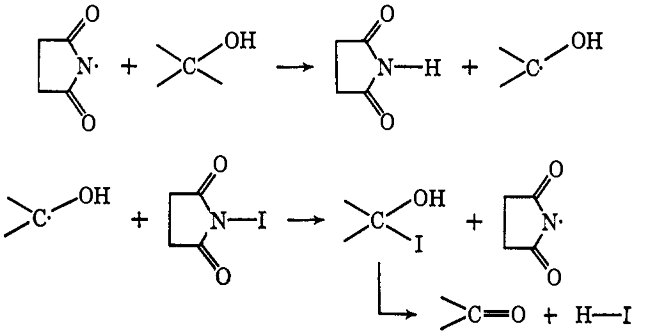
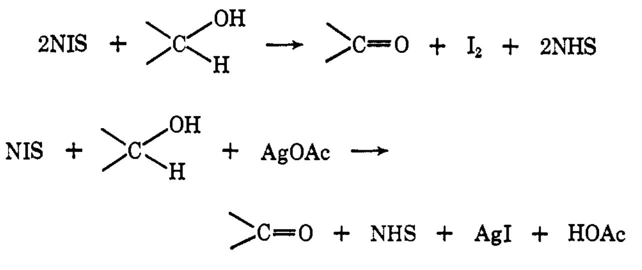
of ketone based upon total NIS, as was observed. Although run II also appeared to be a radical-chain reaction, the formation of iodine slowed the rate of ketone production. This was expected since iodine itself is a known scavenger of free radicals[6] and should decrease the chain length of the radical reaction. Attempts to oxidize the alcohol under the same free-radical conditions but using iodine rather than NIS failed to yield ketone, which supports the idea that the hydrogen-abstracting radical is the succinimidyl radical and not the iodine atom. If the iodine atom were the chain-propagating radical in the NIS reactions, then it would be expected that photolytic or peroxide initiation of the iodine reaction would also oxidize the alcohol. Furthermore, if the iodine atom were the chain-propagating radical, then run II, where iodine was produced as a side product, should have a faster rate than run III, where no iodine was produced due to the presence of silver acetate.

The possibility that the hydrogen-abstracting radical was the β-propionyl isocyanate radical[7] ($\cdot CH_2CH_2COCNO$), formed from the succinimidyl radical by ring cleavage, was ruled out as succinimide was recovered in 80–90% yield from the reaction mixtures. Succinimide was recovered from runs where silver acetate was added and from runs where no silver acetate was added. We propose that the oxidation mechanism involves the succinimidyl radical and is similar to that of Bloomfield's original suggestion.



In runs I and II, where silver acetate was absent, 2 mol of NIS was needed for the production of 1 mol of ketone as the hydrogen iodide product reacted with NIS to produce iodine and succinimide. When silver acetate was present the hydrogen iodide formed silver iodide before it could react with the NIS.



$$2\text{NIS} + {>}\text{C(OH)H} \longrightarrow {>}\text{C=O} + I_2 + 2\text{NHS}$$

$$\text{NIS} + {>}\text{C(OH)H} + \text{AgOAc} \longrightarrow {>}\text{C=O} + \text{NHS} + \text{AgI} + \text{HOAc}$$

The final yield of ketone produced in runs I, II, III, and IV relative to the amount of NIS present in the reaction was 50, 35, 80, and 64%, respectively. Based upon NIS available for oxidation the ketone yield in runs I and II was 100 and 70%.

The leveling off of plots of Figure 1 for runs II and III is attributed to the exhaustion of the supply of benzoyl peroxide which was not added except at the beginning of each reaction. The plot for run IV does not level off, and this is attributed to constant radical production during photolysis.

The rates of reaction were followed by injecting 5-μl samples of the reaction mixture on a 6-ft long vapor-phase chromatograph column holding 3% Carbowax 20-M and 7% SE-30 on Chromosorb P (60–80 mesh).

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Received December 12, 1968

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(6) W. A. Pryor, "Free Radicals," McGraw-Hill Book Co., Inc., New York, N. Y. 1966, p 94.

(7) J. C. Martin and P. D. Bartlett, *J. Am. Chem. Soc.*, 79, 2533 (1957).

