. Couch, K. R. Kopecky, and G. S. Hammond, *J. Org. Chem.*, **29**, 1922 (1964).

(30) (a) pπ–dπ overlap is suggested for the stabilization of carbanions adjacent to heteroatoms. See D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965, pp 71–84. (b) A zinc-complexed carbene, $I^+Zn{=}CH_2$, analogous to the copper-complexed carbene may be involved as an intermediate in the Simons–Smith reaction. See W. G. Dauben and G. H. Berezin, *J. Am. Chem. Soc.*, **85**, 468 (1963), and references therein.

Table I. Relative Amounts of Volatile Products

	Method of decomposition	% XV	% XVI	% XII
1	Irradiation/$C_2H_5OH^{a,b}$	52	26	. . .
2	Irradiation/$(CH_3)_2CHOH^{a,c}$	97	1.5	. . .
3	Irradiation/cyclohexene[a,d,e]	83	. . .	10
4	Thermolysis/cyclohexene	. .	. .	100

[a] In all cases the major product isolated was **VIII**. [b] Propiophenone formed in 22% relative yield. [c] Propiophenone formed in 1.5% relative yield. [d] Propiophenone formed in 7% relative yield. [e] Bicyclohexenyl isolated in 38% yield.

volatile materials (see Table I) were identified as acetophenone (XV), propiophenone, and ethyl phenylacetate (XVIa). When 2-propanol was employed as solvent, a drastic reduction in the ratio of phenylacetic ester to acetophenone occurred. Finally, irradiation in cyclohexene produced benzoylnorcarane (XII) in addition to V. These results are summarized in Table I.

The evidence clearly supports the intermediacy of benzoylmethylene in the photolytic decomposition of I. Although both the singlet and triplet states are probably involved, the available evidence does not allow unambiguous assignment as to which spin state is the precursor of the various products. The singlet carbene must be the intermediate that combines with the ylide I to produce ultimately tribenzoylcyclopropane. Presumably the same species yields the Wolff rearrangement products, XVI.[31] Hammond and coworkers[29] found the major product from triplet benzoylcarbene (generated from diazoacetophenone) in cyclohexene to be acetophenone (XV), but low yields of 7-benzoylnorcarane (XII) were also obtained. Since the ratio of XV:XII (about 7:1) is nearly identical for both the diazoacetophenone and dimethylsulfonium phenacylide decomposition, the same intermediate, triplet ketocarbene, is most likely involved in both cases as the precursor of these two products.

The proposed intermediate XIV was never observed. Thus, the subsequent reaction of XIV with either I or XIII must be fast relative to its formation. Since dibenzoylethylene has a relatively electron-poor double bond, its rapid reaction with the highly electrophilic carbene seems unlikely, especially in the presence of a large excess of the much more reactive olefinic linkage of cyclohexene. Thus, VIII probably arises from the reaction of XIV with I (*vide infra*). A reasonable mechanistic pathway for the formation of propiophenone, a product in all the irradiations, involves a Stevens rearrangement of the ylide followed by the photolytic decomposition of the resultant α-methylthiopropiophenone.[32]

Experimental Section[33]

Preparation of Dimethylsulfonium Phenacylide (I). A solution of 20 g of sodium hydroxide in 250 ml of water was cooled to 5° under an atmosphere of nitrogen. With stirring, 26.0 g (0.100 mole) of dimethylphenacylsulfonium bromide was added portionwise to the base solution. The mixture was stirred at 5° until all the solid dissolved. It was then extracted, and the extracts were dried. After evaporation, a pale yellow oil remained which slowly crystallized *in vacuo* over phosphorus pentoxide. It was washed with cyclohexane and recrystallized from a chloroform–carbon tetrachloride mixture to yield 13.30 g (74% yield) of colorless flakes, mp 78–79°.[34] Its infrared spectrum[35] shows absorptions (cm^{-1}) at 1510 (enolate) and 1585 (benzene ring). The nmr spectrum[36] (in δ) shows a sharp singlet at 2.89 (6 H; SCH_3), a broad singlet at 4.30 (1 H, methine proton), a multiplet centered at 7.36 (3 H, *m*- and *p*-phenyl protons), and a multiplet centered at 7.86 (2 H, *o*-phenyl protons). Its mass spectrum shows a molecular ion peak at *m/e* 180 as well as abundant peaks at 166, 134, 120, 106, 105 (base peak), 91, 78, 77, 75, 62, and 61.

