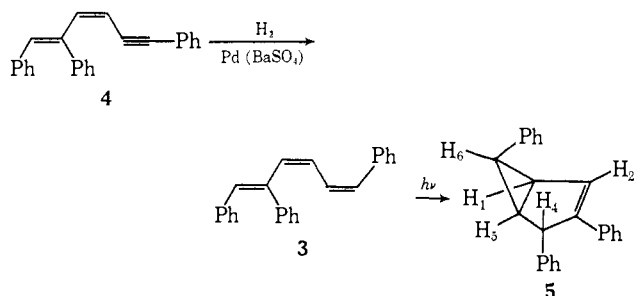


the determination of the following coupling constants; $J_{1,5} = 6.3$ Hz, $J_{1,6} = 2.3$ Hz, $J_{5,6} = 3.6$ Hz, $J_{1,4} = 2.4$ Hz, $J_{2,4} = 1.6$ Hz, and $J_{1,2} = 1.9$ Hz. The magnitude of the coupling implies *trans*-cyclopropyl vicinal coupling^{19,20} and thus requires that the C₆-phenyl group be *exo*. The absence of coupling between H₄ and H₅ implies *trans* vicinal coupling and fixes the C₄-phenyl group in the *exo* position.^{1c,2b,7a}

Bicyclo[3.1.0]hexene **2** is not the expected product from orbital symmetry considerations but is the thermodynamically most favored isomer. In order to determine whether the photoisomerization of a triphenyl-substituted hexatriene is subject to orbital symmetry interpretation, we have investigated the photochemistry of the isomeric 1,2,6-triphenyl-(*Z,Z,Z*)-hexa-1,3,5-triene (**3**). This material was obtained from the catalytic hydrogenation of 1,2,6-triphenyl-(*Z,Z*)-hexa-1,3-dien-5-yne (**4**). Dienes **4** was in turn synthesized from the Wittig reaction of *cis*- α -phenylcinnamyltriphenylphosphonium bromide and phenylpropargyl aldehyde followed by fractional crystallization of the two isomeric dienes. Irradiation of **3** in cyclohexane gave a new



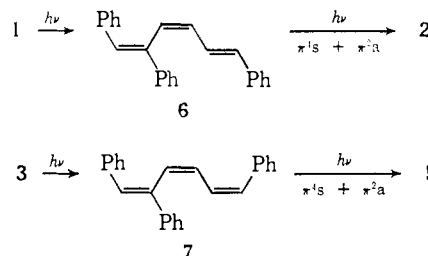
photoisomer (mp 132–133°) whose structure is assigned as 4-*exo*,6-*endo*-3,4,6-triphenylbicyclo[3.1.0]hex-2-ene (**5**) on the basis of its nmr spectrum:¹⁸ δ 2.01 (dd, 1, C₅H), 2.50 (m, 2, C₁H and C₆H), 3.78 (t, 1, C₄H), 6.32 (m, 1, C₂H), and 6.8–7.3 (m, 15, aromatic). Appropriate spin-decoupling experiments showed that $J_{1,2} = J_{1,4} = J_{2,4} = 2.0$ Hz, $J_{1,5} = 6$ Hz, and $J_{5,6} = 8.0$ Hz. The magnitude of the *cis*-cyclopropyl vicinal coupling requires that the C₆-phenyl group be *endo*. In accord with this assignment is the observation that H₆ is no longer shielded by the anisotropy of the double bond and appears 0.8 ppm downfield from C₆H in the *exo,exo* isomer **2**. Again, $J_{4,5} = 0$ Hz, requiring that the C₄-phenyl group be *exo*.

The fact that only **5** was isolated from the irradiation of **3** implies that the stability of the final product is not the major factor governing the photoisomerization in the triphenylhexatriene system. These results indicate that orbital symmetry control must be important in these systems. It should be pointed out, however, that **5** is not the isomer that would be predicted to be formed from the irradiation of **3**. The above observa-

(19) W. G. Dauben and W. T. Wipke, *J. Org. Chem.*, **32**, 2976 (1967).

(20) M. Schneider and R. J. Crawford, *Can. J. Chem.*, **48**, 628 (1970).

tions can be rationalized if it is assumed that the above reactions are consecutive photoreactions involving initial *cis*-*trans* photoisomerization followed by bond reorganization to the bicyclic isomer.