Stable Carbonium Ions. XC.[1] The Octamethylbicyclo[3.3.0]octadienyl Dication, a Dihydropentalene Dication

Sir:

We undertook a study of the protonation of derivatives of tetramethylcyclobutadiene dimer in an attempt to prepare the octamethylhomotropylium ion **2**. This study is a continuation of our work on the protonation of hexamethyl Dewar benzene[2] and also the acid-catalyzed opening of cyclobutane rings.

We examined the protonation of *syn*- and *anti*-octamethyltricyclo[4.2.0.0^{2,5}]octa-3,7-diene (**1a** and **1b**, respectively), octamethylsemibullvalene (**1c**), and octamethylcyclooctatetraene (**1d**)[3] in $HFSO_3$–SbF_5–SO_2 solution at temperatures ranging from −10 to −60°. In every case the major species produced was the octamethylbicyclo[3.3.0]octadienyl dication (**3**). The structural assignment of ion **3** is based on the remarkable simplicity of its nmr spectrum (Figure 1) which consists of three singlets in the ratio 1.96:1.00:1.04 at δ 3.29, 2.30, and 2.05 (relative to capillary TMS). These chemical shifts are consistent with those of a methyl-substituted allylic cation and indicate that a cyclo-

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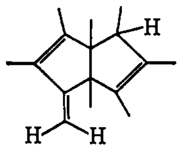
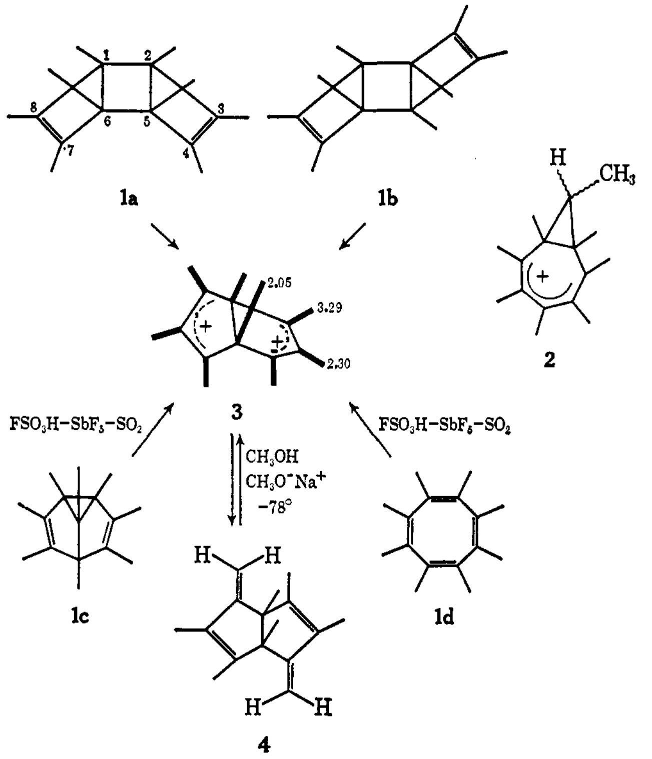
(1) Part LXXXIX: G. A. Olah, J. M. Bollinger, and A. M. White, *J. Amer. Chem. Soc.*, in press.

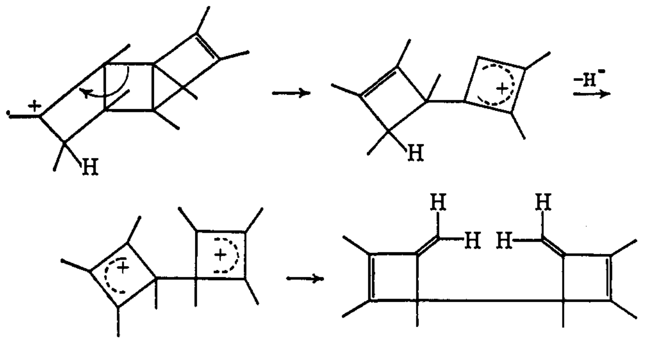
(2) P. A. Paquette, G. R. Krow, J. M. Bollinger, and G. A. Olah, *ibid.*, 90, 7147 (1968).