Anal. Calcd for $C_{10}H_{12}SO$: C, 66.6; H, 6.7; S, 17.8; mol wt, 180. Found: C, 66.3; H, 6.8; S, 17.5; mol wt, 180 (mass spectrum).

Michael Reactions. A. With Chalcone. A solution of 0.4350 g (2.42 mmoles) of dimethylsulfonium phenacylide and 0.500 g (2.40 mmoles) of chalcone in 15.0 ml of benzene was stirred 15 hr at 25° under an atmosphere of nitrogen. The benzene was evaporated to leave a yellow solid residue. Recrystallization from a benzene–pentane mixture produced a yellow solid. This material was then recrystallized from cyclohexane to yield 0.535 g (65.5% yield) of off-white needles, mp 149–150° (lit.[19] mp 151°). Its infrared spectrum[35] showed absorptions (cm^{-1}) at 1675 (C=O), 1600 and 1575 (C=C). A maximum appears at 249 mμ (ε 30,400) in its ultraviolet spectrum.[37] The nmr[36] spectrum (in δ) exhibits a 4 H multiplet centered at 7.95 (*ortho* protons of benzoyl groups), an 11 H multiplet centered at 7.25 (remaining aromatic protons), and an AB_2 pattern (cyclopropane protons) with H_a at 3.52 and H_b at 3.37 and J_{AB} = 6.0 cps. On the basis of this spectral data it was assigned the stereochemistry depicted in IV. The original benzene–pentane mother liquors were evaporated, and the residue was recrystallized from cyclohexane to give 0.2615 (33.2% yield) of off-white needles, mp 114–116° (lit.[19] mp 115°). Its infrared[35] revealed characteristic absorptions (cm^{-1}) at 1655 (C=O), 1600 and 1580 (C=C). A maximum appeared at 250 mμ (ε 27,500) in its ultraviolet spectrum. The nmr[36] spectrum (in δ) exhibits a 4 H multiplet at 8.10 (*ortho* protons of benzoyl groups), a 11 H multiplet centered at 7.40 (remaining aromatic protons), a 1 H triplet (J = 5.5 cps) at 4.25 (benzylic cyclopropyl proton), a 1 H quartet (J = 5.5 and 10.0 cps) at 3.80 (cyclopropyl proton *cis* to phenyl), and a 1 H quartet (J = 5.5 and 10.0 cps) at 3.52 (cyclopropyl proton *trans* to phenyl). Structure III must be assigned from this spectral information.

B. With Dibenzoylethylene. The reaction was performed as described above utilizing 0.360 g (2.00 mmoles) of ylide I and 0.472 g (2.00 mmoles) of dibenzoylethylene in 20 ml of benzene. There was obtained 0.692 g (97.8% yield) of *trans*-1,2,3-tribenzoylcyclopropane, mp 214–216° (lit.[38] mp 215°). The nmr spectrum agreed with that reported for this compound.[39]

C. With Methyl Phenylpropiolate. A solution of 0.180 g (1.00 mmole) of ylide I and 0.160 g (1.000 mmole) of methyl phenylpropiolate in 25.0 ml of benzene was prepared under an atmosphere of nitrogen. Stirring at 25° for 24 hr produced no reaction as indicated by infrared analysis of the mixture. It was refluxed 3 hr with stirring and then allowed to cool slowly to room temperature. A yellow solid precipitated. It was filtered, and the filtrate was con-

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(31) A. Padwa and R. Layton, *Tetrahedron Letters*, 2167 (1965).

(32) (a) To our knowledge, this example represents the first photolytic induced Stevens rearrangement. (b) For a discussion of this type of reaction see D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965, pp 223–233. (c) For a recent example of the photochemical reaction of an α-thioketone and a discussion of the photolytic cleavage of electronegative substituents to a carbonyl group, see A. Padwa and D. Crumrine, *Chem. Commun.*, 506 (1965).

