Table I. Sensitized Photoisomerization of the 1,3-Pentadienes[a]

Sensitizer (E_T)	a	$\phi_{c\rightarrow t}$	$\phi_{t\rightarrow c}$	% [t]$_s$
Benzophenone (68)[b]	1.00[c]	0.55_5	0.44_5	$55._5$
Fluorenone (53)	0.94[c]	0.52	0.31	$67._2$
Pyrene (48)	0.11 ± 0.04[d]	0.04_4	0.03_8	$64._6$

[a] Quantum yields in Tables I and II are independent of diene concentration in the range employed. [b] A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965). [c] From footnote *b* assuming $a = 1.00$ for benzophenone. [d] W. Heinzelmann and H. Labhart, *Chem. Phys. Lett.*, **4**, 20 (1969); pyrene 2×10^{-3} *M*. For 2×10^{-3} *M* pyrene $a = 0.08$ was obtained from the $\phi_{c\rightarrow t}$ value in Table I assuming only s-trans conformer excitation. The $\phi_{t\rightarrow c}$ value obtained for the pyrene–1,3-pentadiene system is higher than expected. Pyrene fluorescence quenching by the dienes was negligible.

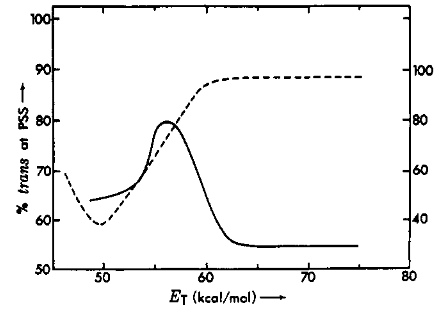
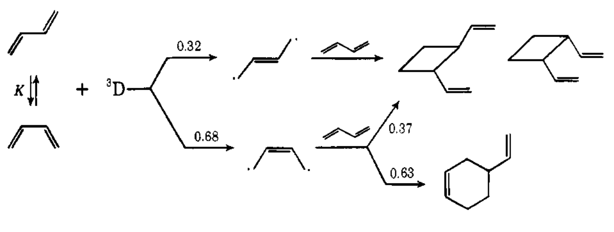


Figure 1. 1,3-Butadiene dimer compositions from ref 1 (dashed line); 1,3-pentadiene photostationary states from ref 4, except for benzil (−69.7%), fluorenone (−67.2%), and pyrene (−64.6%) values which are from this work (solid line).

s-trans conformers is likely for both dienes. Values of $k_3/(k_3 + k_4K)$ and $k_4K/(k_3 + k_4K)$ can be estimated by assuming that the minimum in the dimer plot reflects exactly the reactivity of s-cis triplets, Scheme I.[6] Using eq 10 and the fluorenone $\phi_{t\rightarrow c}/a$ value, $\alpha' = 0.72$ is obtained. This suggests that the decreased trans content in 1,3-pentadiene photostationary states, $E_T <$ 56 kcal/mol, is due to selective formation of s-cis triplets from *trans*-1,3-pentadiene.

Scheme I. Fluorenone-Sensitized 1,3-Butadiene Dimerization



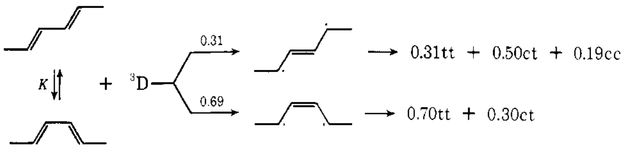
2,4-Hexadienes. Corrected quantum yields for the benzophenone-, the fluorenone-, and the pyrene-sensitized photoisomerizations of the 2,4-hexadienes are compared in Table II. Fluorenone and benzophenone data starting with either *cis,cis*- or *trans,cis*-2,4-hexadiene are similar, suggesting that interaction of fluorenone triplets with these isomers produces mainly *s-trans*-2,4-hexadiene triplets. By contrast, isomerization quantum yields obtained with fluorenone or pyrene as sensitizer for the trans,trans isomer are lower than with benzophenone. It follows that excitation of s-cis diene conformers is important when *trans,trans*-2,4-hexadiene is the acceptor. If s-cis triplets decay only to tt and tc, the ratios of $\phi_{tt\rightarrow cc}/a$ and the decay fractions of the s-trans triplets[7] indicate that 31 and 10% of the fluorenone and pyrene excitation transfer events, respectively, produce s-trans triplets. The resulting values for α'', the decay fraction of s-cis triplets to tt, are 0.70 and 0.69 from the fluorenone and pyrene $\phi_{tt\rightarrow ct}/a$, respectively, in agreement with $\alpha' = 0.72$ for the 1,3-pentadiene triplets. Scheme II summarizes the interpretation of the fluorenone results.