(3) The starting materials were prepared by known methods: *syn*-octamethyltricyclo[4.2.0.0^{2,5}]octadiene: R. Criegee and G. Louis, *Chem. Ber.*, 90, 417 (1957) (we thank Professor Leo A. Paquette for a sample); *anti*-octamethyltricyclo[4.2.0.0^{2,5}]octadiene: R. Criegee and G. Schröder *Ann. Chim.*, 623, 1 (1959); R. Criegee, G. Schröder, G. Maier, and H. G. Fischer, *Chem. Ber.*, 93, 1553 (1960); octamethylsemibullvalene: R. Criegee and R. Askani, *Angew. Chem. Intern. Ed. Engl.*, 1, 537, (1968); R. Criegee, W. O. Wirth, W. Engel, and H. A. Brune, *Chem. Ber.*, 96, 2230 (1963). Octamethylcyclooctatetraene was prepared in 10% yield by the pyrolysis of *anti*-octamethyltricyclooctadiene at 300° (3 mm) in a 38-cm column packed with glass helices. In this reaction 80% of the product was an oil, probably **5**, reported by R. Criegee and G. Louis, *Chem. Ber.*, 90, 424 (1957); 10% of the starting material was recovered unchanged. These materials were readily separated by column chromatography on silica gel.



5





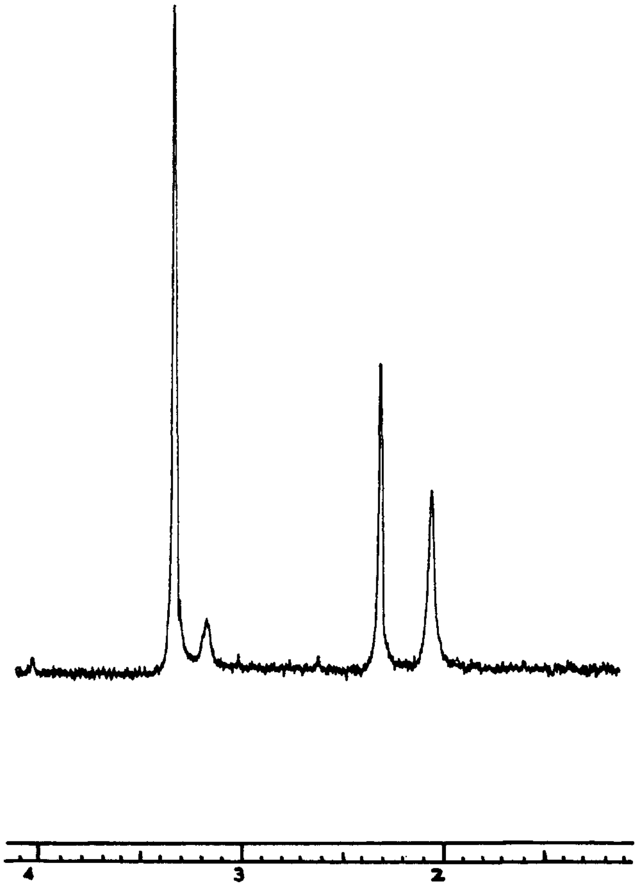


Figure 1. Nmr spectrum of the octamethylbicyclo[3.3.0]octadienyl dication in $HFSO_3$–SbF_5–SO_2 at −60° (prepared from **1c**).

butenyl structure need not be considered for this ion since these show chemical shifts for the corresponding groups at considerably higher field.[4a] This rules out a ring-opening path as indicated below. The dication produced in this way would accommodate the gross features of the spectrum observed for both the ion and its methanolysis product, but the olefinic protons in this latter compound have been reported to appear at considerably higher field[4b] than was found for **4**. Solvolysis of **3** in methanol–sodium methoxide or methanol–potassium carbonate at −78° gave the hydrocarbon **4** reported by Criegee.[5] Protonation of **4** at −78° regenerates **3**, although some broad high-field absorptions are also formed, indicating some polymerization. This is a common problem in attempting to generate carbonium ions from olefins in strong acids.

The best spectrum of **3** was obtained from **1c**. From both **1a** and **1b** several absorptions due to other unidentified ions were observed. The amount of these absorptions was greater from **1b** than from **1a**, but the difference is not enough for us to draw any conclusions concerning the stereochemical preferences of the ring expansion. Ion **3** could also be produced from **5**.

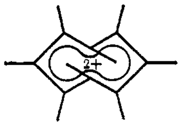
The most probable path of the reactions is through protonation followed by hydride abstraction. Protonation of **1a–1d** in fluorosulfuric acid–sulfur dioxide solution leads to nearly identical, very complex spectra. The absorptions in these spectra are probably due to an allylic monocation since this acid is not strong enough to effect hydrogen abstraction to the dication. When SbF_5 is subsequently added to these solutions and they are allowed to warm to about −10°, the complex spectrum begins to disappear and is replaced by the spectrum of **3**. Simultaneously, hydrogen evolution takes place.

