Syntheses and Reactions of 3-Substituted Tricyclo[3.3.0.0^{2,6}]octanes and of Tricyclo[3.3.0.0^{2,6}]oct-3-ene[1]

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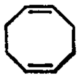
Abstract: Photochlorination of tricyclo[3.3.0.0^{2,6}]octane (**2**) leads to 3-chlorotricyclo[3.3.0.0^{2,6}]octane (**9**), resulting from preferential attack at the secondary positions. Similarly, chromyl acetate oxidation of **2** gives tricyclo[3.3.0.0^{2,6}]octan-3-one (**10**) as the chief product, accompanied by a smaller amount of tricyclo[3.3.0.0^{2,6}]oct-3-yl acetate (**11**). The acetolysis of the corresponding tosylate (**13**) was found to proceed at a rate about 180 times that of bicyclo[2.1.1]hex-2-yl tosylate (**18**), producing a mixture of unrearranged and rearranged products (**11**, **14**, and **15**). These observations are accommodated by consideration of the difference in degree of substitution and in geometry between the tricyclic and bicyclic esters. Finally, tricyclo[3.3.0.0^{2,6}]oct-3-ene (**4**) was obtained *via* tricyclo[3.3.0.0^{2,6}]oct-3-ylamine (**30**) using a Hofmann elimination sequence. Some unexpected features of the nmr and ultraviolet spectra of this strained olefin are described.

In 1963 Srinivasan reported that the gas-phase, mercury-sensitized photoisomerization of *cis,cis*-1,5-cyclooctadiene (**1**) gives tricyclo[3.3.0.0^{2,6}]octane (**2**) in 1% yield.[2] Shortly thereafter,[3,4] he was able to develop a solution photolysis technique which gave a 30% yield of **2**. These developments, along with our continuing interest in the highly strained bicyclo[2.1.1]hexane ring system (**3**), prompted an investigation of the synthesis and reactions of functionalized tricyclo[3.3.0.0^{2,6}]octanes. Some of our specific goals were the introduction of substituents at C_3 of **2**, to permit carbonium ion studies analogous to those already carried out on bicyclo[2.1.1]hexanes.[5-9] Another objective was to use such functionalized derivatives as intermediates for a synthesis of tricyclo[3.3.0.0^{2,6}]oct-3-ene (**4**), analogous to the as yet unknown bicyclo[2.1.1]hex-2-ene. We wish now to present our results in these areas.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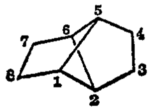

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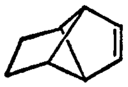
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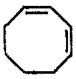
Discussion

To obtain tricyclo[3.3.0.0^{2,6}]octane for extensive study, the irradiation of 1,5-cyclooctadiene was carried out under conditions slightly different from those previously described.[3] By increasing the concentration of 1,5-cyclooctadiene about fourfold and by allowing the conversion to proceed almost to completion, yields of *ca.* 50% and absolute amounts of 15–50 g of **2** could be realized in a single experiment.

Srinivasan found in this initial study that **2** was not the only product of the irradiation of 1,5-cyclooctadiene in solution. Thus, when the reaction was carried out in ether with cuprous chloride or rhodium chloride as catalyst, four products were identified: the tricyclooctane **2**, 1,3-cyclooctadiene (**5**), 1,4-cyclooctadiene (**6**), and bicyclo[4.2.0]octene-7 (**7**).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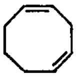
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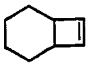
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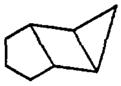
We have found that one previously undetected product consistently comprised about 10% of the reaction mixture. An elemental analysis indicated that this component was another C_8H_{12} isomer. Its nmr spectrum showed no absorption in the olefinic region, but upfield absorption attributable to a cyclopropane grouping was apparent. A comparison of the nmr and infrared spectra of this compound with those of an authentic sample of *cis,anti,cis*-tricyclo[3.3.0.0^{2,4}]octane (**8**) showed two compounds to be identical.[10,11] Although the formation of **8** might be rationalized by a small variation of the free radical chain mechanism proposed recently to account for the formation of **2** from **1**,[12a] it now appears more correct to view this as an independent side reaction rather than as one based upon a common intermediate.[12b]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With **2** readily available we examined methods to functionalize the hydrocarbon skeleton. Since free radical reactions generally occur without structural rearrangement, even in highly strained systems, this was the first type of reaction to be tried. Two free

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[1] The partial support of this resarch by the National Institutes of Health (GM 10090) is acknowledged with pleasure.

[2] R. Srinivasan, *J. Am. Chem. Soc.*, **85**, 819 (1963).

[3] R. Srinivasan, *ibid.*, **85**, 3048 (1963).

[4] R. Srinivasan, *ibid.*, **86**, 3318 (1964).

[5] J. Meinwald and P. G. Gassman, *ibid.*, **85**, 57 (1963).

[6] J. Meinwald, P. G. Gassman, and J. J. Hurst, *ibid.*, **84**, 3722 (1962).

[7] K. B. Wiberg and R. Fenoglio, *Tetrahedron Letters*, 1273 (1963).

[8] K. B. Wiberg, B. R. Lowry, and T. H. Colby, *J. Am. Chem. Soc.*, **83**, 3998 (1961).

[9] K. B. Wiberg and B. R. Lowry, *ibid.*, **85**, 3188 (1963).

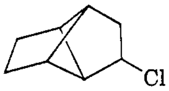
[10] J. Zirner and S. Winstein, *Proc. Chem. Soc.*, 235 (1964).

[11] Private communication, Professor S. Winstein.