Table II. Sensitized Photoisomerization of the 2,4-Hexadienes

Sensitizer	$\phi_{tt\rightarrow ct}/a$	$\phi_{cc\rightarrow ct}/a$	$\phi_{ct\rightarrow tt}/a$	$\phi_{cc\rightarrow tt}/a$	$\phi_{tt\rightarrow cc}/a$	$\phi_{ct\rightarrow cc}/a$
Benzophenone[a]	0.48	0.50	0.33	0.29	0.18	0.16
Fluorenone	0.36	0.52	0.29	0.27	0.05_8	0.12_3
Pyrene[b]	0.33				0.02_0	

[a] J. Saltiel, L. Metts, and M. Wrighton, *J. Amer. Chem. Soc.*, **91**, 5684 (1969). [b] Assuming $a = 0.08$ for 2×10^{-3} *M* pyrene (see footnote *d*, Table I).

Scheme II. Fluorenone-Sensitized Isomerization of *trans,trans*-2,4-Hexadiene



In conclusion, it is encouraging that two independent methods predict almost identical distributions of s-trans and s-cis triplets by excitation transfer from fluorenone, and pyrene, as well as identical decay fractions for the s-cis triplets of two related 1,3-dienes.

Acknowledgment. This research was supported by the donors of the Petroleum Research Fund administered by the American Chemical Society, and by National Science Foundation Grant No. GP-24625.

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(6) The sensitivities of adduct compositions to sensitizer energy changes differ for dimerization and cross-adduct formation reactions suggesting different contributions of s-cis triplets to cyclobutane formation.[2]

(7) J. Saltiel, L. Metts, and M. Wrighton, *J. Amer. Chem. Soc.*, **91**, 5684 (1969).

(8) (a) Alfred P. Sloan Foundation Fellow, 1971–1973; (b) Petroleum Research Fund Fellow; (c) Petroleum Research Fund Scholar.

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Received July 19, 1971

Mechanism of Sulfonium Ylide Reactions. Synthesis of Cyclopropanes and Oxiranes of High Optical Purity[1]

Sir:

Sulfur ylides are popular and practical reagents for the synthesis of oxiranes and cyclopropanes. The

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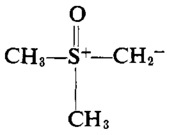
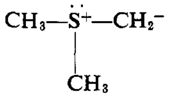
(1) Part XXXIV in the series "Chemistry of Sulfoxides and Related Compounds." We gratefully acknowledge support by the National Science Foundation (GP 19623).

classic reagents are dimethyloxosulfonium methylide (**1**) and dimethylsulfonium methylide (**2**).[2] The com-



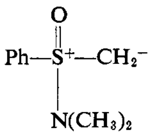
$$\mathrm{CH_3{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle CH_3}{|}}{S}}{}^{+}{-}CH_2^-}$$

1



$$\mathrm{CH_3{-}\overset{..}{\underset{\underset{\displaystyle CH_3}{|}}{S}}{}^{+}{-}CH_2^-}$$

2

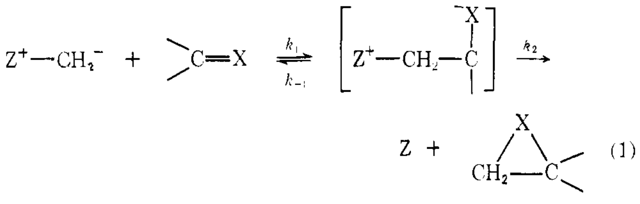


$$\mathrm{Ph{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle N(CH_3)_2}{|}}{S}}{}^{+}{-}CH_2^-}$$

3

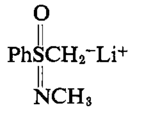
plementary behavior of methylides **1** and **2** in their stereo-[2,3] and regioselectivity[2] is an intriguing, but incompletely explained, phenomenon. This complementary behavior, which appears to be quite general, can be illustrated by a few selected examples from the original work by Corey and Chaykovsky. The reaction of **1** with 4-*tert*-butylcyclohexanone gives the (*Z*)-oxirane, whereas **2** yields the (*E*)-oxirane; **1** reacts with carvone to give the cyclopropyl ketone (from conjugate ylide addition) but with **2** to give the oxirane (1,2 addition at the carbonyl). In this communication we wish to discuss our findings which relate to these matters as well as report exemplary syntheses of an oxirane and a cyclopropane in high optical purity.