One additional feature of the spectrum of **3** which deserved comment is the fact that the high-field signal is broader than the others (Figure 1). Lowering the temperature results in this signal broadening more rapidly than the others, which suggests that rotation of these methyl groups is hindered. Models support this idea. We have not yet succeeded in obtaining a low-temperature spectrum (−110 to −130°) with sufficient resolution to allow analysis of the kinetic process.

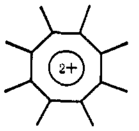
(4) (a) The 1,2,3,4-tetramethylchlorocyclobutenium cation (T. J. Katz and E. H. Gold, *J. Amer. Chem. Soc.*, 86, 1600 (1964)) shows absorptions at 2.92 (6 H), 2.47 (3 H), and 2.32 (3 H) in 1:1 $HFSO_3$–SbF_5 in SO_2 at −60°. A substantial 1,3 interaction (homoaromaticity) is the reason usually given for the fact that the 1- and 3-methyl groups are at higher field and the 2-methyl group at lower field in cyclobutenium cations than the corresponding methyl groups are in open-chain or five-membered ring allylic cations. (b) R. Criegee, J. Dekker, and H. A. Brune, *Chem. Ber.*, 96, 2368 (1963).

(5) We were unable to induce this oily material to crystallize (*cf.* R. Criegee, W. D. Wirth, W. Engel, and H. A. Brune, *ibid.*, 96, 2330 (1963); G. Maier, *ibid.*, 96, 2238 (1963), reports mp 55° (after recrystallization from methanol) and the identity of this material is inferred from the similarity of the nmr spectra and the specific ir absorptions of the two materials. In CCl_4 from internal TMS, **4** shows absorptions at δ 1.09 (6 H), 1.61 (6 H), 1.67 (6 H), 4.64 (2 H), and 4.75 (2 H).

Another structure for this ion which deserved consideration was that of the octamethylcyclooctatrienyl dication **6** which could conceivably exist in two forms, **a** or **b**, as shown below. In **b** one would conclude that the methyl groups should be equivalent. We cannot rigorously exclude **a**, but this structure seems unlikely.

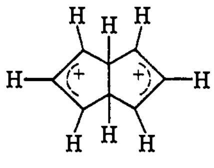


6a



6b

We also considered the possibility that cyclooctatetraene might rearrange to the bicyclo[3.3.0]octadienyl dication (**7**) in the super acid medium HFSO$_3$–SbF$_5$.[6] This was not the case, for when cyclooctatetraene was added to 1 : 1 fluorosulfuric acid–antimony pentafluoride in sulfur dioxide solution, a poorly resolved spectrum of the homotropylium ion was obtained.[7] It was possible to prepare a solution of this ion giving a well-resolved spectra by adding cyclooctatetraene to fluorosulfuric acid in sulfur dioxide and then adding antimony pentafluoride. Aside from slight changes in chemical shifts, the spectrum was identical with that reported for the homotropylium cation. We are continuing our studies on pentalenyl dications and bicyclo[3.3.0.]octadienyl-dications.



7

Acknowledgment. The National Science Foundation and the Petroleum Research Fund administered by the American Chemical Society are thanked for partial support and the Badische Anilin und Soda Fabrik for a gift of cyclooctatetraene.

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(6) Cyclooctatetraene undergoes a thermal rearrangement to dihydropentalene: M. Jones, Jr., and L. O. Schwab, *J. Amer. Chem. Soc.*, **90**, 6549 (1968).

(7) C. E. Kellen and R. Pettit, *ibid.*, **88**, 604 (1966); S. Winstein, C. G. Kreiter, and J. I. Brauman, *ibid.*, **88**, 2047 (1966).