[12] (a) J. E. Baldwin and R. H. Greeley, *J. Am. Chem. Soc.*, **87**, 4514 (1965); (b) I. Haller and R. Srinivasan, *ibid.*, **88**, 5084 (1966).

radical substitutions which proved useful were chlorination and chromyl acetate oxidation.

In the chlorination of acyclic hydrocarbons it has been found that the order of reactivity of aliphatic carbon–hydrogen bonds toward chlorine is tertiary > secondary > primary.[13] In alicyclic compounds, however, this order is not necessarily the same. Thus, in the chlorination of bicyclo[2.2.1]heptane only two products have been isolated, both of which involve attack at the C_2 position.[14] The liquid-phase photochlorination of **2** led to analogous results; the only product detected, isolable in 50% yield, was 3-chlorotricyclooctane (**9**). The glpc of this product on several analytical columns indicated the presence of only one component. Its elemental analysis was compatible with the molecular formula $C_8H_{11}Cl$. The nmr spectrum showed a complex doublet centered at τ 5.46 (1 proton, assignable to that at C_3), and a complex series of peaks, subsequently found to be characteristic of 3-substituted derivatives of **2**, from τ 7.3 to 8.2 (10 protons).



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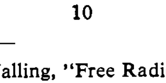
The liquid-phase bromination of **2** was also carried out, but was unexpectedly complex. The reaction may have followed a carbonium ion pathway rather than a free radical pathway. (An example of a hydrocarbon bromination which apparently utilizes a carbonium ion mechanism is provided by the conversion of adamantane to 1-bromoadamantane.[15]) The product, which appeared to contain two bromine atoms, was not fully characterized.

The oxidation of hydrocarbons by chromic acid, chromyl acetate, or chromyl chloride is also reported to be a free radical substitution reaction.[16] The relative rates of attack on aliphatic carbon–hydrogen bonds are typical of rates of free radical reactions, that is, tertiary > secondary > primary.[17] The alcohols formed initially in these reactions are often further oxidized to ketones. This technique provides a useful ketone synthesis when the product is not readily degraded by enolization and subsequent oxidation.[8,18,19]

Chromyl acetate oxidation of **2** gave tricyclo[3.3.0.0^{2,6}]octan-3-one (**10**) and tricyclo[3.3.0.0^{2,6}]oct-3-yl acetate (**11**), characterized as described below. They were formed in a ratio of 9:1, as determined by glpc, in an over-all yield of *ca.* 60% based on the tricyclooctane consumed. The structure of **10** follows from its elemental analysis, from its mass spectrum, which showed a parent peak at *m/e* 122, from its infrared absorption maximum at 5.68 μ (carbonyl stretching), and from a series of reactions, described later, which relate ketone **10** to **2**. The acetate **11** could be separated from the crude ketone by a zone freezing technique, and was shown to be identical with authentic **11**, prepared, as described below, from alcohol **12**.



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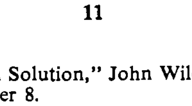

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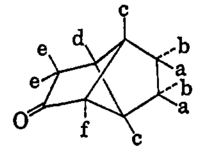
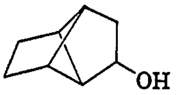
The nmr spectrum of **10** is simplified by a coincidence of chemical shift values. While there are six different types of carbon–hydrogen bonds in the molecule, the spectrum shows only four sharp bands at τ 7.40 (2), 7.78 (2), 7.86 (2), and 8.13 (4). This pattern of absorption can be explained by assuming that all four hydrogens at C_7 and C_8 (a and b, formula **10a**) have the same chemical shift, and that those at C_2 and C_5 (f and d) are also equivalent.



10a

Reduction of **10** with lithium aluminum hydride gave the alcohol **12** in 80% yield. The corresponding tosylate **13** was prepared in 90% yield by the treatment of **12** with *p*-toluenesulfonyl chloride in pyridine. The elemental analyses of **12** and **13** and their infrared and nmr spectra were consistent with the assigned structures.



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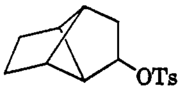

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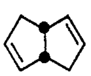
The rate of acetolysis of **13** was determined titrimetrically, at 35.0 and 50.0°, by standard methods.[20,21] Excellent first-order kinetics were observed over several half-lives. Three products were characterized from this acetolysis. The first (20%) was identified as bicyclo[3.3.0]octa-2,6-diene (**14**) by comparison with an authentic sample.[22] Unrearranged acetate **11** was formed in 40% yield, and the ring-opened acetate **15** in 17% yield. The acetates were reduced with lithium aluminum hydride, and the resulting alcohols were separated by preparative glpc. The alcohol from the reduction of **11** was identical in every respect with the previously characterized tricyclic alcohol **12**. The alcohol from the reduction of acetate **15** was hydrogenated over Adam's catalyst. A phenylurethan of this alcohol had the same melting point as that reported for the phenylurethan of **16**.[23] The hydrogenated alcohol was oxidized with N-bromosuccinimide, following a procedure



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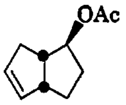

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(13) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, Chapter 8.

(14) E. C. Kooyman and G. C. Vegter, *Tetrahedron*, 4, 382 (1958).

(15) H. Stetter, M. Schwarz, and A. Hirschhorn, *Chem. Ber.*, 92, 1629 (1959).

(16) K. B. Wiberg and R. Eisenthal, *Tetrahedron*, 20, 1151 (1964).

(17) R. Stewart, "Oxidation Mechanisms," W. A. Benjamin, Inc., New York, N. Y., 1964, pp 50–55.

(18) K. B. Wiberg in "Oxidation in Organic Chemistry," K. B. Wiberg, Ed., Academic Press Inc., New York, N. Y., 1965, Chapter 3.