Although a zwitterionic intermediate (eq 1) has been generally accepted,[4] the reversibility[5] of its formation or even its existence has remained speculative.[6] We felt that the best, although permissive, evidence for resolution of this mechanistic problem would be obtained by the independent generation of the proposed intermediates.[8] (Dimethylamino)phenyloxosulfonium methylide (**3**)[7] has been shown to be similar in stability and reactivity to methylide **1**; oxosulfonium betaine intermediates derived from **3** should behave in like fashion to those derived from **1**. Independent synthesis of the former was considered to be a more feasible undertaking.



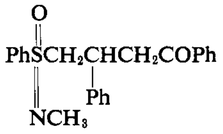
Z = dimethyl sulfide, dimethyl sulfoxide, *N*,*N*-dimethylbenzenesulfinamide, etc.

Lithium (*S*)-*N*-methylbenzenesulfonimidoylmethide (**4**)[9] added in the conjugate manner to *trans*-benzalacetophenone in dimethylformamide to yield, after neutralization, a mixture of diastereomers **5**. After separation on a silica gel column the diastereomeric adducts **5** were methylated with trimethyloxonium fluoroborate to give **6** (mp 98–101°) and **7** (mp 124–125° dec), the conjugate acids of the two diastereomeric betaines expected from ylide **3** and benzalacetophenone. Betaine **8**, generated by treatment of **6** with potassium *tert*-butoxide–*tert*-butyl alcohol, collapsed to give optically pure (+)-(1*S*,2*S*)-*trans*-1-benzoyl-2-phenylcyclopropane (**9**), $[\alpha]^{25}\mathrm{D}$ +393° (*c* 1.02, acetone), mp 66–70°,[10] in 91% yield. Treatment of **7** in a similar manner resulted in a 93% yield, of the enantiomeric cyclopropane, $[\alpha]^{25}\mathrm{D}$ −387 (*c* 1.0 acetone).



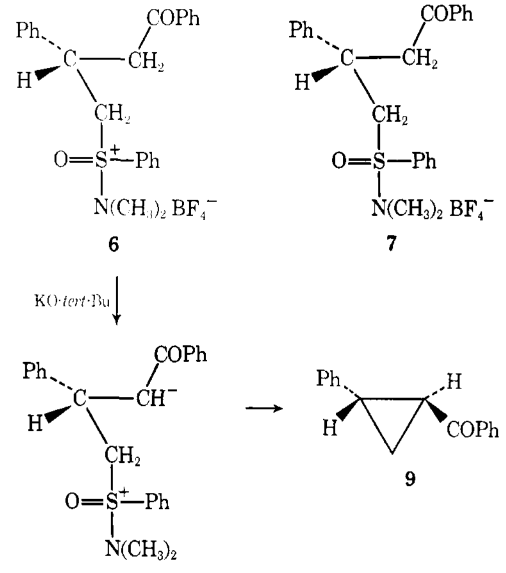
$$\mathrm{Ph\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle NCH_3}{\|}}{S}}CH_2^-Li^+}$$

4

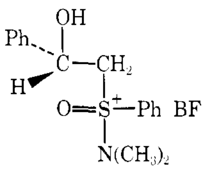


$$\mathrm{Ph\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle NCH_3}{\|}}{S}}CH_2\underset{\underset{\displaystyle Ph}{|}}{C}HCH_2COPh}$$

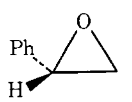
5



The reaction of **4** with benzaldehyde gave a mixture of diastereomers from which one (mp 99–100°) was obtained pure by recrystallization. Methylation of the pure diastereomer with trimethyloxonium fluoroborate gave **10**, mp 115–117°. Treatment of **10** with potas-



10



11

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(2) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **87**, 1353 (1965).

(3) (a) R. S. Bly, C. M. Dubose, and G. M. Konizer, *J. Org. Chem.*, **33**, 2188 (1968); (b) C. E. Cook, R. C. Corley, and M. E. Wall, *Tetrahedron Lett.*, 891 (1965); (c) R. G. Carlson and N. S. Behn, *J. Org. Chem.*, **32**, 1363 (1967); (d) C. E. Cook, R. C. Corley, and M. E. Wall, *ibid.*, **33**, 2791 (1968).

