The Nature of the Base-Induced Decomposition of the *p*-Toluenesulfonylhydrazone of Tricyclo[3.2.1.$0^{3,6}$]octan-2-one

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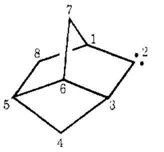
Decomposition of the sodium salt of the tosylhydrazone of tricyclo[3.2.1.$0^{3,6}$]octan-2-one (**5a**) in diglyme in excess sodium methoxide at 145° generates tetracyclo[3.3.0.$0^{2,7}$.$0^{4,6}$]octane (**2**), tetracyclo[3.3.0.$0^{2,4}$.$0^{3,7}$]octane (**3**), and *exo*-2-methoxytricyclo[3.2.1.$0^{3,6}$]octane. Hydrogenolysis of **3** produces tricyclo[3.3.0.$0^{3,7}$]octane (**8**), while similar treatment of **2** results in tricyclo[3.3.0.$0^{2,7}$]octane. Treatment of *exo*-2-chlorotricyclo[3.2.1.$0^{3,6}$]octane (**10**) with sodium in decane at 85–90° generates a C_8 hydrocarbon fraction composed of bicyclo[3.2.1]octene-2 (**11**), tricyclo[3.2.1.$0^{3,6}$]octane, and tetracyclooctane **2**. Tricyclo[3.2.1.$0^{3,6}$]octan-2-one tosylhydrazone-*N-d* (**5b**) decomposes in excess sodium methoxide to provide decreasing ratios of **2**:**3** and decreasing deuterium incorporation as the amount of sodium methoxide is increased. Product composition in the decomposition of **5a** is primarily dependent upon the solvent composition and the base. The decomposition of **5a** is interpreted in terms of competing carbene and ionic pathways.

Our interest in the chemistry of 2-carbenatricyclo[3.2.1.$0^{3,6}$]octane was stimulated by the interesting possibilities for insertion and the prospects for additional studies on the tetracyclooctane insertion products.[1] If one views bivalent intermediate **1** as an isopropylcarbene intermediate,[2–7] then insertion into C-8, C-4, and C-7 leading to tetracyclooctanes **2**, **3**, and **4** is anticipated.



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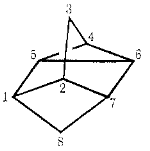

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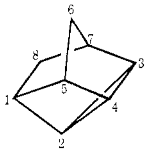

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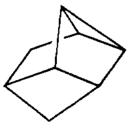

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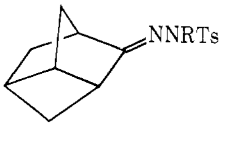
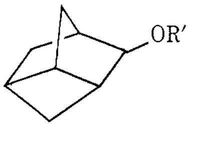
Thermal decomposition of the tosylhydrazone of tricyclo[3.2.1.$0^{3,6}$]octan-2-one (**5a**), in the presence of 6 equiv of $NaOCH_3$ in diglyme at 145°, resulted in the generation of two hydrocarbons and a methyl ether in a yield ratio of 17:33:22. Infrared and nmr spectral comparisons with an authentic sample demonstrated that the methyl ether component is *exo*-2-methoxytricyclo[3.2.1.$0^{3,6}$]octane (**6a**), while elemental and mass spectral measurements (C_8H_{10}, *m/e* 106), coupled with infrared and nmr analysis (absorption above 3000 cm^{-1}, no absorption in the region 1500–1700 cm^{-1}, no absorption below τ 7.3), indicated that the two hydrocarbon components were tetracyclic hydrocarbons.

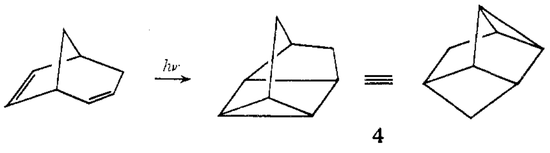


5a, R = H
b, R = D
c, R = Na
d, R = Li



6a, R′ = CH_3
b, R′ = $CH(CH_3)_2$

Structural identification of the two tetracyclic hydrocarbon components was accomplished by an analysis of spin decoupling at 100 MHz as well as by hydrogenolysis. A consideration of the structures of probable insertion products **2**, **3**, and **4** reveals that **2** possesses three pairs of enantiotopic protons and four unique ones (C_s plane through C-2, C-3, and C-4), tetracyclic **3** possesses four pairs of enantiotopic protons and two unique ones (C_s plane through C-3, C-7, and the midpoint of C-1–C-5), while all the protons of tetracyclic **4** are nonequivalent. Spin decoupling carried out on the 33% component demonstrated the presence of three pairs of equivalent protons, appearing at τ 7.68–7.80, 8.47–8.57, and 8.60–8.66, and two pairs of nonequivalent protons appearing at τ 7.90–8.06 and 8.21–8.35, with the largest coupling constant due to the geminal coupling of the protons at C-8 (J = 6.4 Hz), which is consistent with the expectations for structure **2**.[8] Similar decoupling experiments carried out on the 17% hydrocarbon component reveal the presence of four pairs of equivalent protons with absorption bands appearing at τ 7.56–7.66, 7.95–8.07, 8.58–8.73, and 8.99–9.15, and bands for two unique protons at τ 7.44–7.56 and 8.21–8.41. Thus, the nmr spectrum fits very nicely that anticipated for tetracyclooctane **3**, and this assignment of structure is reinforced by the fact that the largest coupling constant observed, J = 9.7 Hz, is readily assignable as the geminal splitting constant of the hydrogens in the enantiotopic methylene groups at C-6 and C-8 in structure **3**. Finally, any lingering doubt that asymmetric **4** might be a structural possibility for either of the two hydrocarbons was removed by infrared and nmr spectral comparison with the corresponding data on the photoisomerization product of bicyclo[3.2.1]octa-2,6-diene, which has been assigned the tetracyclo[4.2.0.$0^{2,4}$.$0^{3,8}$]octane structure (**4**).[9]



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[1] An account of the chemistry of bivalent intermediate **1** has been published in preliminary form: P. K. Freeman, V. N. M. Rao, and G. E. Bigam, *Chem. Commun.*, 511 (1965).

