

ozone to 1-phospha-2,8,9-trioxadamantane. Removal of the solvent from a portion of this solution under vacuum at -40° gave the solid ozonide **3** (0.06 mmol). A 5-ml solution of **1** ($2.8 \times 10^{-3} M$, 0.014 mmol) in the Tris buffer was added to the solid ozonide at -10° . The resulting solution was allowed to warm to ambient temperature over a period of 15 min. The uv spectrum of the solution indicated 63.1% reaction of **1**. A series of four experiments gave an average consumption of **1** of $63.7 \pm 3\%$. The reaction in the presence of 5 mg of SOD gave 63.3% conversion.

We have used the water-soluble 2,3-dicarboxylic acid derivative of 9,10-diphenylanthracene to further test our conclusion that SOD does not quench 1O_2 . A solution (10 ml) of **2** ($8.1 \times 10^{-5} M$) in aqueous Tris buffer (pH 8.8) with 50 mg of \oplus -Rose Bengal was irradiated with stirring under O_2 at 560 nm. The consumption of **2** was monitored by the decrease in the absorption at 380 nm. After 825 min, 50% of **2** had been consumed. The addition of SOD (1 mg/ml, $10^{-5} M$) had no effect on the rate of disappearance of **2** with 49% reaction after 825 min.

The decomposition of ozonide **3** is attended with chemiluminescence. We attribute this chemiluminescence to the singlet oxygen "dimol" emission.¹⁶ We have observed that SOD does not quench the luminescence produced by the decomposition of **3** in H_2O . The details of these experiments will be reported shortly.

We conclude on the basis of the results of the above experiments that superoxide dismutase does *not* quench singlet oxygen. SOD probably protects biological systems from oxidative damage by 1O_2 by removing $O_2^{\cdot-}$ via the SOD catalyzed dismutation reaction (eq 2) and preventing the formation of singlet oxygen.

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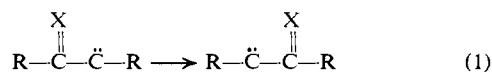
(16) A. U. Khan and M. Kasha, *J. Amer. Chem. Soc.*, **88**, 1574 (1966).
 (17) Alfred P. Sloan Research Fellow, 1974-1976.

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Evidence for the Discrete Existence of a Bicyclo[4.1.0]heptatriene

Sir:

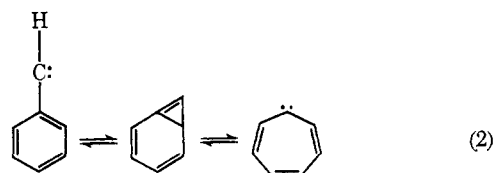
Carbene-carbene rearrangements in which a group migrates to the reaction site with generation of a new carbene (eq 1) are well documented in the now familiar



interconversion of phenylcarbene and its derivatives with cycloheptatrienylenes.^{1,2} Although a number

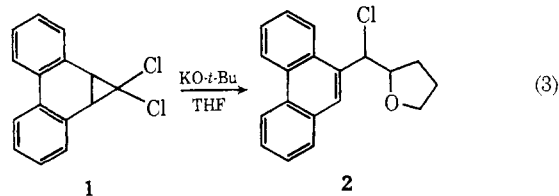
(1) (a) R. C. Joines, A. B. Turner, and W. M. Jones, *J. Amer. Chem. Soc.*, **91**, 7754 (1969); (b) J. A. Myers, R. C. Joines, and W. M. Jones, *ibid.*, **92**, 4740 (1970); (c) W. J. Baron, M. Jones, Jr., and P. P. Gaspar, *ibid.*, **92**, 4739 (1970); (d) P. O. Schissel, M. E. Kent, M. J. McAdoo, and E. Hedaya, *ibid.*, **92**, 2147 (1970); (e) E. Hedaya and M. E. Kent, *ibid.*, **93**, 3285 (1971); (f) T. Mitsuhashi and W. M. Jones, *ibid.*, **94**, 677 (1972); (g) G. G. Vander Stouw, A. R. Kraska, and H. Schechter, *ibid.*,

of attractive mechanisms have been considered,³ one which involves a bicyclo[4.1.0]heptatriene (eq 2) as an



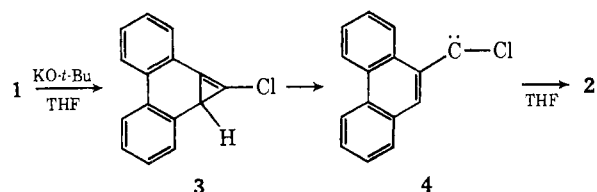
intermediate (or transition state) seems to have gained the most support. In this communication we report evidence for the discrete existence of a bicyclo[4.1.0]heptatriene derivative.

