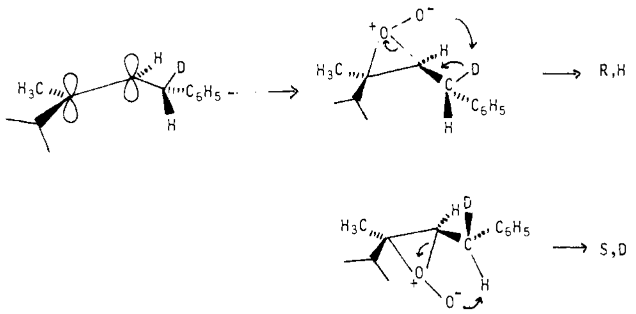
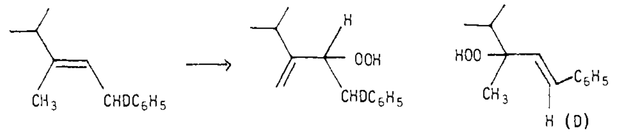
ticipate, in such a formulation, equivalent attack on the top and the bottom olefin faces, leading to equal yields of the two intermediates. Completion of the sequence would thus lead to



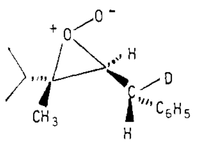
equal yields of the two products, with no apparent isotope effect or enantiomeric excess.

Singlet oxygenation of the opposite geometrical isomer, **6**, of this olefin leads to interestingly different results. The methyl group is now placed on the reactive disubstituted side[3] of the olefin π system and competes efficiently with the chiral center.

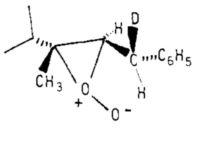


6 56% 44%

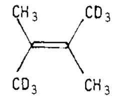
In this case one now anticipates, and finds, an isotope discrimination. Again, using the formalism of the perepoxide for purposes of discussion, one sees that, in **7**, the system has a choice of abstracting D from the chiral center or reacting with methyl C–H bonds and, in **8**, a choice of –H or the methyl C–H. We find an isotope effect of 1.2. This is exactly half the effect (1.4) found for the system **9**, which is ideally suited for



7



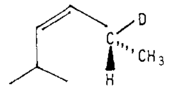
8



9

cis competition on both top and bottom faces. Again, in this case the enantiomeric ratio in the products (1.2) matches the isotopic ratio.

In our earlier study[4] on **10**, below, we reported completely analogous results when this reaction was carried out in acetone;



10

R/*S* and D/H ratios matched and were near unity for the allylic alcohol products. We also reported a novel solvent effect in which methanol was postulated to participate in the hydrogen abstraction step, while acetone did not. This provided an explanation for the high isotope effects (~2), but low enantiomeric ratios in the products obtained in methanol. This result can be duplicated in the present trisubstituted series if galvinoxyl is omitted from the reaction medium. Thus we believe that these results can be attributed to radical-chain processes (i.e., a hydrogen abstraction–allyl radical sequence) and are unrelated to the singlet oxygen mechanism.

The present results confirm that the singlet oxygen-ene reaction is a highly stereospecific suprafacial process. The absence of an isotope effect of any significant magnitude makes it difficult to argue for a traditional concerted transformation. We use the perepoxide here for discussion purposes only. We will present a comprehensive mechanism shortly which we believe is consistent with all recent data.

Acknowledgment. The work was supported by the National Science Foundation through Grants CHE 77-12744 (to CWRU) and CHE 78-21153 (to USC). The authors express appreciation to J. Hoover for moral support and experimental assistance.

References and Notes

(1) (a) A. A. Gorman, G. Lovering, and M. A. J. Rodgers, *J. Am. Chem. Soc.*, **101**, 3030 (1979); (b) R. D. Ashford and E. A. Ogryzlo, *Can. J. Chem.*, **52**, 3544 (1974); *ibid.*, **97**, 3604 (1975); (c) D. J. Bogan, R. S. Sheinson, R. G. Gann, and F. W. Williams, *ibid.*, **97**, 2560 (1975); (d) D. J. Bogan, R. S. Sheinson, and F. W. Williams, *ibid.*, **98**, 1034 (1976).

(2) The synthesis proceeds through the key intermediate, 2-deuterio-2-phenylethanol, a compound whose synthesis and chiroptical properties have been completely documented by R. L. Elsenbaumer and H. S. Mosher, *J. Org. Chem.*, **44**, 600 (1979).

(3) (a) M. Orfanopoulos, M. Bellarmine Grdina, and L. M. Stephenson, *J. Am. Chem. Soc.*, **101**, 275 (1979); (b) K. H. Schulte-Elte, B. L. Muller, and V. Rautenstrauch, *Helv. Chim. Acta*, **61**, 2777 (1978).