[2] W. Kirmse, H. D. von Scholz, and H. Arold, *Justus Liebigs Ann. Chem.*, **711**, 22 (1968).

[3] L. Friedman and H. Shechter, *J. Amer. Chem. Soc.*, **81**, 5512 (1959).

[4] W. Kirmse and W. von E. Doering, *Tetrahedron*, **11**, 266 (1960).

[5] E. Taeger and C. Fielder, *Justus Liebigs Ann. Chem.*, **696**, 42 (1966).

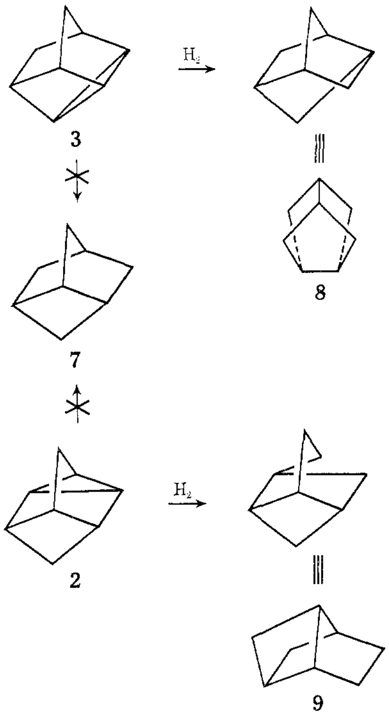
[6] A. M. Mansoor and I. D. R. Stevens, *Tetrahedron Lett.*, 1733 (1966).

[7] L. Friedman and J. G. Berger, *J. Amer. Chem. Soc.*, **83**, 492, 500 (1961).

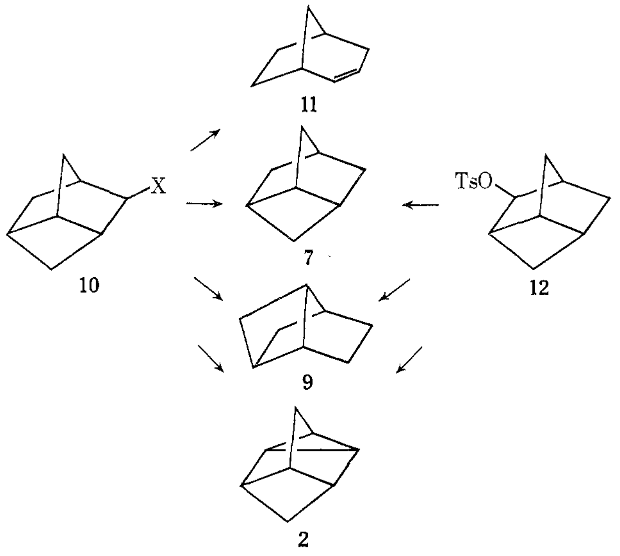
[8] The geminal C-5 protons on the bicyclo[2.1.1]hexane ring system exhibit a similar splitting constant, J = 5.4 Hz: K. B. Wiberg, B. R. Lowry, and B. J. Nist, *J. Amer. Chem. Soc.*, **84**, 1594 (1962).

[9] Professor S. Winstein, private communication.

Hydrogenolysis of the 17% component over platinum in methanol occurred rapidly, yielding only one product, mp 105–105.5°. Elemental and mass spectral analysis (C_8H_{12}, m/e 108) combined with a consideration of the infrared spectrum, which exhibited no evidence for cyclopropane, methyl, or unsaturation, suggested that the hydrogenolysis product must be tricyclic as a result of fission of a cyclopropane bond. Hydrogenolysis of the enantiotopic bonds C-2–C-3 or C-3–C-4 in **3** does not occur, since the spectral data of the hydrogenolysis product do not agree with the data for tricyclo[3.2.1.0^{3,6}]octane (**7**), synthesized by Wolff–Kishner reduction of tricyclo[3.2.1.0^{3,6}]octan-2-one. The remaining possibility is fission of the C-2–C-4 bond, which is the transannular bond of a bicyclo[2.1.0]pentane moiety and thus subject to facile cleavage.[10] The nmr spectrum (100 MHz) of this tricyclic hydrocarbon is striking, revealing only two broadened singlets at τ 7.72 and 8.68 in the ratio of 1:2 and thus is consistent with the D_{2d} symmetry of tricyclo[3.3.0.0^{3,7}]octane (**8**). Formation of **8** reinforces the assignment of **3** to the 17% component, since **8** cannot be formed from reductive bond fission of **2** or **4**. Hydrogenation of tetracyclooctane **2** over platinum in methanol proceeds readily to yield a single C_8H_{12} tricyclic hydrocarbon. Reductive bond fission of the C-5–C-6 bond did not occur, as determined by spectral comparison with data of authentic **7**. Since no cyclopropane absorption is evident above 3000 or near 1020 cm^{-1} in the infrared, cleavage of the C-4–C-6 (or C-4–C-5) bond must have occurred, generating tricyclo[3.3.0.0^{2,7}]octane. The nmr spectrum (60 MHz) exhibits complex absorption bands at τ 7.62–7.95 (4 H) and 8.12–8.93 (8 H).



With the structure of the products of the thermal decomposition of the sodium salt of **5a** established, and thus with a tentative view of the reaction routes followed by 2-carbenatricyclo[3.2.1.0^{3,6}]octane, or a combination of bivalent **1** and the related carbonium ion, attention was focused on the possibility of generation of a carbenoid intermediate related to **1** by an α-elimination pathway. *exo*-2-Chlorotricyclo[3.2.1.0^{3,6}]octane (**10**) was prepared by treatment of the corresponding alcohol[11] with thionyl chloride. Chloride **10** appeared to be homogeneous by vpc and was assigned the exo unrearranged structure on the basis of the appearance of a sharp singlet at τ 6.00 for the hydrogen α to chlorine in the nmr spectrum. A heart-cut sample of chloride **10**, collected by vapor phase chromatography on a 30-ft Carbowax 20M column, was allowed to react with sodium in decane at 85–90°.[7,12] Distillation of the volatile hydrocarbon fraction directly from the reaction mixture resulted in a 44% yield of C_8 hydrocarbons. A combination of vpc and spectral analyses revealed that the C_8 hydrocarbon fraction was composed of 72% bicyclo[3.2.1]octene-2 (**11**), 22% tricyclo[3.2.1.0^{3,6}]octane (**7**), 3% tetracyclooctane **2**, a 3% unidentified liquid component, and a trace (<1%) of tricyclooctane **9**.