(19) P. von R. Schleyer and R. D. Nicholson, Abstracts, 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1961, p 750.

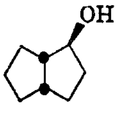
(20) S. Winstein, E. Grunwald, and L. I. Ingraham, *J. Am. Chem. Soc.*, 70, 821 (1948).

(21) S. Winstein, C. Hanson, and E. Grunwald, *ibid.*, 70, 812 (1948).

(22) W. von E. Doering and W. R. Roth, *Tetrahedron*, 19, 715 (1963).

(23) A. C. Cope, H. E. Petree, and M. Brown, *J. Am. Chem. Soc.*, **80**, 2852 (1958).

of Cope,[23] to give a ketone, the 2,4-dinitrophenylhydrazone of which had the same (broad) melting point as that of the known derivative of ketone **17**.[24] Thus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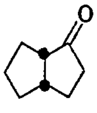
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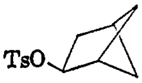
the *cis* fusion of the rings and the position of the oxygen is certain, as is the *exo* configuration of the alcohol, although a small amount of the *endo* alcohol might have gone unobserved. The position of the double bond of **15** is assigned on mechanistic grounds and on the basis of the great similarity of the nmr spectra of **14** and **15** in the olefinic proton region.

To rationalize both the rate of solvolysis of **13** and the products formed, we may compare these results with those obtained for carbonium reactions at C_2 in the bicyclo[2.1.1]hexane series. The relative rates for the acetolysis of bicyclo[2.1.1]hexyl 2-tosylate (**18**), 5,5-dimethylbicyclo[2.1.1]hexyl 2α-tosylate (**19**), and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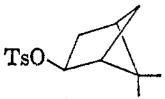
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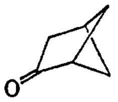
tosylate **13** (extrapolated to 75°) are 1:36:180.[5,25] A major factor influencing the rate of ionization is the internal angle at the carbon atom where the ionization occurs.[26–28] Although knowledge of the pertinent molecular geometry from direct physical measurement is often lacking, estimates are available from a correlation of carbonyl stretching frequencies with included angle.[28] The carbonyl stretching band of both **20** and **21** is found at 1764 cm^{-1}, while that of **13** is at 1758 cm^{-1}. These frequencies lead to calculated angles of 95.5° for **20** and **21**, and 98.5° for 10. If the internal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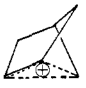
angles were the only determining factor in the rates of acetolysis, then one would expect **18** and **19** to have the same solvolysis rate, and **13** to have a rate *ca.* 15 times faster. A possible explanation for the difference in rate between **18** and **19** may be found in the hypothesis that these esters yield bridged, delocalized ions in which positive charge is distributed over three positions.[5,25] The bridged carbonium ion **22**, derived from **18**, would spread its charge to a primary carbon in one of its contributing forms, whereas the bridged carbonium ion **23**, derived from **19**, has two additional methyl groups providing a tertiary site in place of the primary site in **22** to help stabilize the positive charge. If a similar type of bridged ion were formed in the solvolysis of **13**, a reasonable model for comparison would be the presently unknown ester **24**, with one methyl substituent to aid the leaving of the tosylate group. In both the hypothetical bridged carbonium ion which would be formed from **24** and that expected from **13**, the electron deficiency would be shared by a secondary carbon. To predict the rate of acetolysis of **24** relative to the rate of **18** and **19**, we will simply choose the average of that for **18** and **19**, which is 18. This would make the relative rates of **24**:**13** 18:180, or 1:10. Correcting for the difference in angle at C_2 of the bicyclo[2.1.1]hexane nucleus and C_3 of the tricyclo[3.3.0.0^{2,6}]octane nucleus,[26,28] the expected relative rates for the hypothetical model and **13** become 1.4:1. On the basis of these crude estimates, the acetolysis rate of **13** agrees well with expectations.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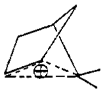
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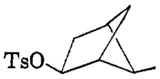
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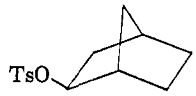
It should be noted that this type of argument, which appears plausible for the cases just discussed, cannot be applied successfully to the bicyclo[2.2.1]heptyl analogs of **18** and **19**, **18a** and **19a**.[29] Thus, in the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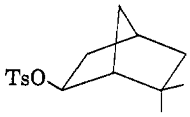
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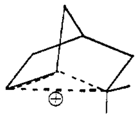
23a

bicyclo[2.2.1]heptyl series, Schleyer, *et al.*, found that 6,6-dimethyl-2-*exo*-bicyclo[2.2.1]heptyl tosylate (**19a**) was *less* reactive than 2-*exo*-bicyclo[2.2.1]heptyl tosylate (**18a**) by a factor of *ca.* 14 at 75°. These results are contrary to those which might have been expected if a bridged ion (**23a**) with significant contribution from the resonance form with positive charge on the tertiary site (C_6) were produced. Schleyer, *et al.*,[29] have rationalized the deactivation of **19a** by assuming that the *endo*-6-methyl substituent suffers unfavorable steric interactions in going to a bridged transition state (**23a**). Since the geometric situation is quite different in **19** and **23**, however, this steric effect may well not be felt. In fact, the C_1–C_5 bond loosening implied in structure **23**, which corresponds to partial opening of a cyclobutane ring, with concomitant strain relief, could be a factor operating in the opposite direction, encouraging contribution from the resonance form with positive charge at C_5 in the bicyclo[2.1.1]hexyl series.