Treatment of 7,7-dichlorodibenzo[*a;c*]bicyclo[4.1.0]heptane (**1**)⁴ with a suspension of KO-*t*-Bu (2 equiv) in THF at 0° gives a yellow viscous oil identified as **2**^{5,6} (mixture of diastereomers) in 72% yield (eq 3).



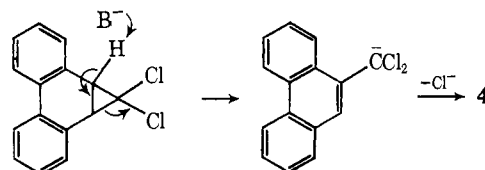
This observation is readily understood in terms of the dibenzobicycloheptatriene (**3**) shown in Scheme I,

Scheme I



although a mechanism which by-passes **3** is shown in Scheme II. Formation of the solvent insertion product

Scheme II



can, of course, be taken as evidence for formation of the carbene **4**.

In order to distinguish between these two mechanisms, an attempt was made to trap the cyclopropene

94, 1655 (1972); (h) K. E. Krajca, T. Mitsuhashi, and W. M. Jones, *ibid.*, **94**, 3661 (1972); (i) W. M. Jones, R. C. Joines, J. A. Myers, T. Mitsuhashi, K. E. Krajca, E. E. Waali, T. L. Davis, and A. B. Turner, *ibid.*, **95**, 826 (1973), and references cited therein.

(2) For similar rearrangements involving nitrenes see: C. Wentrup and K. Wilczek, *Helv. Chim. Acta*, **53**, 1459 (1970); W. D. Crow and C. Wentrup, *Chem. Commun.*, 1387 (1969); R. J. Sundberg and S. R. Suter, *J. Org. Chem.*, **35**, 827 (1970), and references cited therein.

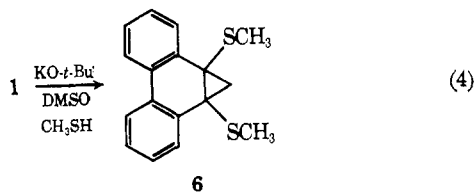
(3) For several views see ref 1a-g.

(4) Prepared as described by Joshi; see G. C. Joshi, N. Singh, and L. M. Pande, *Synthesis*, 317 (1972).

(5) Spectral data are: nmr (CCl_4) δ 1.70-2.20 (m, 4 H), 3.65-4.10 (m, 2 H) 4.40-4.80 (m, 1 H), 5.50-5.71 (one diastereomer exhibits a doublet at 5.53, 1 H, $J = 5$ Hz); the remaining diastereomer has the doublet at 5.63 (1 H, $J = 5$ Hz) and 7.30-8.80 (m, 9 H); ir (neat) 745 (s), 1060 (s), 1450 (s), 1498 (m), 1690 (s) cm^{-1} ; elemental composition was provided by high resolution mass spectroscopy, 296.0984 (m^+), calcd 296.0967.

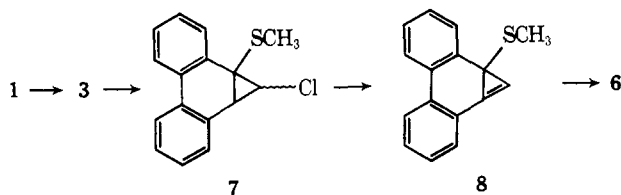
(6) Using nmr as a limit of detection insertion into the β position in THF was not observed.

before it rearranged to the carbene. The result of this study is shown in eq 4. Compound **6'** almost



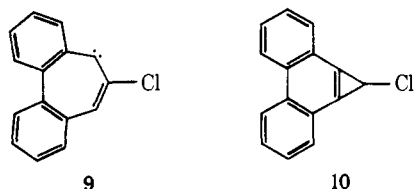
certainly arises by addition of the mercaptide to the cyclopropenes **3** and **8**⁸ (Scheme III). The addition of

Scheme III



nucleophiles such as mercaptide and alkoxide to cyclopropene double bonds is well preceded in the work of Shields and Gardner⁹ who have shown that these reactions are quite general.¹⁰

It is interesting that the cyclopropene **3** must be so unstable that it rearranges even at temperatures as low as 0° to give the arylcarbene, a species normally considered to be one of high energy. On the other hand, it must be sufficiently long-lived to experience addition of the nucleophile. The strain associated with **3** and the increase in resonance energy upon ring opening is probably sufficient to place the carbene at a lower energy than the cyclopropene. This is consistent with other examples of low temperature bicycloheptatriene → arylcarbene rearrangements.¹¹ We did not observe insertion products arising from the cycloheptatrienyldiene **9**, but this is not surprising since bicycloheptatriene → cycloheptatrienyldiene rearrangements normally occur at much higher temperatures (250–600°). Another fate of **3** would be base-catalyzed isomerization to the cyclopropene **10**; however, this requires a cyclopropene



anion¹¹ intermediate which is probably too energetic to be formed under these conditions.