Since an understanding of the base-induced decomposition of tosylhydrazone **5a** as well as the reaction of chloride **10** with sodium depends upon an accurate assessment of the relative importance of carbene as well as carbonium ion pathways in the thermal decomposition of the sodium salt of **5a**, a more detailed analysis of this reaction was undertaken. Tricyclo[3.2.1.0^{3,6}]octan-2-one tosylhydrazone-*N-d* (**5b**) was decomposed in the presence of varying amounts of sodium methoxide and the ratio of insertion products **2** and **3**, as well as the deuterium content of **2** and **3**, was measured (Table I). In a second series of decompositions of **5a**, **5c**, and **5d**, thermal reactions were carried out in various solvents and without solvent and a photolytic decomposition in diglyme was investigated (Table II).

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(10) K. B. Wiberg in "Advances in Alicyclic Chemistry," Vol. 2, H. Hart and G. J. Karabatsos, Ed., Academic Press, New York, N. Y., 1968, p 185.

(11) R. R. Sauers and R. A. Parent, *J. Org. Chem.*, **28**, 605 (1963); R. R. Sauers, R. A. Parent, and S. B. Damle, *J. Amer. Chem. Soc.*, **88**, 2257 (1966).

(12) P. K. Freeman, D. E. George, and V. N. M. Rao, *J. Org. Chem.*, **29**, 1682 (1964); E. A. Hill, *ibid.*, **37**, 4008 (1972); H. G. Richey, Jr., and E. A. Hill, *ibid.*, **29**, 421 (1964); W. Kirmse and W. von E. Doering, *Tetrahedron*, **11**, 266 (1960); P. S. Skell and A. P. Krapcho, *J. Amer. Chem. Soc.*, **83**, 754 (1961).

TABLE I

DECOMPOSITION OF TRICYCLO[3.2.1.0^{3,6}]OCTAN-2-ONE TOSYLHYDRAZONE-N-d^a AT 160° IN TETRAGLYME

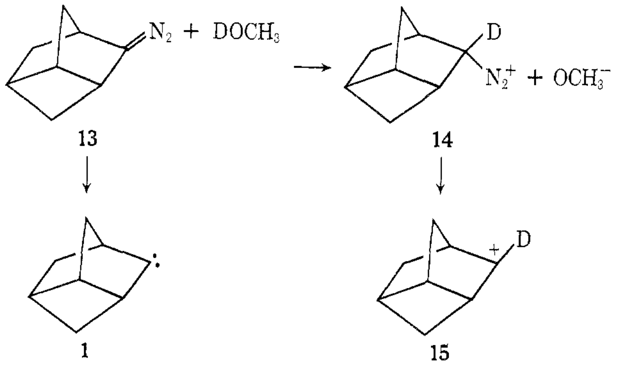
Run	Equiv of $NaOCH_3$	% 2 (% d_1)	% 3 (% d_1)
1	0.48	86 (46 ± 4)	14 (30 ± 6)
2	1.07	87 (31 ± 2)	13 (15 ± 2)
3	1.97	78 (16 ± 2)	22 (7 ± 2)
4	3.16	69 (5 ± 1)	31 (2^b)
5	11.62	62 (3 ± 1)	38 (2 ± 1)

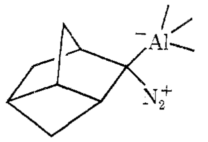
^{a} 68% d_1. ^{b} Only one run.

Discussion

The product ratios and the extent of deuteration found in these experiments listed in Tables I and II provide convincing evidence that 2-carbenatricyclo-[3.2.1.0^{3,6}]octane undergoes insertion into the γ C–H bonds at C-8 and C-4 to generate tetracyclooctanes **2** and **3** in an approximate ratio of 3:2. Convergence of the **2**:**3** product ratio with increasing quantities of sodium methoxide (Table I) to that observed in the dry lithium or sodium salt pyrolyses (Table II), as well as the low level recorded for the deterium concentration in **2** and **3** in the high methoxide runs (4 and 5 in Table I), substantiates this view.

One can consider these results in terms of two major competing reaction pathways. Decomposition of sodium salt **5c** yields **13**, which can decompose by loss of nitrogen to form carbene **1** or react with methanol-d to give diazonium ion **14**, which, in turn, may generate labeled carbonium ion **15**. Thus with a large excess of sodium methoxide complete conversion to **5c** is assured and aprotic conditions are achieved with minimum incorporation of deuterium label; carbene **1** is nearly the sole product-determining intermediate. In protic solvents (run 4, Table II), diazoalkane **13** is converted to diazonium ion **14** and either ion **14** or **15** is the major product-determining intermediate. A similar result to that of run 4 is obtained by using Al(i-OPr)$_3$ as the base (run 9). Apparently the aluminum alkoxide, acting as a Lewis acid, generates a carbenoid, perhaps similar in structure to **16**, which undergoes insertion in a pattern similar to that followed by ion **15** (or perhaps diazonium ion **14**). Even though **14** or **15** favors insertion at C-8, the deuterium incorporation at low methoxide concentration (run 1, Table I) suggests that the carbonium ion (or diazonium ion) also undergoes insertion at C-4.