The acetolysis product obtained from **18**, after reduction with lithium aluminum hydride, is bicyclo[2.1.1]hexan-2-ol (**26**), whereas the product of the acetolysis of **19**, after reduction, is the ring-opened tertiary alcohol, **27**. The formation of **26** and **27** is consistent with the bridged carbonium ion hypothesis. Acetic acid could be expected to attack ions **22** and **23** at the positions of greatest positive charge density.[30] Attacked in this way, **22** would yield the acetate of **26**. In the case of **23**, bonding of a solvent molecule to the position of greatest positive charge density (tertiary) would give the acetate of **27**. Similarly, ion **28** formed from the solvolysis of **13** has no obvious position of "greatest" charge density, since all relevant positions are secondary.

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[24] A. C. Cope and W. R. Schmitz, *J. Am. Chem. Soc.*, 72, 3056 (1950).

[25] Doctoral dissertation submitted to Cornell University, J. K. Crandall, 1963.

[26] P. von R. Schleyer, *J. Am. Chem. Soc.*, 86, 1854 (1964).

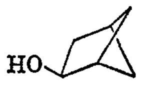
[27] J. A. Halford, *J. Chem. Phys.*, 24, 830 (1950).

[28] C. S. Foote, *J. Am. Chem. Soc.*, 86, 1853 (1964).

[29] P. von R. Schleyer, M. M. Donaldson, and W. E. Watts, *ibid.*, 87, 375 (1965).

[30] J. A. Berson, *Tetrahedron Letters*, 16, 17 (1960).

On this basis, solvent attack at both C_2 and C_6 with concomitant ring opening appears reasonable.



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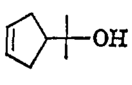

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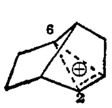

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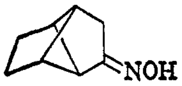
Another very significant experimental difference between the bicyclo[2.2.1]heptyl and bicyclo[2.1.1]hexyl series is that **19a** suffers acetolysis, giving exclusively the *unrearranged* 6,6-dimethyl-2-*exo*-bicyclo[2.2.1]heptyl acetate,[29] while **19** yields *ring-opened* acetate as at least 98% of the acetate produced.[25] Thus, the *differences* between the effects of *gem*-dimethyl substitution in **19** and **19a** are apparent from both the kinetic results and the products obtained.

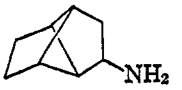
The introduction of a double bond into the tricyclo[3.3.0.0^{2,6}]octane nucleus was another objective of this study. One of the reasons for our interest in this olefin is that all attempts to synthesize the closely related bicyclo[2.1.1]hexenes have as yet been unsuccessful.[31] A series of reactions which led to the successful preparation of **4** are described below.

Ketone **10** reacted with hydroxylamine to give oxime **29** in 95% yield. This oxime was reduced with lithium aluminum hydride in tetrahydrofuran to give amine **30** in 80% yield. (It has been shown that adamantylamine hydrochloride (**31**) has both *in vitro* and *in vivo* antiviral activity.[32] It will be of interest to see whether the somewhat related hydrochloride of **30** is associated with similar biological activity.)

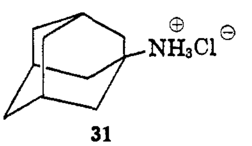
Amine **30** was converted to the dimethylamine **32** in 80% yield by the Eschweiler–Clarke technique.[33] Methyl iodide in ether converted **32** to the trimethylammonium iodide **33a**, which was then treated with a suspension of silver oxide to form the trimethylammonium hydroxide **33b**. This product decomposed in a nitrogen atmosphere at *ca.* 100° (12 mm) to give **4** in 29% yield, accompanied by 53% of recovered **32**.



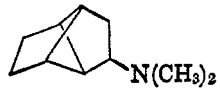
29



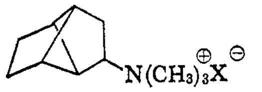
30



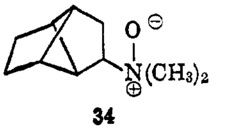
31



32



33a, $X^- = I^-$
33b, $X^- = OH^-$

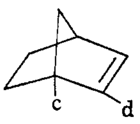


34

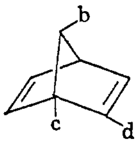
(The formation of **32** corresponds to a common side reaction in many Hofmann elimination reactions.[34]) In an attempt to obtain better yields of **4**, the amine oxide **34** was prepared from **32** and 30% hydrogen peroxide. Disappointingly, the decomposition of **32** required unusually high temperatures (180–210°), and gave as its main product not **4**, but an unidentified product which seemed to be aromatic. This study of **34** was not carried further.

The olefinic product obtained from **33b** had the expected elemental analysis, and its molecular formula was confirmed by its mass spectrum, which showed a parent peak at *m*/*e* 106. A small sample of **4** was hydrogenated over Adams' catalyst, and the product was found to be identical with the parent tricyclooctane **2**, as shown by nmr and infrared spectra, and by glpc comparisons. This reaction proved that the basic tricyclic nucleus had remained unchanged throughout the series of reactions which culminated in the formation of **4**.