(4) For a review of sulfonium ylide chemistry, including mechanistic interpretations, see A. W. Johnson, "Ylid Chemistry," Academic Press, New York, N. Y., 1966, Chapter 9.

(5) For discussions of how reversibility of betaine formation might affect product stereochemistry, see ref 3a, b, and A. W. Johnson, V. J. Hruby, and J. L. Williams, *J. Amer. Chem. Soc.*, **86**, 918 (1964).

(6) It has been reported[7] that ylide **3** reacts with dimethyl maleate to give only *trans*-dimethyl 1,2-cyclopropanedicarboxylate. Excess maleate was isomerized in part to dimethyl fumarate. These results are consistent with the reversible formation of a long-lived betaine intermediate.

(7) C. R. Johnson, M. Haake, and C. W. Schroeck, *J. Amer. Chem. Soc.*, **92**, 6594 (1970).

(8) For a similar approach in a study of phosphonium ylide mechanisms, see D. E. Bissing and A. J. Speziale, *ibid.*, **87**, 2683 (1965).

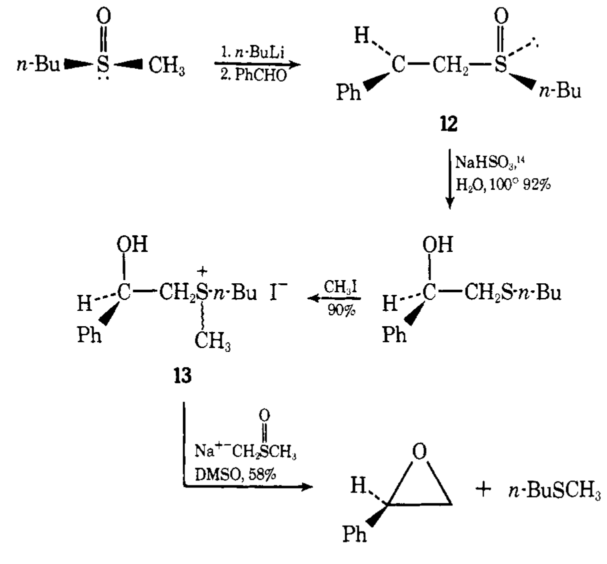
(9) This anion was prepared by treating (+)-(*S*)-*N*,*S*-dimethyl-*S*-phenylsulfoximine, $[\alpha]^{25}\mathrm{D}$ +183° (*c* 1.02, acetone) [C. W. Schroeck and C. R. Johnson, *ibid.*, **93**, 5305 (1971)], with butyllithium in ether.

(10) This material nonfractionally crystallized after chromatography on silica gel to remove the sulfinamide. From related work we have obtained an optically pure sample of **9**, $[\alpha]^{25}\mathrm{D}$ +390.5° (*c* 1.0, acetone), mp 70–71°.

sium *tert*-butoxide-*tert*-butyl alcohol gave (−)-(*S*)-styrene oxide (71%), $[\alpha]^{25}D$ −1.46° (*c* 4.7, acetone), of 22% optical purity.[11] This lowered value of optical purity is the same order of magnitude that would be expected from the direct reaction of optically pure ylide **3** and benzaldehyde,[11] which suggests that the betaine from **10** is in equilibrium with **3** and benzaldehyde. This suspicion was confirmed by generating the betaine (NaH, DMSO) in the presence of 1 equiv of a more reactive ylide substrate, *trans*-benzalacetophenone; an 80% yield of cyclopropane **9** was observed by vpc analysis of the reaction mixture. The ylide **3** was also trapped by protonation; the betaine conjugate acid **10**, when dissolved in aqueous sodium carbonate, was quantitatively converted to benzaldehyde and (dimethylamino)methylphenyloxosulfonium fluoroborate.[12]

Beginning with (+)-(*S*)-*n*-butyl methyl sulfoxide, $[\alpha]^{25}D$ +112° (*c* 1.02, isooctane, 94% optically pure),[13] the reactions summarized in Scheme I were completed.