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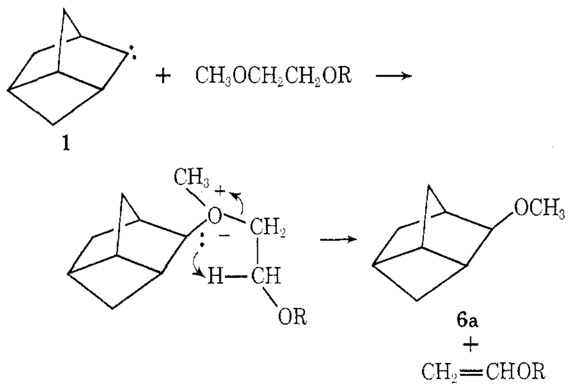
The generation of methyl ether **6a**, in run 1 (Table II), at first glance intrigued us, as one possible route to **6a** is through intermolecular reaction of bivalent **1** with methoxide ion, methyl alcohol, or perhaps diglyme *via* an ylide elimination mechanism[13-16] (Scheme I). The ylide mechanism variation was tested by substituting diethylcarbitol for diglyme as the solvent (run 2, Table II). The formation of methyl rather than ethyl ether in this run rules out the ylide mechanism. In run 3, the sodium salt of the tosylhydrazone was formed by treatment with sodium hydride and the decomposition of the sodium salt was run in the presence of 6 equiv of sodium methoxide. The complete lack of methyl ether in this run demonstrates that methyl alcohol is required for the generation of **6a**. One might reasonably anticipate a mild electrophilicity for dialkylcarbene **1**[17] and, therefore, expect that, if bivalent intermediate **1** does not react intermolecularly with methoxide ion, an insertion into methanol would be unlikely. The role of the methanol must be to create a carbonium ion (or diazonium ion) component of the reaction, which then results in ether formation.

SCHEME I



The related reaction of chloride **10**-Cl with sodium in decane at 85–90° may be explained in terms of the formation of sodium alkyl **10**-Na, which may undergo cleavage at the C-3–C-6 bond followed by proton abstraction to yield major product **11** or abstract a proton from the α position of **10**-Cl to generate hydrocarbon **7** and a carbenoid related to bivalent **1**, which undergoes insertion to produce tetracyclooctane **2**. The trace of tricyclic **9** is believed to be due to the presence of a small amount of Wagner–Meerwein rearranged chloride present in **10**-Cl. Additional evidence pointing to this conclusion is found in the fact that, when a chloride sample prepared in the reaction of **10**-OH with thionyl chloride, but not purified by taking a vpc heart-cut,

(13) G. B. R. deGraaf, J. H. van Dijck-Rothius, and G. van deKolbe, *Recl. Trav. Chim. Pays-Bas*, **74**, 143 (1955); G. B. R. deGraaf and G. Van deKolbe, *ibid.*, **79**, 48 (1960).

(14) V. Franzen, *Justus Liebigs Ann. Chem.*, **627**, 22 (1959); V. Franzen and L. Fikentscher, *ibid.*, **617**, 1 (1958); V. Franzen and H. Kuntze, *ibid.*, **627**, 15 (1959).

(15) M. Saunders and R. W. Murray, *Tetrahedron*, **11**, 1 (1960).

(16) W. Ando, T. Yagihara, and T. Migita, *Tetrahedron Lett.*, 1983 (1969); W. Ando, T. Yagihara, S. Tozune, and T. Migita, *J. Amer. Chem. Soc.*, **91**, 2786 (1969); W. Ando, K. Nakayama, K. Ichibori, and T. Migita, *ibid.*, **91**, 5164 (1969); W. Ando, S. Kondo, and T. Migita, *ibid.*, **91**, 6516 (1969).

(17) W. M. Jones, M. H. Grasley, and W. S. Brey, Jr., *J. Amer. Chem. Soc.*, **85**, 2754 (1963).

TABLE II

DEPENDENCE OF PRODUCT COMPOSITION ON REACTION CONDITIONS IN THE DECOMPOSITION OF TOSYLHYDRAZONE **5a** AND TOSYLHYDRAZONE SALTS **5c** AND **5d**

Run	R	Solvent, conditions	Equiv base	Temp, °C	Yield, %			
					2/3	2 + 3	6a	6b
1	H	Diglyme, Δ	6 NaOMe	145	1.96	50	22	
2	H	Diethylcarbitol, Δ	6 NaOMe	145	2.01	29	17	
3	H	Diglyme, Δ	1.25 NaH, then 6 $NaOCH_3$	145	2.07	24	0	
4	H	Ethylene glycol, Δ	6 NaOMe	145	22.4	8	3	
5	Li	None, Δ		200	1.64	78		
6	Li	None, Δ		160	1.63	76		
7	Na	None, Δ		160–175	1.50	39		
8	Li	Diglyme, $h\nu$		20	2.03	3		
9	H	Diglyme, Δ	8 Al(*i*-OPr)$_3$	145	18	13		44

was employed, a considerably larger fraction of **9**, amounting to 15% of the volatile hydrocarbon fraction, was produced.

In a related experiment solvolysis of the exo tosylate **12** in bis(2-ethoxyethyl) ether at 90° in the presence of lithium aluminum hydride generated a 32% yield of C$_8$ hydrocarbons, which consisted of tricyclic **7**, tricyclic **9**, and tetracyclic **2** in a ratio of 60:27:13. Thus Wagner–Meerwein rearrangement does occur in contrast to the result of acetolysis of **12** at 105°[11] and the reaction pattern of the carbonium ion reveals that insertion into C-8–H is highly favored over C-4–H in accord with the pattern uncovered for the decomposition of **5a** in a protic solvent (run 4, Table II). Carbenoid **16** also exhibits a marked preference for C-8 insertion, but the related species formed by α-proton abstraction from **10**-Cl forms **2** in too low a yield to establish the insertion pattern with certainty.

Assuming a singlet state precursor for the carbene insertion products,[18] it might have been reasonable to expect a similar insertion pattern for both the bivalent and carbonium ion intermediates, since each should be approximately sp^2 hybridized at C-2 and interact with the σ bond of the migrating hydrogen by electrophilic attack of an empty C-2 p orbital. The contrasting patterns revealed in the ratios of **2**:**3** (22 *vs.* 1.5–1.6) suggest that the product-determining intermediates may be rather different.