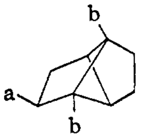
The nmr spectrum of **4** shows four groups of absorption bands centered at τ 3.93 (2 protons), 6.53 (2 protons), 8.15 (2 protons), and 8.27 (4 protons). A tentative assignment of these absorption bands, based upon the chemical shifts of closely related absorption bands in bicyclo[2.2.1]heptene,[35] bicyclo[2.2.1]heptadiene,[35] and tricyclooctane, is given below. The spin–spin couplings are described in the Experimental Section. Although the coupling pattern appears to be rationalized, it should be noted that this spin–spin coupling may be "deceptively simple."[36] One interesting aspect of the nmr spectrum of **4**, assuming the above assignment of the absorption bands, is the long-range coupling (*J* = *ca.* 2 cps) between the olefinic (τ 3.93) and homoallylic (τ 8.15) protons, d and b. These protons do not have the "W" geometry usually associated with four-bond proton–proton coupling.[37] The alternate explanation that the coupling of the olefinic protons is actually with the adajacent allylic rather than with the homoallylic protons would appear at first to require quite unusual chemical shift assignments, as shown in formula **4a**. Interesting precedent for these unexpected assignments, however, is provided by the nmr spectrum of benzvalene (**35**), which has recently been synthesized, and which appears to have its allylic proton resonance



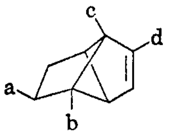
c = τ 7.15
d = τ 4.04



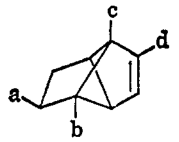
c = τ 6.53
d = τ 3.35
b = τ 8.05



a = τ 8.27
b = τ 8,18



a = τ 8.27
b = τ 8.15
c = τ 6.53
d = τ 3.93



4a
a = τ 8.27
b = τ 6.53
c = τ 8.15
d = τ 3.93

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(31) J. Meinwald and J. K. Crandall, *J. Am Chem. Soc.*, **88**, 1292 (1966).

(32) W. L. Davis, R. R. Grunert, R. F. Haff, J. W. McGahen, E. M. Neumayer, M. P. Shock, J. C. Watts, T. R. Wood, E. C. Hermann, and C. E. Hoffmann, *Science*, **144**, 862 (1964).

(33) M. L. Moore, *Org. Reactions*, **5**, 301 (1949).

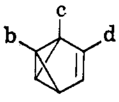
(34) A. C. Cope and E. R. Trumbull, *ibid.*, **11**, 317 (1960).

(35) P. Laszlo and P. von R. Schleyer, *J. Am. Chem. Soc.*, **86**, 1171 (1964).

(36) R. J. Abraham and H. J. Bernstein, *Can. J. Chem.*, **39**, 216 (1961).

(37) A. Rassat, C. W. Jefford, J. M. Lehn, and B. Waegell, *Tetrahedron Letters*, 233 (1964).

ca. 1.5 ppm upfield from that of the homoallylic protons.[38] The problem of distinguishing between these two possible rationalizations of the nmr spectrum of **4** is a subtle one, and clarification of the assignment of the τ 8.15 and 6.53 bands will have to await further investigation.



35
b = τ 6.47
c = τ 8.16
d = τ 4.05

The nmr spectrum of **4** affords an opportunity to estimate the degree of s character in the vinyl carbon–hydrogen bonds on the basis of the corresponding H–^{13}C coupling constant.[39] The coupling constant $J_{^{13}C-H}$ depends upon the bond order, and varies from J = 125 cps for an sp^3 bond to J = 250 cps for an sp bond.[39] The carbon–hydrogen spin–spin coupling constants of molecules closely related to **4**, and of **4**, itself are collected in Table I.[40] It would appear from these data that **4** has more s character in its vinyl carbon–hydrogen bonds than does bicyclo[2.2.1]heptene, and less than bicyclo[2.2.1]heptadiene.

Table I

Compd	$J_{^{13}C-H}$, cps	$J_{-HC=CH-}$, cps
Cyclopentene	160.5	5.8
Cyclopentadiene	170	. . .
Ethylene	156.8	11.4
Bicyclo[2.2.1]heptene	165.5	6.0
Bicyclo[2.2.1]heptadiene	172.5	5.2
Tricyclo[3.3.0.0^{2,6}] octene	167 ± 1	5.1

The ultraviolet absorption spectrum of **4** appears to be of particular interest. Its longest wavelength band starts at *ca.* 251 mμ, whereas the comparable absorptions start at *ca.* 208 mμ in cyclopentene, at *ca.* 213 mμ in bicyclo[2.2.1]heptene, and at *ca.* 221 mμ in bicyclo-[2.2.1]heptadiene.[41,42] This ultraviolet spectrum is now receiving more careful examination, and will be discussed elsewhere.[43]

Summing up, tricyclooctane **2** has been functionalized at C_3, and the acetolysis of the corresponding 3-tosyloxy derivative has been studied. In addition, tricyclooctene **4** has been synthesized for the first time. This olefin, which shows several unexpected spectral properties, provides the first example of a simple bicyclo-[2.1.1]hexene.

Experimental Section

All boiling points and melting points are uncorrected. Column chromatography was carried out on Woelm neutral alumina. Microanalyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark, and by the Galbraith Laboratories, Knoxville, Tenn.

Gas–Liquid Partition Chromatography (Glpc). Analytical determinations were carried out on Aerograph Models 600 Hy-Fl and 660 Hy-Fl. Columns of the following liquid phases on Firebrick were used: 30% Ucon oil nonpolar; BDS (15% butanediol succinate); 30% Carbowax 20M; TCEP (20% 1,2,3-tris(2-cyanoethoxy)propane).

A Beckman GC-2 gas chromatograph was used for preparative glpc. The following columns were used: Carbowax, 10 ft of 30% Carbowax 20M; TCEP, 12 ft of 20% 1,2,3-tris(2-cyanoethoxy)propane.

Infrared Spectra. Most infrared spectra were run on a Perkin-Elmer Infracord Model 137 B. The carbonyl stretching frequencies of ketones **10** and **20** were measured on a Perkin-Elmer Model 521.

Nuclear Magnetic Resonance Spectra. Nmr spectra were taken on a Varian A-60 spectrometer, in carbon tetrachloride, unless otherwise noted.