In order to gain further evidence for the above scheme, trienes **6** and **7** were independently synthesized.²¹ When subjected to irradiation, **6** gave only **2** and **7** afforded **5** as predicted. Furthermore, in the partial photolysis of **1**, the presence of **6** could be detected by nmr spectroscopy.

It appears that photoisomerization about the 1,2 double bond to relieve *cis*-diphenyl nonbonded interactions is rapid relative to symmetry-allowed concerted cyclization. In both cases the cyclization is observed to occur only *via* the $\pi^4s + \pi^2a$ route.²² This perhaps is a reflection of the somewhat greater steric requirements of the $\pi^4a + \pi^2s$ path. Closure by the $\pi^4s + \pi^2a$ route would also be expected from consideration of the nodal structure of the lowest π^* level of the *transoid* conformer of the hexatriene. Further work on the importance of orbital symmetry control in 1,3,5-hexatriene photochemistry in related systems is currently under way and will be the subject of future reports.

Acknowledgment. We gratefully acknowledge support of this work by the National Science Foundation (Grant GP-9385).

(21) Triene **6** was synthesized from the Wittig reaction of *trans*- α -phenylcinnamyltriphenylphosphonium bromide and *trans*-cinnamyl aldehyde. Triene **7** was obtained from the catalytic hydrogenation of 1,2,6-triphenyl-(*E,Z*)-hexa-1,3-dien-5-yne. The diene was obtained from the Wittig reaction of *trans*- α -phenylcinnamyltriphenylphosphonium bromide and phenylpropargyl aldehyde followed by chromatographic separation of the two isomers.

(22) It should be pointed out that even though the photoreaction is stereospecific it is not necessarily concerted, even though it is allowed to be so. The concertedness of the reaction still has to be experimentally verified.

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The Photolysis of Sulfur Ylides. Diphenylsulfonium Allylide

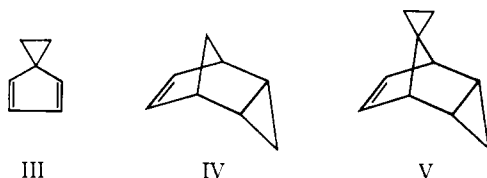
Sir:

The utility of sulfur ylides in organic synthesis depends upon a definition of their reactivity and the availability of diverse ylides. In our work directed toward these goals, we have examined the thermal, photochemical, and catalyzed decomposition of dimethylsulfonium phenacylide¹ as well as the properties

of other new sulfur ylides.² One aspect of ylide reactivity that remains to be defined is their ability to undergo α elimination. In this paper, we wish to report a new reaction of a sulfur ylide which relates to this important question.

Allyldimethylsulfonium salts upon base treatment had been found to principally undergo rearrangement to derivatives of 4-methylthio-1-butene and thus precluded studies of the corresponding allylides.^{2c,3} On the other hand, diphenylsulfonium allylide (II) can readily be generated from its corresponding salt I.⁴ If α elimination to vinylcarbene occurred, intramolecular trapping to yield cyclopropene would be expected. Thus, providing such an intramolecular olefin trap should avoid the problem of intermolecular trapping of the carbene by starting sulfur ylide.

Thermal (from -78 to 100°) and metal-catalyzed decomposition of the ylide generated no cyclopropene. Two methods of detection were employed. In the first technique, all volatiles were passed through a pentane solution containing cyclopentadiene at 0° —a method shown independently to trap cyclopropene quantitatively. Alternatively, spiro[4.2]hepta-2,4-diene (III) was employed in the reaction mixture. Both dienes have been shown to produce the endo Diels-Alder adducts IV and V.