Nickon and Werstiuk prefer a diazonium ion precursor for the Bamford–Stevens reaction of norcamphor tosylhydrazone in ethylene glycol,[19] and thus it is reasonable to consider endo diazonium ion **14** as the product-determining intermediate in the present case. It turns out that a syn-periplanar transition state for 1,3 elimination in the preferred U-shaped configuration[20] is more easily achieved with the endo C-8 hydrogen than with the corresponding hydrogen at C-4, although the difference is not large. Perhaps the greater selectivity of the diazonium ion is due to a major extent to a greater sensitivity to product strain, which might be expected in a comparison of a diazonium ion with a free carbene. An alternative view in the case of tosylhydrazone decomposition in protic solvent is that the ionic intermediate is indeed a free carbonium ion, but is delocalized, which is consistent with the anchimeric assistance found for acetolysis of **12** ($10^{2.8}$)[11] and the Wagner–Meerwein rearrangement observed in the present study. Such delocalization should provide stabilization and a geometry with a shortened C-2–C-8 distance, which would be expected to enhance insertion at C-8. Such a view would have the advantage of encompassing the ionic pathways of the several variations discussed.

Experimental Section

All melting points and boiling points reported are uncorrected. Microanalyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, 5251 Elbach über Engelskirchen, West Germany, or Chemalytics, Inc., Tempe, Ariz. 85282. Infrared spectra were recorded on a Beckman Model IR-8 infrared spectrophotometer and nmr spectra were determined on a Varian Associates A-60 or HA-100 nmr spectrometer. Mass spectra were obtained using an Atlas CH7 mass spectrometer. Vapor phase chromatographic analyses and collections were carried out using either an F & M Model 700 or an Aerograph Model A-90-P chromatograph equipped with thermal conductivity detectors. Columns employed were made with aluminum tubing and contained the following: A, 9 ft × 0.125 in. 5% Carbowax 20M on 70/80 Anakrom ABS; B, 8 ft × 0.25 in. 15% Carbowax 20M and 2% XF-1112 on 30/60 Chromosorb P (AW); C, 20 ft × 0.125 in. 10% β,β'-oxydipropionitrile on 30/60 Chromosorb P (AW); D, 30 ft × 0.125 in. 5% Carbowax 20M on 70/80 Anakrom ABS; E, 25 ft × 0.25 in. 25% Carbowax 20M on 30/60 Chromosorb P. Product ratios and percentage yields calculated from chromatographic data are based on relative peak areas and were corrected, when necessary, for differences in molecular weight by the method of Eastman.[21] Peak areas were determined by electronic integration using a Hewlett-Packard Model 3373-B integrator unless stated otherwise. Solvents used in tosylhydrazone decompositions were distilled from lithium aluminum hydride or calcium hydride and stored over 4-Å molecular sieves, but only for short periods.

Tricyclo[3.2.1.0^{3,6}]octan-2-one *p*-Toluenesulfonylhydrazone (5a).—A mixture of tricyclo[3.2.1.0^{3,6}]octan-2-one (4.08 g, 32.9 mmol) and *p*-toluenesulfonylhydrazine (6.35 g, 34.1 mmol) in 26 ml of pyridine was heated on a steam bath for 1.5 hr. Subsequent dilution with 125 ml of cold water with vigorous stirring yielded 8.05 g (85%) of **5a**, mp 149–160°. A pure product was obtained by effecting solution of the crude solid in a hot 1:1 DMF–H$_2$O solution (10 g of solution per gram of crude tosylhydrazone), filtering, then allowing the solution to cool slowly to room temperature. The resulting crystals were collected, washed with three aliquots of 1:1 DMF–H$_2$O and three aliquots of water, and then dried. Recovery gave about 85% of pure **5a**: mp 161–164° dec; ir (CHCl$_3$, 0.1 mm) 3257, 3031, 2994, 2899, 1669, 1600, 1394, 1340, 1164, 1092, 1021, 918, 811, 659 cm^{-1}.

Anal. Calcd for C$_{15}$H$_{18}$N$_2$O$_2$S: C, 62.04; H, 6.24. Found: C, 61.80; H, 6.02.

Decomposition of Tricyclo[3.2.1.0^{3,6}]octan-2-one *p*-Toluenesulfonylhydrazone (5a) in Sodium Methoxide–Diglyme.—In a

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[18] There is no evidence for products derived from the triplet state in the reactions of the closely related 2-carbena-6,6-dimethylnorbornane, generated by pyrolysis of the lithium salt of the tosylhydrazone of 6,6-dimethylnorbornan-2-one: P. K. Freeman and T. A. Hardy, *J. Amer. Chem. Soc.*, submitted.

[19] A. Nickon and N. H. Werstiuk, *J. Amer. Chem. Soc.*, **94**, 7081 (1972); A. Nickon and N. H. Werstiuk, *ibid.*, **88**, 4543 (1966).

[20] A. Nickon and N. H. Werstiuk, *J. Amer. Chem. Soc.*, **89**, 3914, 3915, 3917 (1967).

[21] R. Eastman, *J. Amer. Chem. Soc.*, **79**, 4243 (1957).

dry 25-ml flask fitted with a reflux condenser and nitrogen inlet, a mixture of 1.00 g (3.45 mmol) of tosylhydrazone **5a**, 1.12 g (21.7 mmol, 6 equiv) of sodium methoxide, and 15 ml of dry diglyme was stirred at ambient temperature for 1 hr under a nitrogen atmosphere. The flask was then plunged into a 145° oil bath and held at that temperature for 5 hr. Initially a red-brown color appeared, which dissipated after *ca.* 15 min, leaving a pale milky-pink suspension. Allowing the mixture to cool, followed by dilution with an equal volume of pentane and subsequent extraction with five aliquots of water, yielded a pentane extract which was dried over anhydrous Na_2SO_4 and concentrated by distillation of the pentane through a 10-cm Vigreux column. The concentrated solution in the pot was analyzed by vpc on column A, and contained three components. The first two were identified as tetracyclo[3.3.0.0^{2,7}.0^{4,6}]octane (**2**) and tetracyclo[3.3.0.0^{2,4}.0^{3,7}]octane (**3**) in a yield ratio of 33:17 (determined by quantitative gas chromatography relative to a norbornane internal standard introduced after product isolation) by the ir and nmr analysis described in the Discussion section. Analytical samples of tetracyclic **2** and **3** were separated by vpc.