Mass Spectra. All mass spectra were run on a CEC 21-103A spectrometer. Each spectrum was calibrated with a compound of known mass.

Ultraviolet Spectra. All ultraviolet spectra were taken on a Cary Model 14 spectrophotometer in the specified solvent.

Tricyclo[3.3.0.0^{2,6}]octane (2).[3] A solution of 1,5-cyclooctadiene (25.3 g, 0.234 mole) and cuprous chloride (0.1 g) in ether (1.8 l.) was irradiated in a 2-l. Vycor flask (equipped with a condenser and drying tube) by a bank of 16 GE 68T5 lamps placed around the flask. After 1 day a green precipitate had formed. The reaction mixture was filtered and the flask washed with nitric acid. The filtrate was returned to the flask and irradiated for an additional 4 days. By the end of this period, a black, finely divided precipitate had formed and coated the walls of the flask. The reaction mixture was again filtered and returned to the cleaned flask. This procedure was repeated again after the tenth day, and fresh cuprous chloride (50 mg) was added. After 15 days of irradiation, the ratio of **2** to 1,5-cyclooctadiene was estimated to be 15:1 by glpc (30% Ucon oil nonpolar at 80°) and irradiation was stopped. The reaction mixture was distilled through a 60-cm spinning-band column and gave five fractions: (1) 0.7 g, bp 65–117°; (2) 0.5 g, bp 117–120°; (3) 4.6 g, bp 120–125°; (4) 10.2 g, bp 125–126°; (5) 3.1 g, bp 126–140°. Fractions 3 and 4 were estimated to be *ca.* 90% **2**. Fraction 5 contained *ca.* 50% **2** and 50% of other C_8H_{12} isomers. The undistilled material (7.3 g) was discarded. The product could be further purified by refluxing with a solution of potassium permanganate (20 g) in 200 ml of water for 1 hr. Hydrocarbon **2** was recovered by steam distillation from the permanganate solution. Extraction of the water layer with *n*-pentane, followed by distillation, yielded 11.5 g (45%) of *ca.* 98% pure **2**. The infrared and nmr spectra agreed with the published data.[2]

***cis,anti,cis*-Tricyclo[3.3.0.0^{2,4}]octane (8).** From several preparations of **2**, fractions equivalent to fraction 5 were collected and redistilled through a spinning-band column. A sample, bp 133–135°, was collected which was estimated to be 60% **8** by glpc (Ucon oil nonpolar). This fraction was further purified by preparative glpc (20% TCEP), yielding a sample of **8** *ca.* 95% pure. An nmr spectrum of **8** showed absorption bands centered at τ 7.9, 8.5, 8.98, and 9.45. A sample collected from the preparative glpc was analyzed.

Anal. Calcd for C_8H_{12}: C, 88.82; H, 11.18. Found: C, 88.72; H, 11.27.

A comparison of the nmr and infrared spectra of **8** with those of an authentic sample of *cis,anti,cis*-tricyclo[3.3.0.0^{2,4}]octane,[10,11] obtained directly from Professor S. Winstein, showed the two compounds to be identical.

Tricyclo[3.3.0.0^{2,6}]octan-3-one (10). Acetic acid (200 ml) and acetic anhydride (200 ml) were added to a 2-l. three-necked flask which was equipped with a Teflon stirrer and a thermometer. Chromium trioxide (40 g) was added to the solution with stirring, to prevent the formation of a solid mass. Heat was evolved as the chromium trioxide reacted with the acetic anhydride to form chromyl acetate. After being stirred for 1 hr, the reaction mixture was cooled to 0° and hydrocarbon **2** (27.8 g, 0.228 mole) of *ca.* 98% purity was added dropwise at such a rate that the temperature remained below 3°. After being stirred for 15 hr at 0–3°, the reaction mixture was warmed slowly to 15° and then heated to 75°. Water (200 ml) was added to the reaction mixture and heating was continued at 100° for 2 hr. The reaction mixture was cooled and a solution of sodium hydroxide (360 g) in 500 ml of water (enough base to neutralize 90% of the acetic acid) was carefully added, with

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(38) K. E. Wilzbach, J. S. Ritscher, and L. Kaplan, *J. Am. Chem. Soc.*, **89**, 1031 (1967).

(39) N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 768, 1471 (1959).

(40) K. Tori, R. Muneyuki, and H. Tanida, *Can. J. Chem.*, **41**, 3142 (1963).

(41) M. B. Robin, R. R. Hart, and N. A. Kuebler, *J. Chem. Phys.*, **44**, 1803 (1966).

(42) M. B. Robin and N. A. Kuebler, *ibid.*, **44**, 2664 (1966).

(43) For a discussion of the relationship between C=C stretching frequencies and bond angles, see C. F. Wilcox and R. R. Craig, *J. Am. Chem. Soc.*, **83**, 3866 (1961).

cooling. The reaction mixture was diluted with water and extracted with ether six times. The ethereal solution was washed with saturated sodium bicarbonate solution until the washings remained basic, then with saturated sodium chloride solution, and was finally dried over sodium sulfate. The dried ethereal solution was distilled through a Podbielniak-type column to remove solvent, and the undistilled residue was redried over magnesium sulfate and finally distilled to yield ketone **10** and acetate **11** [bp 90° (32 mm)] in a 9:1 ratio as estimated by glpc (15% BDS at 120°). The yield of the ketone-acetate mixture was *ca.* 60% based on the amount of hydrocarbon consumed. A small sample of the product mixture was purified by zone freezing, and the ketone, whose melting point was slightly below room temperature, was analyzed. The infrared spectrum (neat) of **10** showed absorption maxima at 3.4, 5.69, 7.05, 7.80, 8.08, 8.30, 8.65, 9.00, 9.9, 11.20, 12.1, and 12.3 μ. The nmr spectrum exhibited singlets at τ 7.40 (2) 7.78 (2), 7.85 (2), and 8.13 (4).