Photolysis of the ylide solution containing the diene III at -78° decolorized the bright yellow solution in less than 1 hr.⁵ Vpc analysis revealed two peaks. The shorter retention time peak (50% relative yield) corresponded to V; a collected sample was identical in every respect with an authentic sample of V (see Scheme I). The second peak (50% relative yield) corresponded to three compounds in the ratio of 10:3:1. Preparative thick layer chromatography separated the components. Each was isomeric with

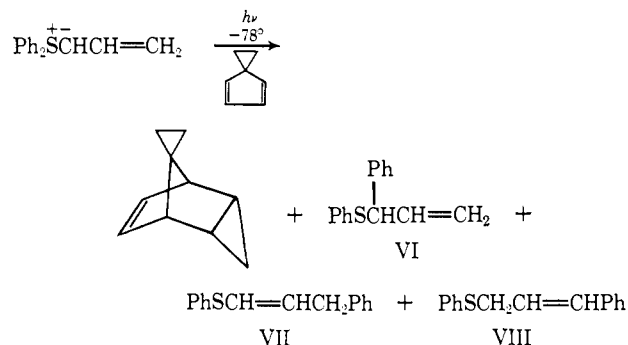
(1) B. M. Trost, *J. Amer. Chem. Soc.*, **89**, 138 (1967); **88**, 1587 (1966).
 (2) (a) J. Adams, L. Hoffman, Jr., and B. M. Trost, *J. Org. Chem.*, **35**, 1600 (1970); (b) B. M. Trost, R. LaRoche, and R. C. Atkins, *J. Amer. Chem. Soc.*, **91**, 2175 (1969); (c) B. M. Trost and R. LaRoche, *Tetrahedron Lett.*, 3327 (1968); (d) B. M. Trost and R. C. Atkins, *ibid.*, 1225 (1968); (e) C. Kaiser, J. Berson, J. Weinstock, and B. M. Trost, *J. Org. Chem.*, **30**, 3972 (1965).

(3) (a) J. E. Baldwin and R. E. Hackler, *J. Amer. Chem. Soc.*, **91**, 3646 (1969); (b) J. E. Baldwin, R. E. Hackler, and D. P. Kelly, *Chem. Commun.*, 537, 538, 1083 (1968); (c) J. E. Baldwin and D. P. Kelly, *ibid.*, 899 (1968); (d) J. E. Baldwin, R. E. Hackler, and D. P. Kelly, *J. Amer. Chem. Soc.*, **90**, 4758 (1968); (e) R. B. Bates and D. Feld, *Tetrahedron Lett.*, 417 (1968); (f) G. M. Blackburn, W. D. Ollis, J. D. Plackett, C. Smith, and I. O. Sutherland, *Chem. Commun.*, 186 (1968); (g) G. M. Blackburn and W. D. Ollis, *ibid.*, 1261 (1968); (h) G. M. Blackburn, W. D. Ollis, C. Smith, and I. O. Sutherland, *ibid.*, 99 (1969); (i) R. W. C. Cose, A. M. Davies, W. D. Ollis, C. Smith, and I. O. Sutherland, *ibid.*, 293 (1969); (j) W. Kirmse and M. Kapps, *Chem. Ber.*, **101**, 994, 1004 (1968); (k) W. Ando, K. Nakayama, K. Ichibori, and T. Migita, *J. Amer. Chem. Soc.*, **91**, 5164 (1969).

(4) For an alternative course during preparation of allyl diphenylsulfonium fluoroborate, see J. E. Baldwin and R. E. Plavy, *Tetrahedron Lett.*, 5029 (1968).

(5) For photolyses of stabilized sulfur ylides see ref 1 and (a) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **86**, 1640 (1964); (b) Y. Kishida, T. Hiraoka, and J. Ide, *Tetrahedron Lett.*, 1139 (1968); (c) R. H. Fish, L. C. Chow, and M. C. Caserio, *ibid.*, 1259 (1969); (d) W. Ando, T. Yagihara, S. Tozune, and T. Migita, *J. Amer. Chem. Soc.*, **91**, 2786 (1969); (e) A. W. Johnson and R. T. Amel, *J. Org. Chem.*, **34**, 1240 (1969); (f) T. Kunieda and B. Witkop, *ibid.*, **91**, 7751, 7753 (1969).