In conclusion, although this study does not provide any evidence which implicates bicycloheptatrienes in the arylcarbene → cycloheptatrienyldiene rearrange-

(7) Product **6**, mp 149–149.5°, was produced in 84% yield. Nmr (CCl₄) δ 1.21 and 1.80 (ABq, J_{AB} = 5.5 Hz, 2 H, cyclopropyl), 2.1 (s, 6 H, SCH₃), 7.1–7.6 (m, 2H, aromatic) and 7.9–8.7 (m, 1 H, aromatic), mass spectral 284.0688 (m⁺), calcd 284.0692.

(8) The reaction was run with a sufficiently high concentration of KO-*t*-Bu and CH₃SH to minimize the formation of **7**. Experiments to trap the proposed bicycloheptatrienes with dienes are in progress.

(9) T. C. Shields and P. D. Gardner, *J. Amer. Chem. Soc.*, **89**, 5427 (1967).

(10) The regioselectivity of the addition of methylmercaptide to the cyclopropenes **3** and **8** is somewhat puzzling, since one might have expected that the anion would have added to give the more stable benzylic carbanion.

(11) R. Breslow, "Organic Reaction Mechanism," W. A. Benjamin, New York, N. Y., 1966, p 26.

ments that have been reported,¹ we believe that the evidence provided for the discrete existence of such a species is rather compelling. Additional results in this area will be provided shortly in a full paper.

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(12) Alfred P. Sloan Foundation Fellow, 1973–1975.

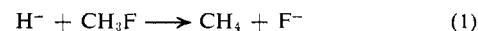
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Activation Energies in Nucleophilic Displacement Reactions Measured at 296°K *in Vacuo*

Sir:

Recent theoretical studies^{1,2} of the evolution of the energy of the reactants in several bimolecular nucleophilic displacement (S_N2) reactions have inferred the presence of measurable activation energies. Computational difficulties have limited such studies to reactions proceeding *in vacuo*, *i.e.*, in the absence of solvent. Consequently, comparisons with experimental measurements made in solution, where solvation of either the nucleophile or the fragment ion in the transition state can raise or lower the activation energy, are of limited value. We wish to report in this communication experimental measurements of S_N2 reactions made in the gas phase which allow, for the first time, direct comparisons with theoretical calculations. The experimental results are consistent with the prediction by theory^{1,2} of energy barriers for the reactions



and also suggest the presence of energy barriers for several other S_N2 reactions which may be amenable to calculation.

The experiments were performed in a flowing after-glow³ and were of the type described previously.^{4,5} The nucleophiles were all generated by the dissociative ionization of *ca.* 40 eV electrons: H⁻ and NH₂⁻ from NH₃ and CH₃NH₂, OH⁻ from H₂O, F⁻ from CF₄ and CH₃F, C₂H⁻ from C₂H₂, and CN⁻ from CH₃NH₂. Thermalization of the anions to the ambient room temperature of 296 ± 2°K prior to the reaction region was ensured by allowing the anions to undergo many thousands of collisions with the helium buffer gas molecules prior to their entry into the reaction region. The buffer gas was at a pressure of *ca.* 0.35 Torr. The methyl fluoride and methyl chloride reagent gases had minimum purities (liquid phase) of 99.0 and 99.5%, respectively. The measured rate constants which have an estimated³ accuracy of ±20% are summarized in Tables I and II. Contributions to the rate constants

(1) A. Dedieu and A. Veillard, *J. Amer. Chem. Soc.*, **94**, 6730 (1972).

(2) R. F. Bader, A. J. Duke, and R. R. Messer, *J. Amer. Chem. Soc.*, **95**, 7715 (1973).

(3) D. K. Bohme, R. S. Hemsworth, H. W. Rundle, and H. I. Schiff, *J. Chem. Phys.*, **58**, 3504 (1973).

(4) D. K. Bohme and L. B. Young, *J. Amer. Chem. Soc.*, **92**, 7354 (1970).

(5) L. B. Young, E. Lee-Ruff, and D. K. Bohme, *J. Chem. Soc., Chem. Commun.*, 35 (1973).