Scheme I



Diastereomer **12**, mp 113.5–114.5°, was obtained pure by fractional recrystallization. Iodide **13** was produced and used as a mixture of diastereomers, mp 95.5–97.5°. By fractional distillation to separate *n*-butyl methyl sulfide, a 58% yield of styrene oxide, $[\alpha]^{25}D$ +32° (*c* 0.96, *dl*-styrene oxide, 90.3% optically pure)[11] was obtained.

The data cited in the foregoing three paragraphs clearly implicate betaine intermediates in nucleophilic methylene transfer reactions of sulfur ylides. Furthermore, it can be concluded that the initial attack of an oxosulfonium ylide at a carbonyl site is "reversible" (eq 1, $k_{-1} \geq k_2$), whereas attack by a simple sulfonium ylide is "irreversible" ($k_{-1} \ll k_2$). Since oxosulfonium ylides (*e.g.*, **1**) are known to be more stable than simple sulfonium ylides (*e.g.*, **2**), it is not surprising that the oxosulfonium ylides are better "leaving groups."[3b] The high optical purity of cyclopropane **9** and its enantiomer indicates that for collapse of their betaine precursors $k_2 \gg k_{-1}$. All comparative results in this and earlier studies seem to be consistent with the hypothesis that simple sulfonium ylides result in products dictated by kinetic control of betaine formation, whereas oxosulfonium ylides result in products predicted by thermodynamic considerations.

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(11) Optical data for an authentic sample assumed to be optically pure; $[\alpha]D$ +6.64° (*c* 4.9, acetone), +35.2° (neat). Highest reported value, $[\alpha]D$ +34.2° (neat) [D. J. Pasto, C. C. Cumbo, and J. Fraser, *J. Amer. Chem. Soc.*, **88**, 2194 (1966)]. The 5% optical purity of styrene oxide reported [C. R. Johnson and C. W. Schroeck, *ibid.*, **90**, 6852 (1968)] from an optically active ylide and benzaldehyde should read "23% optically pure."

(12) A similar sequence of reactions has been accomplished employing heptaldehyde rather than benzaldehyde.

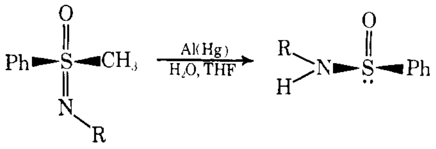
(13) The synthesis of this substance will be reported in a future paper.

(14) C. R. Johnson, C. C. Bacon, and J. J. Rigau, to be published.

Aluminum Amalgam Reduction of Aryl Sulfoximines and Related Compounds[1]

Sir:

Aluminum amalgam has been employed in organic syntheses for a variety of reductive transformations,[2] including the hydrogenolysis of organosulfur compounds. This mild reagent was used for desulfurization in the structural investigation of the antibiotic gliotoxin.[3] Amalgamated aluminum foil in aqueous tetrahydrofuran has been shown to be an excellent reagent for the hydrogenolysis of β-keto sulfoxides,[4,5] sulfones,[4] and sulfonamides.[4] We wish to report new results with this reagent in the reduction of a number of tetracoordinate hexavalent sulfur compounds. Our reactions were carried out under the conditions of Corey and Chaykovsky,[4] except that in all cases the temperature was kept at 25° or below. An excess of aluminum amalgam was added to a dilute solution of the sulfur compound in 10% water–90% tetrahydrofuran. The results of these reductions are summarized in Table I; the reactions proceed with better than 95% stereospecificity.



1, R = CH_3
2, R = H
3, R = p-$CH_3C_6H_4SO_2$

4, R = CH_3
5, R = H

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[1] Part XXXI in the series "Chemistry of Sulfoxides and Related Compounds." We gratefully acknowledge support by the National Science Foundation (GP 19623).

(2) For a review see L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Vol. I, Wiley, New York, N. Y., 1967, pp 20–22; Vol. II, 1969, p 19. See also E. J. Corey, N. H. Andersen, R. M. Carlson, J. Paust, E. Vedejs, I. Vlattas, and R. E. K. Winter, *J. Amer. Chem. Soc.*, **90**, 3245 (1968).

(3) J. D. Dutcher, J. R. Johnson, and F. W. Bruce, *ibid.*, **67**, 1736 (1945); J. R. Johnson and J. P. Buchanan, *ibid.*, **75**, 2103 (1953).

(4) E. J. Corey and M. J. Chaykovsky, *ibid.*, **86**, 1639 (1964); **87**, 1345 (1965).

(5) P. B. Gassman and G. D. Richmond, *J. Org. Chem.*, **31**, 2355 (1966).