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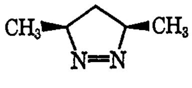
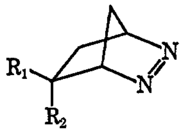
Thermolysis of *exo*-6,7-Diazatricyclo[3.2.1.0^{2,4}]-6-octene

Sir:

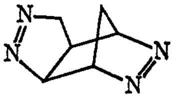
It is well established that simple alkyl cyclic azo compounds such as **1** and **2** thermally decompose in a stepwise manner by extrusion of molecular nitrogen to give 1,3-diradical-like intermediates which then form products.[1,2] As we reported recently,[3] **3** decomposes with an appreciable contribution from a reverse Diels–Alder reaction pathway which does not involve nitrogen loss. We now wish to record evidence that *exo*-6,7-diazatricyclo[3.2.1.0^{2,4}]-6-octene (**4**) decomposes by yet another mechanism. In this connection, **4** *shows an enormous reactivity ratio of* 10^{11} compared to structurally related **2**.



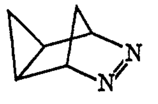
1



2a, R$_1$ = H; R$_2$ = H
b, R$_1$ = OCH$_3$; R$_2$ = H
c, R$_1$ = H; R$_2$ = OCH$_3$



3

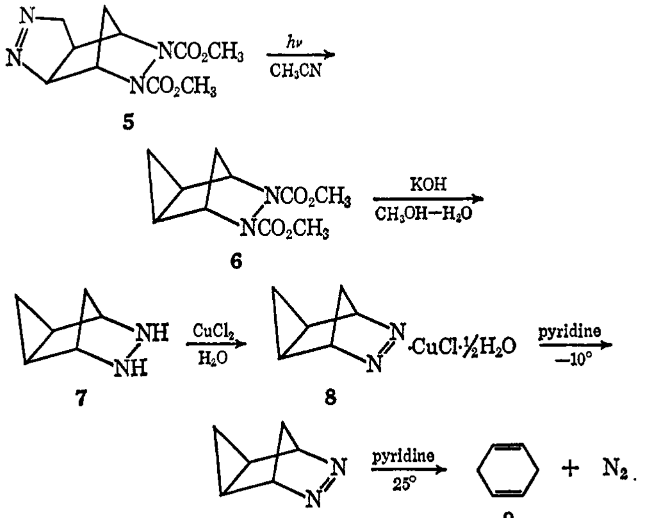


4

Scheme I outlines the synthetic sequence used to convert **5**[4] to **4**.[5] Irradiation of **5** in acetonitrile solution with 3500-Å light for 48 hr produced **6** in near-quantitative yield: mp 84–86° (from dichloromethane–pentane after column chromatography on Florisil); $\lambda_{max}^{CCl_4}$ 3.30 μ (cyclopropyl); nmr, τ_{CDCl_3} 9.59 (2 H, multiplet), 8.72 (4 H, multiplet), 6.33 (6 H, singlet), and 5.46 (2 H, broad singlet). The assignment of the *exo* configuration to **6** follows from the known structure of **5** with its *exo* locked-C$_8$ carbon.[4]

Hydrolysis-decarboxylation of **6** with hot potassium hydroxide in aqueous methanol led to hydrazine **7**. Exposure of this compound to air or mercuric oxide resulted in immediate oxidation with the accompanying formation of nitrogen and 1,4-cyclohexadiene (**9**). Treatment of **7** with cupric chloride in water gave the brick red cuprous chloride complex **8**:[5] 56% (from **6**); decomposes slowly at ~100°; λ_{max}^{KBr} 6.74 μ (-N=N-);[4] $\lambda_{max}^{CH_3CN}$ 348 mμ (ϵ ~200).[4] Azo compound **4** was liberated by dissolving **8** in pyridine at temperatures $< -10°$. The nmr spectrum of the solution showed

Scheme I



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(1) R. J. Crawford and B. H. Al-Sader, *Can. J. Chem.*, **46**, 3301 (1968); R. J. Crawford and D. M. Cameron, *ibid.*, **45**, 691 (1967); R. J. Crawford and G. L. Erickson, *J. Amer. Chem. Soc.*, **89**, 3907 (1967); R. J. C awford and L. H. Ali, *ibid.*, **89**, 3908 (1967); R. J. Crawford and A. Mishra, *ibid.*, **88**, 3963 (1966); and other papers in the series.

(2) E. L. Allred and R. L. Smith, *ibid.*, **89**, 7133 (1967).

(3) J. C. Hinshaw and E. L. Allred, *Chem. Commun.*, 72 (1969).

(4) The synthesis and characterization of **5** have been reported elsewhere: E. L. Allred and J. C. Hinshaw, *J. Amer. Chem. Soc.*, **90**, 6885 (1968).

(5) Satisfactory elemental analyses were obtained for **6** and **8**.