Anal. Calcd for C_8H_{10} (**2**): C, 90.51; H, 9.49. Found: C, 90.31; H, 9.57.

Anal. Calcd for C_8H_{10} (**3**): C, 90.51; H, 9.49. Found: C, 90.31; H, 9.29.

The third component was identified as *exo*-2-methoxytricyclo[3.2.1.0^{3,6}]octane (**6a**) by ir and nmr spectral comparison with spectra of an authentic sample.

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.04; H, 10.09.

A 106-mg sample of tetracyclic hydrocarbon **3** was hydrogenated in methanol over platinum oxide in a semimicro hydrogenation apparatus. Hydrogen take-up was rapid and approximately 1 molar equiv of hydrogen was absorbed in 30 min. Vpc analysis of the product on column E at 90° indicated the presence of only one product. Purification of this product by vapor phase chromatography gave a white solid, mp 105–105.5. The infrared spectrum of this hydrogenated material was very simple, indicating that the product is symmetrical. There are no absorptions above 3000 cm^{-1} or near 1022 cm^{-1}, and no evidence of methyl absorptions, thus indicating that the cleavage of the ring must have occurred in one of the cyclopropyl bonds. A parent peak at m/e 108 is exhibited in the mass spectrum. The nmr spectrum showed two singlets at τ 7.72 and 8.68 in the ratio 1:2. The data are consistent with the identification of this hydrocarbon as tricyclo[3.3.0.0^{3,7}]octane.

Anal. Calcd for C_8H_{12}: C, 88.81; H, 11.19. Found: C, 88.93; H, 11.37.

A 106-mg sample of tetracyclic hydrocarbon **2** was hydrogenated in methanol over platinum oxide in a semimicro hydrogenation apparatus. Approximately 1 molar equiv of hydrogen was absorbed. Vpc analysis of the hydrogenated mixture on a 25-ft Carbowax 20M column at 90° indicated the presence of only one product component. An infrared spectrum showed no olefinic absorption and there were no absorptions above 3000 cm^{-1} or near 1020 cm^{-1}, indicating the absence of a cyclopropane ring. Absorption corresponding to a methyl group was also absent. The nmr spectrum of this component exhibits complex absorption bands at τ 7.62–7.95 (4 H) and 8.21–8.93 (8 H), while the mass spectrum reveals a weak parent peak at m/e 108. The spectral data of this compound were different from that of tricyclo[3.2.1.0^{3,6}]octane; consequently, the hydrogenated product was identified as tricyclo[3.3.0.0^{3,6}]octane.

Anal. Calcd for C_8H_{12}: C, 88.81; H, 11.19. Found: C, 88.95; H, 11.29.

Preparation of *exo*-2-Methoxytricyclo[3.2.1.0^{3,6}]octane (6a).—In a sealed reaction vessel were stirred 0.15 g (1.23 mmol) of *exo*-tricyclo[3.2.1.0^{3,6}]octan-2-ol, 0.56 g (2.4 mmol) of Ag_2O, 0.34 g (3.6 mmol) of methyl iodide, and 2 ml of dimethylformamide at ambient temperature for 5 days with exclusion of light. Dilution of the resulting solution with 1:1 pentane–ether (5 ml) followed by extraction with five aliquots of H_2O yielded, after solvent removal at reduced pressure, a residue which contained two components by vpc analysis on column B.

The minor component (30%) was identified as starting alcohol. The major component (70%) had ir and nmr spectra consistent with the assigned structure, *exo*-2-methoxytricyclo[3.2.1.0^{3,6}]octane (**6a**) and was formed in 65% yield based on unreacted alcohol: ir (CCl_4) ν 2959, 2875, 2833, 1449, 1366, 1199, 1120, 1106, 1094, 1078, 971 cm^{-1}; nmr (100 MHz, CCl_4) δ 3.24 (s, 1 H), 3.17 (s, 3 H), 2.74 (broad s, $W_{1/2}$ = 9 Hz, 1 H), 2.60 (broad s, $W_{1/2}$ = 7 Hz, 1 H), 2.18 (m, 3 H), 1.80 (doublet of doublets, J = 11, 1.7 Hz, 1 H), 1.56 (doublet of multiplets, J = 11 Hz, 1 H), 1.36 (s, 1 H), 1.23 (s. 1 H), 1.12 (m, 1 H).

Preparation of Tricyclo[3.2.1.0^{3,6}]octan-2-one *p*-Toluenesulfonylhydrazone-*N-d* (5b).—Deuterium exchange was effected by vigorously shaking 3.0 g (10.3 mmol) of tosylhydrazone **5a**, 25 ml of $CHCl_3$, 30 ml of 99.8% D_2O, and a catalytic amount of sodium methoxide in a 125-ml separatory funnel. Monitoring the amount of N-*h* *vs.* N-*d* by observation of the 3.1-μ band in the infrared revealed that a maximum d_1 incorporation occurred after only a few minutes—continued shaking caused a diminution of the amount of N-*d* owing to exchange of the chloroform proton. Precipitation of the tosylhydrazone by pentane addition yielded 1.74 g (6 mmol, 58%) of **5b**, mp 156–157° dec. Quantitative ir analysis using the resolved C=N stretching absorption at 6.0 μ as an internal standard in comparison to the NH stretching frequency at 3.1 μ indicated 68% deuterium incorporation at the desired position. Mass spectral analysis at 16 eV likewise revealed 68 ± 3% d_1 incorporation, determined from nine scans.

Preparation of *N*-Lithiotricyclo[3.2.1.0^{3,6}]octan-2-one *p*-Toluenesulfonylhydrazone (5d).—The tosylhydrazone lithium salt was prepared by addition of 1 equiv of methyllithium (1.95 *M* in ether) to tosylhydrazone **5a** in ether under nitrogen in a glove bag, followed by removal of solvent at reduced pressure and at room temperature with swirling of the solution such that the salt forms a thin coat on the inside of the reaction vessel. The last traces of ether were very difficult to remove, but extended subjection of the salt to a pressure of less than 0.01 mm, while warming to 40°, seemed moderately effective. No attempt was made to separate the tosylhydrazone lithium salt from the lithium bromide (1 equiv/mol of methyllithium) present in the commercial methyllithium solution used.