(33) Melting points were taken on a Thomas–Hoover melting point apparatus and are corrected. Infrared spectra were determined on a Beckman IR-8 spectrophotometer, and ultraviolet spectra were recorded on Cary Model 11 and Model 15 spectrophotometers. Nmr spectra were determined on a Varian Associates Model A-60 spectrometer fitted with a variable-temperature probe. Chemical shifts are given in ppm relative to TMS as an internal standard. Mass spectra were taken on a CEC 103 C mass spectrometer at an ionizing current of 40 ma and ionizing voltage of 70 v. Analyses were performed by Spang Microanalytical Laboratory and Micro-Tech Laboratories, Inc. Unless otherwise indicated, extractions were performed with chloroform and magnesium sulfate was employed as a drying agent. Vpc analyses were performed on an Aerograph Model 90P instrument.

(34) We erroneously reported[1] mp 57–59° for this ylide. The hygroscopic ylide forms a hydrate which has this lower melting point.

(35) Determined as a solution in chloroform.

(36) Determined as a solution in deuteriochloroform.

(37) Determined as a solution in ethanol.

(38) G. Maier, *Chem. Ber.*, **95**, 611 (1962).

(39) J. D. Graham and M. T. Rogers, *J. Am. Chem. Soc.*, **84**, 2249 (1962).

Table II. Thermolyses Conditions[a]

Expt	Amt of I, mmoles	Solvent	Time, hr	Added salt
1	1.00	$CHCl_3$	144	None
2	1.00	Benzene-cyclohexanone	144	None
3	1.00	$CHCl_3$	72	None
4	2.22	Cyclohexene	24	$CuSO_4$
5	2.22	Cyclohexene	48	ZnI_2

[a] All reactions were performed twice.

centrated to yield additional product. Recrystallization from ethanol yielded 0.175 g (52% yield) of pale yellow flakes, mp 194–195° dec. The infrared spectrum[40] had absorptions at 1650 (CO_2CH_3), 1575 ($>C{=}C<$), and 1545 ($>C{=}C(O^-)-$)cm^{-1}. The ultraviolet spectrum[37] had maxima at 359 mμ (ε 4010) and 253 mμ (ε 22,600) which shifted to 276 mμ (ε 23,400) in an HCl–ethanol mixture.

Anal. Calcd for $C_{20}H_{20}SO_3$: C, 70.6; H, 5.9; S, 9.4. Found: C, 70.5; H, 6.0; S, 9.3.

D. With Dimethyl Acetylenedicarboxylate. A solution of 1.80 g (10.0 mmoles) in 50.0 ml of anhydrous benzene under nitrogen was cooled to 5°. To this solution, 1.42 g of dimethyl acetylenedicarboxylate was added dropwise with stirring. The mixture immediately became red, and the color deepened with each additional drop. A yellow precipitate slowly formed. Upon completion of the addition, the mixture was stirred for 24 hr during which time it was allowed to warm to room temperature. The solid was filtered and recrystallized from benzene to give 1.36 g (40% yield) of pale yellow powder, mp 137–139° dec. Its infrared spectrum[35] showed absorptions at 1710 (conjugated CO_2CH_3), 1675 (CO_2CH_3 conjugated with anion), and 1550 (C=C) cm^{-1}. The ultraviolet spectrum[37] showed maxima at 242 mμ (ε 13,700), 272 mμ (sh, ε 6260), and 342 mμ (ε 8070). The compound was identified as a 60:40 mixture of isomers VIIa and b and VIIc and d from its nmr spectrum (in δ): for VIIa and b, 2.72, singlet, CH_3–S; 3.37, singlet, CH_3O; 3.72, singlet, CH_3O; 5.56, singlet, =CH; 7.35, singlet, aromatic H; for VIIc and d, 2.61, singlet, CH_3–S; 3.28, singlet, CH_3O; 3.80, singlet, CH_3O; 6.42, singlet, =CH; 7.30, singlet, aromatic H.

Anal. Calcd for $C_{16}H_{18}SO_5$: C, 59.6; H, 5.6; S, 9.9. Found: C, 59.2; H, 5.7; S, 9.6.