(4) L. M. Stephenson, D. E. McClure, and P. K. Sysak, *J. Am. Chem. Soc.*, **95**, 7888 (1973).

M. Orfanopoulos
Department of Chemistry, Case Western Reserve University
Cleveland, Ohio 44106

L. M. Stephenson*
Hydrocarbon Research Institute
University of Southern California
Los Angeles, California 90007

Received July 2, 1979

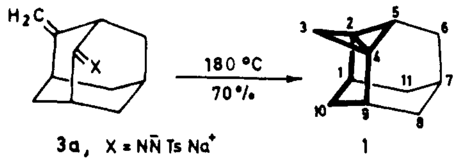
2,4-Methano-2,4-dehydroadamantane. A [3.1.1]Propellane[1]

Sir:

We report the first synthesis and characterization of 2,4-methano-2,4-dehydroadamantane[2] (**1**), a derivative of [3.1.1]propellane. This is the smallest carbocyclic propellane system which has been prepared.

Small-ring propellanes possess three rings fused together at the central bond containing two carbons with inverted tetrahedral geometry.[3] Decrease in ring sizes parallels increase in p character of the central bond, which approximates a p-p σ bond in smallest ring propellanes.[3-5] Carbocyclic propellanes containing three, four, and five bridge carbons ([1.1.1], [2.1.1], [3.1.1], and [2.2.1]) have not been synthesized so far. Propellane systems containing six bridge carbons, ([4.1.1],[6] [3.2.1],[3] and [2.2.2])[7] have been prepared rather recently and found to be very reactive. Large-ring propellanes, however, contain no inverted carbon and behave chemically like "normal" polycyclic hydrocarbons.[8]

2,4-Methano-2,4-dehydroadamantane (**1**) was prepared by the intramolecular cycloaddition of 4-methylene-2-adamantylidene (**2**) to the olefinic bond. Thus, treatment of 4-hydroxy-2-adamantanone[9] with methyl Grignard reagent, followed by Jones oxidation and acid-catalyzed dehydratation, afforded 48% 4-methylene-2-adamantanone[10] (**3**). Pyrolysis of the dry sodium salt of the tosylhydrazone derived from ketone **3** (**3a**) at 180 °C and 0.02 mmHg produced 70% **1**. The

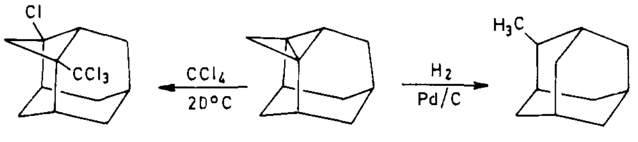


3a, X = N$\bar{\text{N}}$Ts Na$^+$ **1**

product sublimed into a trap cooled by liquid nitrogen and was found to be more than 95% pure by ^{13}C NMR.

The structure proof for **1** is based on the mass spectrum[11a] (*m/e* 146 (M$^+$)), the IR spectrum[11a] (ν 3040 cm^{-1}), the ^{1}H NMR spectrum ((C_6D_6) δ 2.36–1.06 (multiplet and two distinctive doublets at δ 2.12 and 1.08, J = 4 Hz[11b])), and the ^{13}C NMR spectrum ((C_6D_6) δ 64.4 (d, J = 166 Hz, 1 C; C-5), 50.1 (t, J = 129 Hz, 1 C; C-10 or C-6), 40.9 (dd, J = 151 and 169 Hz, 1 C; C-3), 44.0 (d, J = 138 Hz, 2 C; C-1, C-9), 34.2 (t, J = 128 Hz, 2 C; C-8, C-11), 30.8 (t, J = 129 Hz, 1 C; C-6 or C-10), 26.6 (d, J = 133 Hz, 1 C; C-7), and 24.2 (s, 2 C; C-2, C-4)). The C–H coupling constants of the ^{13}C NMR dd signal at δ 40.9 are typical of the methylene carbon in the bicyclobutane system.[13] In the ^{13}C NMR spectrum of 2,4-methano-*3,3-d*$_2$-2,4-dehydroadamantane (**1a**)[12] this signal is absent, which strongly supports the structure proof for **1**.