Decomposition of Tricyclo[3.2.1.0^{3,6}]octan-2-one *p*-Toluenesulfonylhydrazone (5a) in Sodium Methoxide–Ethylene Glycol.—Decomposition of 1.00 g (3.45 mmol) of tosylhydrazone **5a** was effected under conditions in all respects identical with those above, except that ethylene glycol (distilled from sodium) was substituted for diglyme as the solvent. Isolation and analysis of the resulting product mixture was also done in a fashion identical with the diglyme decomposition. Ether **6a** was found in only 2.0% yield, and a mixture of hydrocarbons **2** and **3** in the ratio of 90:4 was found in 7.8% yield using an internal norbornane reference. Two additional peaks, eluting before **2** or **3**, were found in 0.13 and 0.36% yield in order of elution and were not identified.

Decomposition of *N*-Lithiotricyclo[3.2.1.0^{3,6}]octan-2-one *p*-Toluenesulfonylhydrazone (5d) in the Absence of Solvent.—A reaction vessel containing the lithium salt **5d** was connected to a trap and cooled to −78° in a Dry Ice–2-propanol bath, and the system was evacuated to 0.01 mm. Immersion of the flask in a 200° silicone oil bath for 1 hr yielded a clear pyrolysate which collected in the −78° trap. This product mixture was analyzed in the same manner as the two preceding decomposition product mixtures. Hydrocarbons **2** and **3** were found in a ratio of 59:36 in a 74% yield in addition to an unidentified component, in 4% yield, which eluted after both **2** and **3** on column C (this component was not present when the same reaction was carried out at 160°).

Photolysis of *N*-Lithiotricyclo[3.2.1.0^{3,6}]octan-2-one *p*-Toluenesulfonylhydrazone in Diglyme.—The lithium salt was prepared by addition of 1.1 equiv of methyllithium (2.13 *M* in ether) to tosylhydrazone **5a** dissolved in diglyme. Irradiation of the resulting suspension in a quartz reaction vessel, equipped with a magnetic stirrer, a cold finger, and $CaCl_2$ drying tube, with a 450-W Hanovia high-pressure mercury lamp for 5 hr at a distance of 1 in., followed by dilution with pentane and extraction several times with water, yielded a solution which was analyzed by vpc as in the above thermal decompositions of **5a**. Both tetracyclic C_8 hydrocarbons **2** and **3** were formed, in a ratio of 67:33 but in only 3% yield as determined by an internal norbornane standard. The low yield was attributed to a low conversion of tosylhydrazone salt to hydrocarbon owing to the heterogeneity of the mixture.

Decomposition of Tricyclo[3.2.1.0^{3,6}]octan-2-one *p*-Toluenesulfonylhydrazone (5a) in Aluminum Isopropoxide–Diglyme.—Decomposition of 0.88 g of tosylhydrazone **5a** was effected under conditions in all respects identical with those for the methoxide–diglyme experiment above, except that 8 equiv of freshly distilled aluminum isopropoxide was substituted for sodium methoxide as the base. Isolation and analysis, also as above, indicated a very low yield (13%) of the two tetracyclic isomers **2** and **3** in the ratio of 18:1. The two volatile peaks observed in the ethylene glycol decomposition were again noticed in similar relative yields.

Decomposition of Tricyclo[3.2.1.0^{3,6}]octan-2-one *p*-Toluenesulfonylhydrazone (5a) in Sodium Methoxide-Bis(2-ethoxyethyl) Ether.—Decomposition and analysis of 0.68 g of tosylhydrazone **5a** under conditions identical with those for the methoxide-diglyme decomposition above, except for a change in solvent to bis(2-ethoxyethyl) ether, gave ether **6a** in 17% yield, and tetracyclic hydrocarbons **2** and **3** in the ratio of 2:1 in 29% yield.

Decomposition of Tricyclo[3.2.1.0^{3,6}]octan-2-one *p*-Toluenesulfonylhydrazone-*N*-*d* (5b) with Various Equivalents of Sodium Methoxide.—In a 15-ml round-bottomed flask fitted with nitrogen inlet and condenser were mechanically stirred 0.290 g (1.0 mmol) of tosylhydrazone **5b**, 5 ml of tetraglyme, and various amounts of sodium methoxide at room temperature for 15 min. The entire apparatus was lowered into a 160 ± 5° oil bath and held there for 30 min. After cooling, the pot was diluted with pentane, filtered, washed six times with water, dried over anhydrous Na_2SO_4, and reduced in volume by distillation of the pentane through a 10-cm Vigreux column. Vpc analysis on column D connected directly to an Atlas CH-7 mass spectrometer operated at 13 eV gave ratios of **2** to **3** and per cent deuterium incorporation reported in Table I. The values reported are the average and average deviation of three scans of each sample.

***exo*-2-Chlorotricyclo[3.2.1.0^{3,6}]octane.**—In a 100-ml, three-necked flask, provided with a magnetic stirrer, a condenser, a pressure-equalizing dropping funnel, and a nitrogen inlet, was placed 9.5 g (0.798 mol) of redistilled thionyl chloride in 20 ml of anhydrous ether. To this mixture was added at ambient temperature with stirring a mixture of 9.0 g (0.725 mol) of *exo*-tricyclo[3.2.1.0^{3,6}]octan-2-ol[11] and 1 drop of piperidine in 30 ml of anhydrous ether during 30 min. The ether solution was heated at reflux for 2 hr, at the end of which period the ether was removed by distillation and the product was distilled under reduced pressure. A 43.6% yield of *exo*-2-chlorotricyclo[3.2.1.0^{3,6}]octane (5.1 g), bp 66-67° (15 mm), was obtained: ir (0.025 mm) 2980, 1442, 1319, 1266, 1240, 1058, 920, 874, 799, 759, 748 cm^{-1}; nmr (CCl_4) δ 3.98 (s, 1 H), 2.92 (broad s, 1 H), 2.67 (broad s, 1 H), 2.55-1.20 (m, 8 H).