Alkylation of I with Sulfonium Salt. A mixture of 0.2730 g (1.51 mmoles) of dimethylsulfonium phenacylide and 0.1311 g (0.50 mmole) of dimethylphenacylsulfonium bromide in 10.0 ml of chloroform was stirred at 25° for 10 hr with no apparent reaction (followed by infrared spectrophotometry). It was subsequently refluxed until the suspended solid had dissolved (4 hr) and then evaporated to yield 0.1609 g (90.8% yield) of *trans*-1,2,3-tribenzoylcyclopropane, mp 214–216° after recrystallization from benzene.

Thermal Reactions of the Ylide I. The thermolyses were performed by refluxing about 0.5 *M* solution of the ylide I in the stated solvent under nitrogen. In those cases where a copper salt was also employed, a twofold excess of anhydrous cupric sulfate was suspended in the medium. Upon completion of the refluxing, any suspended solid (the copper salts) was removed by filtration, and the salts were washed thoroughly with solvent. Distillation eliminated excess solvent. The residue was diluted with chloroform to a volume of 10.0 ml, and the solution was divided into two equal parts. To one part, biphenyl was added as an internal standard and the mixture was analyzed by vpc.[41] The components were identified by comparison of vpc retenton times and infrared spectra of collected samples with authentic materials. In some cases, mass spectral comparisons were also employed. The second fraction was evaporated to dryness. Recrystallization of the remaining solid from benzene–pentane yielded pure *trans*-1,2,3-tribenzoylcyclopropane. The results of these experiments are summarized in Tables II and III.

Table III. Thermolyses Products[a]

Expt	% XII	% VIII
1	No reaction	
2	No reaction	
3	No reaction	
4	4.9	90.0
5	. . .	95.1

[a] The average of two runs.

Photolytic Decomposition of Ylide I. The photolyses were performed with a Hanovia high-pressure mercury lamp employing a Pyrex filter sleeve. In all cases ~0.5 *M* solution (50 ml) of ylide I was irradiated in the stated solvent for 3 hr in a nitrogen atmosphere. Distillation removed excess solvent, and the residue was diluted with chloroform to a volume of 10.0 ml. It was then divided into two equal parts. To the first fraction, biphenyl was added as an internal standard, and the solution was analyzed by gas chromatography.[41] The products were identified by comparison of vpc retention times and infrared spectra of collected samples with authentic samples. The second aliquot was evaporated to dryness. Recrystallization of the residue from benzene–pentane produced pure *trans*-1,2,3-tribenzoylcyclopropane. A summary of these analyses appears in Tables IV and V.

Table IV. Photolytic Reactions[a]

Expt	Amount of ylide, mmoles	Solvent	Time, hr
1	2.22	Ethanol	3
2	2.22	2-Propanol	3
3	2.22	Cyclohexene	3
4	2.22	Benzene	3

[a] All experiments were performed twice.

Table V. Photolytic Products[a]

Expt	% XV	% XVI	% XII	% VIII	% Propiophenone
1	34	1.3	. .	44	2.8
2	49	0.8	. .	34	0.8
3[b]	37	. .	5	40	3.2
4	. .	. .	. .	92	. .

[a] The average of two runs. [b] Bicyclohexenyl formed in 38% yield.

Preparation of an Authentic Sample of 7-Benzoylnorcarane. A mixture of Δ^2- and Δ^3-norcarene-7-carboxylic acids[42] was hydrogenated by the method of Berson and Hand.[43] A solution of 0.500 g (3.57 mmoles) of 7-norcaranecarboxylic acid in 25 ml of dry ether was cooled to 0° under an atmosphere of nitrogen. With vigorous stirring, 10.0 ml of 1.02 *M* (10.2 mmoles) phenyllithium was added dropwise. After stirring 1 hr at 25°, the solution was cautiously poured into dilute aqueous hydrochloric acid. The mixture was extracted with ether, and the combined ether extracts were washed with water and aqueous sodium bicarbonate. After drying and evaporation of solvent, the residue distilled at 130–135° (0.5 mm) (lit.[29] 140° (<1 mm)). Its spectral properties agreed with those reported.[29]

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(40) Determined as a Nujol mull.

(41) Columns packed with silicone oil and diethylene glycol succinate were employed for these analyses.

(42) We wish to thank Professor Jerome A. Berson for a generous supply of these compounds.

(43) J. A. Berson and K. S. Hand, *J. Am. Chem. Soc.*, **86**, 1978 (1966).