The chemistry of **1** is in accord with the structure of small-ring propellanes. At room temperature **1** decomposed slowly even in benzene solution under a nitrogen atmosphere. It reacted rapidly with oxygen and instantly with moisture, methanol, and bromine to give complex mixtures of products.[14] With carbon tetrachloride **1** reacted instantaneously at room temperature yielding 100% single product (≥98% pure by GLC), the spectral data[15] of which indicated that it was 2-chloro-4-trichloromethyl-2,4-methanoadamantane (**4**). Compound **4** was thermally stable [bp 110 °C (0.01 mm)] and inert to bromine (at 20 °C for 24 h). Hydrogenolysis of **1** with Pd/C in benzene solution at 20 °C and 1 atm produced 2-methyladamantane (**5**) as the major product (≥90%).[17] Interestingly, the central bond in **1** appears not to be cleaved in the first step, since this would lead to the stable 2,4-methanoadamantane.[18]



4 1 5

The carbene center in 4-methylene-2-adamantylidene (**2**) is not "ideally" situated[19] for the intramolecular cycloaddition to the olefinic bond. The angle between the axes of the carbene center p orbital and the olefinic bond p orbitals is ~60°. The arrangements of the carbene center and the γ-CH bonds in **2** and 2-adamantylidene are essentially equal, and the latter inserts readily into the γ-CH bonds.[20] Nevertheless, **2** yields exclusively the intramolecular cycloaddition product, **1**.

Acknowledgments. This work was supported by the Research Council of the Republic of Croatia (SIZ II). We thank Dr. Z. Meić for recording the ^{13}C NMR spectra.

References and Notes

(1) Presented in part at the 6th Meeting of Chemists of Croatia, Feb 1979, Zagreb, Yugoslavia.
(2) Pentacyclo[5.3.1.0^{2,4}.0^{2,5}.0^{4,9}]undecane.
(3) Wiberg, K. B.; Burgmaier, G. J. *J. Am. Chem. Soc.* **1972**, *94*, 7396; *Tetrahedron Lett.* **1969**, 317.
(4) Aue, D. H.; Reynolds, R. N. *J. Org. Chem.* **1974**, *39*, 2315, and references therein.
(5) The hybridization of the central bond in carbocyclic [1.1.1]-, [2.1.1]-, [3.1.1]-, [2.2.1]-, [3.2.1]-, [2.2.2]-, [3.3.1]-, [3.2.2]-, [3.3.2]-, and [3.3.3]propellanes has been calculated to be sp$^{43.9}$, sp$^{17.1}$, sp$^{10.8}$, sp$^{9.3}$, sp$^{6.7}$, sp$^{6.1}$, sp$^{5.3}$, sp$^{4.8}$, sp$^{4.0}$, and sp$^{3.5}$, respectively; see Herr, M. L. *Tetrahedron* **1977**, *33*, 1897.
(6) Szeimies-Seebach, U.; Szeimies, G. *J. Am. Chem. Soc.* **1978**, *100*, 3966.
(7) Eaton, P. E.; Temme G. H. III *J. Am. Chem. Soc.* **1973**, *95*, 7508. Wiberg, K. B.; Epling, G. A.; Jason, M. *Ibid.* **1974**, *96*, 912. Dannenberg, J. J.; Prociv, T. M.; Hutt, C. *Ibid.* **1974**, *96*, 913.
(8) Liebman, J. F.; Greenberg, A. *Chem. Rev.* **1976**, *76*, 311.
(9) Faulkner, D.; McKervey, M. A. *J. Chem. Soc. C* **1971**, 3906.
(10) **3:** mp 135–138 °C; ^{13}C NMR (CCl_4) δ 209.7 (s), 152.5 (s), 104.9 (t), 57.9 (d), 45.6 (d), 41.7 (t), 38.8, 38.0, 37.7, 37.2, 27.5 (d); ^{1}H NMR ($CDCl_3$) δ 4.65 (dd, 2 H), 3.15 (br s, 1 H), 2.63 (br s, 2 H), 2.25–1.85 (m, 9 H); IR (KBr) ν 3075 (m), 2920 (s), 2855 (s), 1725 (s), 1652 (m), 1450 (m), 1225 (m), 1065 (m) cm^{-1}; MS *m/e* 162 (M$^+$, 59%), 134 (29), 119 (28), 105 (43), 93 (100), 92 (100), 91 (100).
(11) (a) MS *m/e* 146 (M$^+$, 65%), 131 (85), 118 (60), 105 (91), 104 (83), 92 (46), 91 (100); IR (KBr) ν 3040 (m), 2905 (s), 2850 (m), 1462 (m), 1450 (m), 1190 (m), 1070 (m), 1020 (m) cm^{-1}. (b) These doublets are absent in the ^{1}H NMR spectrum of 2,4-methano-*3,3-d*$_2$-2,4-dehydroadamantane (**1**a).[12]
(12) Compound **1**a was prepared by pyrolysis of the tosylhydrazone sodium salt of 4-methylene-*d*$_2$-2-adamantanone.
(13) Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972; p 335.
(14) The study of the chemistry of **1** is in progress and will be published in a full paper.
(15) ^{13}C NMR (C_6D_6) δ 105.1 (s, 1 C), 62.4 (s, 1 C), 57.3 (s, 1 C), 51.4 (d, J = 145 Hz, 1 C), 43.0 (dd, J = 140 and 146 Hz, 1 C),[16] 39.2 (d, J = 138 Hz, 1 C), 35.8 (dd, —, 1 C), 34.0 (t, J = 128 Hz, 1 C), 31.3 (d, J = 135 Hz, 1 C), 31.0 (t, J = 126 Hz, 1 C), 27.2 (t, J = 126 Hz, 1 C), 24.9 (d, J = 135 Hz, 1 C); ^{1}H NMR (CCl_4) δ 3.05–1.25 (multiplet and two distinctive doublets[16] at δ 2.64 and 2.23, J = 9 Hz); IR (neat) ν 3010 (m),[16] 2920 (s), 2855 (m), 1465 (m), 1450 (m), 1157 (s), 920 (m), 890 (s), 783 (s), 760 (s) cm^{-1}; MS *m/e* 298 (M$^+$, 5%), 300 (6), 302 (3), 264 (100), 262 (100), 229 (45), 227 (70), 115 (50), 91 (79), 79 (73), 77 (83).
(16) This signal(s) is absent in the spectrum of 2-chloro-4-trichloromethyl-2,4-methano-*3,3-d*$_2$-adamantane (obtained from **1a**).
(17) The product was identified by comparing its ^{13}C NMR, ^{1}H NMR, IR, and mass spectra with those of an authentic sample of 2-methyladamantane.
(18) Sasaki, T.; Eguchi, S.; Hirako, Y. *J. Org. Chem.* **1977**, *42*, 2981.
(19) Hoffmann, R. *J. Am. Chem. Soc.* **1968**, *90*, 1475. Bodor, N.; Dewar, M. J. S.; Wasson, J. S. *Ibid.* **1972**, *94*, 9095.
(20) Udding, A. C.; Strating, J.; Wynberg, H.; Schlatmann, J. L. M. A. *Chem. Commun.* **1966**, 657.