Anal. Calcd for $C_8H_{11}Cl$: C, 67.36; H, 7.77. Found: C, 67.52; H, 7.90.

Reaction of *exo*-2-Chlorotricyclo[3.2.1.0^{3,6}]octane with Sodium.—A solution of 4.0 g (0.028 mol) of *exo*-2-chlorotricyclo[3.2.1.0^{3,6}]octane in 15 ml of redistilled *n*-decane was allowed to react with 1.28 g (0.056 g-atom) of sodium in a manner described previously for 5-chloromethylbicyclo[2.2.1]hept-2-ene.[22] When the reaction was complete, the mixture was distilled through a Claisen head at 40 mm and 6.2 g of a distillate was obtained. From the distillate, a total of 1.39 g (42.4%) of C_8 hydrocarbons was isolated by redistillation on an 18-in. semimicro spinning band column at 90 mm. The mixture was analyzed on column E and showed the presence of seven components in the ratio 1:15:17:11:46:8:4. A sufficient quantity of the 1% component was not obtained to make a positive identification. The 15% component was a low-melting solid. The infrared and the nmr spectra of the solid were identical with those of an authentic sample of tricyclo[3.3.0.0^{2,7}]octane. The 17% component was a white solid at room temperature, mp 120-121.5°. The infrared spectrum showed no evidence of any unsaturation. The absence of a cyclopropyl group was indicated by no absorptions above 3000 cm^{-1} or near 1020 cm^{-1}. The nmr spectrum was identical with that of a sample obtained by the Wolff-Kishner reduction of tricyclo[3.2.1.0^{3,6}]octan-2-one. Two purifications by vapor phase chromatography raised the melting point of the solid to 140-141°. The 11% component was a liquid at room temperature. The spectral data of this component were identical with those of a sample of tetracyclo[3.3.0.0^{2,7}0.^{4,6}]octane. The 46% component was a low-melting solid. The infrared and the nmr spectra of this component were identical with those of an authentic sample of bicyclo[3.2.1]octene-2.[23] The 8% component was a liquid at room temperature. The infrared spectrum of this sample exhibited olefinic absorption at 1580 and 1630 cm^{-1}. In addition, it also had absorptions at 3045 and 3070 cm^{-1}, although there was no absorption corresponding to a nortricyclene type of ring structure near 800 cm^{-1}. The nmr spectrum indicated that this component was probably a mixture of more than one constituent. Owing to the paucity of material, further identification of this component was not carried out. The 4% component was a low-melting solid. The infrared spectrum of this component was very simple, suggestive of a symmetrical hydrocarbon. It exhibited characteristic absorptions at 3100 and 1022 cm^{-1}, suggestive of a nortricyclene type of ring skeleton. In addition, it also exhibited olefinic absorption at 1610 cm^{-1} and sharp absorptions at 915 and 720 cm^{-1}. The nmr spectrum of this compound showed four sets of absorptions, a triplet at τ 4.22, corresponding to two protons, a one-proton multiplet centered at 3.52, a five-proton peak between 8.3 and 8.81, and two singlets at 9.21 and 9.41, whose integrated area corresponded to two protons, and is identical with the spectrum of authentic tricyclo[3.2.1.0^{2,7}]oct-3-ene.[24]

When a heart-cut sample of *exo*-2-chlorotricyclo[3.2.1.0^{3,6}]octane was allowed to react with sodium, a 44.2% yield of C_8 hydrocarbons was obtained. Analysis of this mixture on column E showed only four peaks in the ratio 22:71:3:3. The 22% component was tricyclo[3.2.1.0^{3,6}]octane, the 71% component was bicyclo[3.2.1]octene-2, and the 3% component was tetracyclo[3.3.0.0^{2,7}0.^{4,6}]octane. The other 3% component was not identified.

Solvolysis of *exo*-Tricyclo[3.2.1.0^{3,6}]octan-2-yl *p*-Toluenesulfonate.—In a 50-ml three-necked flask provided with a nitrogen inlet, a mechanical stirrer, and a condenser was placed 1.39 g (0.005 mol) of the title tosylate in 10 ml of bis(2-methoxyethyl) ether. To this mixture was added 0.38 g (0.01 mol) of lithium aluminum hydride in 10 ml of dry bis(2-methoxyethyl) ether in one portion. The mixture was heated under a nitrogen atmosphere with stirring at a temperature of 90° for 72 hr. The mixture was cooled; water and wet sodium sulfate were added; and the mixture was extracted with three 25-ml portions of pentane. The pentane solutions were combined, washed with three 50-ml portions of water, and dried over anhydrous magnesium sulfate. The pentane was removed on an 18-in. semimicro spinning band column to leave a residue which weighed 0.17 g (32.2%). Analysis of this residue on column E at 90° showed the presence of three peaks in per cent ratios 27:60:13.

The 27% peak was identified as tricyclo[3.3.0.0^{2,7}]octane by comparison of its infrared and nmr spectra with those of a known sample of the same hydrocarbon. The 60% component was likewise identified as tricyclo[3.2.1.0^{3,6}]octane and the 13% component was identified as tetracyclo[3.3.0.0^{2,7}0^{4,6}]octane.

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Registry No.—**2**, 5078-81-9; **3**, 4582-22-3; **5a**, 41564-15-2; **5b**, 41564-17-4; **5d**, 41564-16-3; **6a**, 41564-18-5; **7**, 250-22-6; **8**, 444-26-8; tricyclo[3.2.1.0^{3,6}]octan-2-one, 6239-87-8; *p*-toluenesulfonylhydrazine, 1576-35-8; *exo*-tricyclo[3.2.1.0^{3,6}]-octan-2-ol, 6239-90-3; methyl iodide, 74-88-4; *exo*-2-chlorotricyclo[3.2.1.0^{3,6}]octane, 41564-23-2.

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(22) P. K. Freeman, V. N. M. Rao, D. E. George, and G. L. Fenwick, *J. Org. Chem.*, **32**, 3958 (1967).

(23) D. E. George, Ph.D. Thesis, University of Idaho, 1963.

(24) We thank Professor R. R. Sauers for this identification.