Scheme I. Photolysis of Diphenylsulfonium allylide

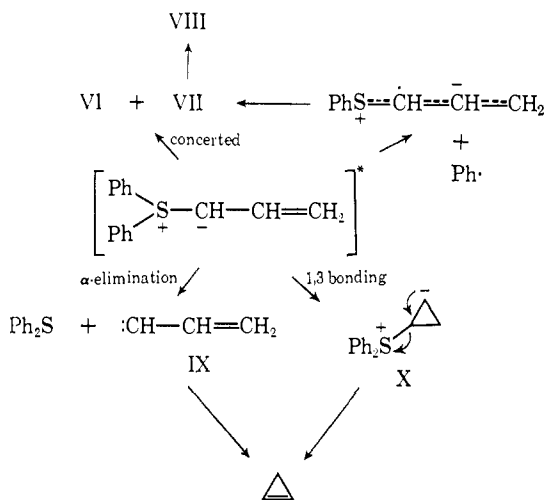


starting ylide II.⁶ The major material exhibited nmr absorptions at δ 4.69 (doublet, 1 H, $J = 7.3$ Hz), 4.95 (doublet with fine splitting, 1 H, $J = 17$ Hz), 5.02 (doublet with fine splitting, 1 H, $J = 9.5$ Hz), 6.0 (multiplet, 1 H), and 7.2 (multiplet, 10 H). Its mass spectrum showed a molecular ion peak at m/e 226 as well as a base peak at m/e 117 corresponding to loss of PhS. Its ultraviolet spectrum had λ_{\max} nm (ϵ) at 252 (4240) indicative of a thiophenyl ether chromophore. The data clearly support structure VI. The remaining two components were present in smaller amounts. Compound VII (the second most abundant component) exhibited a pair of doublets at δ 3.43 ($J = 7.0$ Hz) and 3.65 ($J = 7.5$ Hz) for a total of 2 H, a multiplet at 6.0 for 2 H, and aromatic absorptions for 10 H centered at 7.2. The mass spectrum shows a molecular ion at m/e 226 as well as intense peaks for loss of PhS (117), PhSCH=CH (91), and PhSCH=CHCH₂ (77). Its ultraviolet spectrum with λ_{\max} nm (ϵ) at 248 (6500) and 264 (6700) was quite similar to phenylpropenyl sulfide. These data clearly indicate the assigned structure VII present as a mixture of cis and trans isomers. Compound VIII showed a doublet further split for 2 H at δ 3.62 ($J = 6$ Hz), a multiplet for 2 H at 6.2, and an aromatic multiplet for 10 H centered at 7.2. Its mass spectrum possesses in addition to a molecular ion peak at m/e 226 relatively intense peaks for loss of Ph (149), PhS (117), and PhSCH=CH (91). The ultraviolet spectrum shows a single maximum at 252 nm (ϵ 5100) indicative of overlapping PhS and styryl chromophores. The structure shown was assigned on this basis; it probably is a mixture of cis and trans isomers.

The formation of phenyl-migrated products could arise either by a concerted or nonconcerted path. For the former, we can treat our system as a butadiene occupied by five electrons and a phenyl radical. Depending on the electronic configuration of the excited state either 1,2 or 1,4 migration would be a symmetry-allowed process. Furthermore, since d orbitals are undoubtedly involved in bonding of sulfur ylides their role in determining the preferred pathway obscure interpretations based on orbital symmetry. Scheme II outlines a nonconcerted path for the rearrangement. Simple homolysis of the phenyl-sulfur bond followed by recombination would generate the observed products. Preferential coupling would be expected to occur at the α carbon since it is the site of highest electron density. The formation of cinnamylphenyl sulfide in addition to 1-phenylthio-3-phenylpropene

(6) All new compounds exhibited satisfactory analytical data.

Scheme II. Mechanistic Interpretations



was not unexpected since base-catalyzed double bond isomerizations proceed readily in such systems.

The formation of the Diels-Alder adduct III demonstrates the intermediacy of cyclopropene. However, such a discovery does not unambiguously indicate the intermediacy of the carbene IX. Alternatively, 1,3 bonding in the ylide to generate the cyclopropyl anion X followed by β elimination also yields cyclopropene. The great endothermicity associated with such a ring closure in the present case (going from a highly stabilized anion to a highly localized charge-separated species) either suggests the improbability of such a path or that 1,3 bonding occurs during internal conversion (*i.e.*, as the energy of the excited state dissipates by non-radiation processes). Such a ring closure is unprecedented. The apparent ability of other sulfur ylides to undergo α elimination during photolysis suggests the likelihood of the carbene pathway in the present case. The present results clearly rule out the intermediacy of carbenes in thermal decompositions of sulfur ylides. The present results also illustrate the utility such α eliminations may play in synthesis since the yield of trapped cyclopropene (25% yield based on ylide) is greater than other corresponding α eliminations (*e.g.*, allyl chloride or vinyl diazomethane). Since the spiro-diene III can be demonstrated to trap only about one-third to one-half of the formed cyclopropene, the actual yield of such an α elimination is much higher than that of the isolated adduct.