Katica Mlinarić-Majerski, Zdenko Majerski*
Rudjer Bošković Institute, 41001 Zagreb
Croatia, Yugoslavia

Received July 23, 1979

Primary Quantum Yields of Ketyl Radicals in Photoreduction by Amines. Abstraction of H from N

Sir:

We report here laser flash photolysis studies which show that the primary reaction of benzophenone triplet with common aliphatic amines in benzene solution gives benzophenone ketyl radical with quantum yield φ = 0.9–1.0. Thus, significant quenching and return to ground-state ketone do not occur in an initially formed exciplex, and a modification of the proposed mechanism for photoreduction by amines is required.[1]

Ketone–amine solutions in benzene in 1 × 1 cm Pyrex cells were degassed by freeze–thaw cycles, placed under 1 atm of argon, and subjected to pulsed-laser photolysis at 347 nm. Flash apparatus and procedures were as described.[2] Transient spectra over the range of 360–700 nm and decay kinetics with time resolution ~50 ns identified the initial and final flash intermediates as benzophenone triplet and ketyl radical, respectively.[3,4] Triplet and radical decay were followed at 530 nm, where the short-lived triplet absorbs more strongly than the long-lived radical (Figure 1). The time resolution of the measurement permits use of such high concentrations of amine that over 90% of the triplet, calculated from triplet lifetimes in absence and presence of donor, decayed via reaction with the amine.[5] The resulting pseudo-first-order rate constant, k_d, was linear in concentration of donor, and the primary reaction rate constant, k_{ir}, was obtained from the slope (eq 1).

$$k_d = k_d{}^0 + k_{ir}[\text{amine}] \qquad (1)$$

The yield of radical from triplet is proportional to the ratio, $r = \Delta D_R{}^\infty / \Delta D_T{}^0$, where $\Delta D_T{}^0$ is the initial increment in absorbance immediately following the flash and $\Delta D_R{}^\infty$ is the change in absorbance corresponding to total formation of radical after decay of triplet is complete (Figure 1). Since the lifetime of the neutral radical is very much greater than that of the triplet, $\Delta D_R{}^\infty$ is obtained by a short extrapolation of the initial portion of the radical decay curve back to zero time,[5] and the ratio r may be measured with good precision. To convert values of r into quantum yields, we take φ_{ketyl} = 2 for

0002-7863/80/1502-1419$01.00/0