Acknowledgment. We wish to express our gratitude to the National Institutes of Health for their generous support of our work.

(7) National Institutes of Health Predoctoral Fellow.

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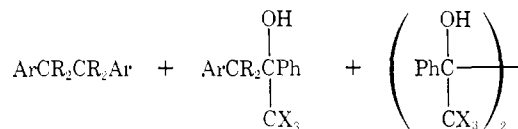
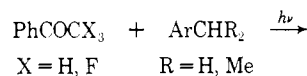
Photoreduction of α -Trifluoroacetophenone by Alkylbenzenes. Another Charge-Transfer Process

Sir:

Although photoreduction of ketones is probably the most studied of photochemical reactions, there have

been relatively few studies of the inductive effects of substituents on excited state reactivity.¹ We have compared the behavior of α -trifluoroacetophenone to that of acetophenone itself^{1,2} and find that the excited triplet of the former is photoreduced by electron transfer from such weak donors as alkylbenzenes.

The actual reduction proceeds similarly for both ketones, in that bibenzyls, pinacols, and cross-coupling products account for all the reacted ketone. Quantum



yields of product formation were measured for both ketones in degassed benzene solutions as a function of concentration of toluene, cumene, and *p*-xylene. Results plotted according to eq 1 gave linear plots with the slopes and intercepts indicated in Table I. Y_{BB} repre-

$$\Phi_{\text{BB}}^{-1} = Y_{\text{BB}}^{-1}P^{-1} \left(1 + \frac{k_d}{k_t[\text{S}]} \right) \quad (1)$$

sents the actual yield of bibenzyl; P , the probability that intermediates other than the excited state proceed on to products rather than reverting to ground states of reactants; $[\text{S}]$, the concentration of alkylbenzene; k_d , the

Table I. Kinetic Data for Photoreduction of Acetophenone and α -Trifluoroacetophenone by Alkylbenzenes in Benzene

Ketone	Substrate	Y_{BB}	$Y_{\text{BB}}P^a$	k_d/k_t^b	k_r ,	k_d ,
					$M^{-1} \text{ sec}^{-1} \text{ }^c$	$10^6 \text{ sec}^{-1} \text{ }^d$
PhCOCH ₃	<i>p</i> -Xylene	0.44	0.10	1.0	0.70 ^c	0.7 (0.5)
PhCOCH ₃	Cumene	0.39	0.18	2.5	0.28	0.7
PhCOCH ₃	Toluene	0.39	0.13	5.8	0.12	0.7
PhCOCF ₃	<i>p</i> -Xylene	0.35	0.04	0.09	97.0 ^c	9.0 (7.0)
PhCOCF ₃	Cumene	0.34	0.06	2.7	3.3	9.0
PhCOCF ₃	Toluene	0.32	0.05	1.2	7.5	9.0
PhCOCF ₃	Toluene- α -d ₃	0.31	0.015	1.2	7.5	9.0

^a Reciprocal of intercept of plots according to eq 1. ^b Slope/intercept of plots according to eq 1. ^c Slope of plots according to eq 2. ^d Values in parentheses are the intercepts of plots according to eq 2.

rate of radiationless decay of the ketone triplet; k_r , the rate constant for interaction of ketone triplet with substrate. Reduction of both ketones at 3660 Å was quenched with naphthalene at various concentrations of *p*-xylene. Stern-Volmer plots were linear, as were plots of $1/\tau$ (calculated from the S-V slopes) vs. $[\text{S}]$, the slopes of which equal k_r . The k_r values for the other substrates were determined from the measured k_d/k_r values and the assumed constant value of k_d .

$$1/\tau = k_d + k_r[\text{S}] \quad (2)$$

(1) For one example, see N. C. Yang and R. Dusenbery, *Mol. Photochem.*, **1**, 159 (1969).

(2) For previous studies on acetophenone, see (a) S. G. Cohen and B. Green, *J. Amer. Chem. Soc.*, **91**, 6824 (1969); (b) C. Walling and M. J. Gibian, *ibid.*, **87**, 3361 (1965).