Anal. Calcd for $C_8H_{10}O$: C, 78.65; H, 8.25. Found: C, 78.75; H, 8.21.

A semicarbazone, mp 199–200°, was prepared from **10** and recrystallized for analysis from absolute ethanol.

Anal. Calcd for $C_9H_{13}N_3O$: C, 60.31; H, 7.31; N, 23.45. Found: C, 60.45; H, 7.32; N, 23.50.

A 2,4-dinitrophenylhydrazone, mp 206–207°, was prepared from **10** and recrystallized for analysis from ethyl acetate.

Anal. Calcd for $C_{14}H_{14}N_4O_4$: C, 55.62; H, 4.67; N, 18.54. Found: C, 55.85; H, 4.85; N, 18.68.

Tricyclo[3.3.0.0^{2,6}]octen-3-ol (12). Ketone **10** (885 mg, 7.25 mmoles) in anhydrous ether (10 ml) was added dropwise to a stirred suspension of lithium aluminum hydride (200 mg) in ether (25 ml). The reaction mixture was refluxed for 15 min, then cooled. Water (1 ml) was cautiously added. After being stirred for a further 30 min, the reaction mixture was filtered, and the precipitated salts were washed three times with ether. The ethereal solution was dried (magnesium sulfate) and filtered and the ether removed to yield a colorless oil (750 mg) which crystallized on standing. When the reaction product was sublimed, it yielded alcohol **12** (700 mg, 78%), mp 33–34°. The infrared spectrum (neat melt) showed absorption maxima at 3.0, 3.38, 3.47, 7.4, 7.8, 8.73, 9.10, 9.5, 9.7, 9.85, and 11.8 μ. The nmr spectrum showed a one-proton doublet (J = 7 cps) at τ 5.58 (HCO), a singlet at τ 5.96, and a complex series of peaks from τ 7.45 to 8.6 (10 protons).

Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.47; H, 9.79.

3-Acetoxytricyclo[3.3.0.0^{2,6}]octane (11). Alcohol **12** was acetylated in the usual way, by treatment with acetic anhydride and pyridine. After the usual work-up, the product was distilled through a Podbielniak-type column to yield **11**, bp 65° (2.5 mm) (5.6 g, 75%). An infrared spectrum showed acetate absorption maxima at 5.67 and 8.00 μ.

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.45; H, 8.53.

Tricyclo[3.3.0.0^{2,6}]octan-3-ol *p*-Toluenesulfonate (13). Alcohol **12** (1.07 g, 0.0086 mole) and *p*-toluenesulfonyl chloride (1.82 g, 0.01 mole) were dissolved in pyridine (5 ml) at 0°. To the reaction mixture, after standing for 18 hr at 5°, was added a small piece of ice to destroy any remaining tosyl chloride. After remaining 30 min more at 5°, the reaction mixture was poured into ice. A white precipitate quickly formed. The white solid was filtered, washed with water, and dried to yield crude **13** (2.19 g). The crude **13** was recrystallized from 2-methylbutane (175 ml) by cooling the solution to −40°, which yielded the tosylate **13** as a white crystalline solid (2.03 g), mp 65–66°. A second crop of crystals (0.08 g), mp 64–65°, was obtained by removal of two-thirds of the solvent and cooling to −78°. The total yield of **13** was 2.11 g (88%). An infrared spectrum ($CHCl_3$) showed bands at 6.22, 7.3–7.4, 8.52, and 10.3 μ, which correspond to a *p*-toluenesulfonate ester. A sample of **13**, mp 65–66°, was recrystallized from 2-methylbutane for analysis.

Anal. Calcd for $C_{15}H_{18}SO_3$: C, 64.73; H, 6.52; S, 11.50. Found: C, 64.58; H, 6.62; S, 11.61.

Kinetic Measurements of Acetolysis of 13. The solvolysis reactions were run in anhydrous acetic acid solution that was 0.0549 *N* in sodium acetate. In both runs a specified amount of **13** was dissolved in 25.00 ml of the solvent, and samples were withdrawn from the reaction flask with a 1.00-ml pipet. The samples were titrated with 0.0328 *N* perchloric acid in acetic acid using bromophenol blue as indicator. The buret used had a 2-ml capacity with a micrometer drive that could be read to the nearest 0.001 ml; at 35.0°, $k = 4.08 \times 10^{-5}$ sec^{-1}; at 50.0°, $k = 2.52 \times 10^{-4}$ sec^{-1}.

Characterization of Acetolysis Products Derived from 13. Tosylate **13** (5.6 g) was dissolved in a solution of glacial acetic acid (100 ml) which contained acetic anhydride (6 ml) and was 0.5 *N* in sodium acetate. The solution was heated at 95° for 0.5 hr; water (5 ml) was added, and heating was continued for 0.5 hr at 95°. The reaction mixture was cooled and poured into a separatory funnel, and water and ether were added. The aqueous layer was extracted four times with ether. The ethereal solution was washed with a saturated sodium carbonate solution until the washings remained basic, then with saturated sodium chloride solution. It was finally dried over magnesium sulfate. The ether was removed by distillation and the residue distilled, yielding three fractions: (1) 0.40 g, bp 41° (32 mm); (2) 1.82 g, bp 73° (5 mm); (3) 0.09 g, bp 73° (5 mm). Fraction 1 (20% yield over-all) was shown to be identical with bicyclo[3.3.0]octadiene-2,6 by infrared and nmr spectral comparison.[22] Fractions 2 and 3 (57% over-all) were shown to be acetates by their infrared spectra. They were reduced by lithium aluminum hydride in the usual fashion. The alcohols (*ca.* 1 g of the mixture) were separated by preparative glpc (30% Carbowax at 160°). The major product (70% of the alcohols; 40% over-all) was shown to be tricyclooctan-3-ol **12** by infrared comparison with an authentic sample. The minor alcohol (30% of the alcohols; 17% over-all) showed infrared absorption at 3.0 and 3.28 μ. The nmr spectrum showed bands centered at τ 4.67 (2), 6.25 (1), 6.66 (1), and a complex series of bands from τ 7.3 to 8.95. A glpc purified sample was analyzed.

Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 77.14; H, 9.72.

A sample of the unknown alcohol was hydrogenated over prereduced Adams' catalyst in methanol. The reaction mixture was poured into a separatory funnel and water and pentane were added. The aqueous layer was extracted twice with pentane. The pentane layer was dried over sodium sulfate and filtered, and the pentane removed, leaving an alcohol with infrared absorption maxima at 2.95, 6.87, 7.42, 9.0, 9.3–9.4, 9.83, 10.02, 10.2, and 10.67 μ. A phenylurethan was prepared from this alcohol and appeared as a white, crystalline solid, mp 71–76°. The white solid was recrystallized once from pentane, yielding a phenylurethan, mp 73–76° (lit.[23] *exo*-bicyclo[3.3.0]octan-2-ol phenylurethan, mp 75–76°). About 100 mg of the hydrogenated alcohol was oxidized in acetone by N-bromosuccinimide, according to the procedure of Cope.[23] A 2,4-dinitrophenylhydrazone was prepared from the crude ketone. This derivative was chromatographed over activity 1 alumina, using benzene as the eluent. The first 8 fractions were combined, the solvent was removed, and the somewhat purified product was rechromatographed on a silica gel thin layer plate, using pentane–ethyl acetate (95:5) as the eluent. The orange band, which had separated from a colorless band, was removed from the plate and the product extracted from the silica gel with chloroform. The chloroform was removed and the derivative crystallized upon standing. It was recrystallized once from ethanol to give a sample with mp 111–120°. The 2,4-dinitrophenylhydrazone of bicyclo[3.3.0]octan-2-one is reported to have a similar melting point range, 110–114.5°, attributed to a mixture of the *syn* and *anti* isomers.[23,24]

3-Chlorotricyclo[3.3.0.0^{2,6}]octane (9). Tricyclooctane **2** (9.74 g, 0.090 mole) was added, in the dark, to a flask which contained a solution of benzene (107 g) and chlorine (*ca.* 3.5 g, 0.05 mole). The flask was then placed in a beaker of ice and set in the sunlight. After 1 min the color of the chlorine had disappeared. Nitrogen was bubbled through the reaction mixture to remove most of the hydrochloric acid. The solution was extracted once with a saturated sodium bicarbonate solution and finally dried over sodium sulfate. The reaction mixture was distilled through a spinning-band column (60 cm) and yielded hydrocarbon **2** (4.89 g) and chlorocarbon **9** (3.52 g, 55%), bp 68° (10 mm). An infrared spectrum (neat) showed absorption maxima at 3.39, 3.48, 6.91, 7.78, 7.98, 8.06, 9.15, 10.72, 10.92, 11.15, 13.8–13.9, and 14.0 μ. The nmr showed a complex one-proton doublet (J = *ca.* 7 cps) at τ 5.5 (HCCl) and a complex series of peaks from τ 7.3 to 8.6 (10 protons).

Anal. Calcd for $C_8H_{11}Cl$: C, 67.37; H, 7.78; Cl, 24.85. Found: C, 67.20; H, 7.92; Cl, 24.71.

Bromination of Tricyclo[3.3.0.0^{2,6}]octane. To a three-necked flask, equipped with stirrer, condenser, and dropping funnel, was added tricyclooctane **2** (2.9 g, 0.027 mole) and bromine (8 ml). The reaction mixture was heated, and at *ca.* 40° hydrogen bromide started to evolve. Heating was continued at 60° for 8 hr; the reaction mixture was diluted with carbon tetrachloride (25 ml). The reaction mixture was cooled and poured into a beaker which contained a solution of sodium sulfite. After the bromine had reacted, the reaction mixture was poured into a separatory funnel the layers were separated, and the organic layer was washed with a saturated sodium bicarbonate solution until the washings remained basic. The reaction mixture was dried over sodium sulfate. The solution was decanted from the drying agent and the carbon tetrachloride and **2** were removed by means of a rotary evaporator. The remaining oil (4.32 g) was distilled to give a pale yellow oil, bp 64–71° (0.5 mm) (1.79 g). An nmr spectrum showed a complex absorption from τ 4.5 to 8.7. A sample was redistilled for analysis.

Anal. Calcd for $C_8H_{10}Br_2$: C, 36.12; H, 4.06; Br, 59.82. Found: C, 34.45; H, 4.36; Br, 61.08.

Tricyclo[3.3.0.0^{2,6}]octan-3-one Oxime (29). To a 50-ml flask was added ketone **10** (2.08 g, 0.017 mole), hydroxylamine hydrochloride (1.75 g, 0.019 mole), potassium hydroxide (1.8 g), water (15 ml), and methanol (5 ml). Concentrated hydrochloric acid was added to the reaction mixture, after standing at room temperature for 2 days, until the mixture became acidic. The methanol was removed by means of a rotary evaporator, and the remaining mixture of oily oxime and water was extracted twice with ether. The ethereal solution was washed once with saturated sodium chloride solution, dried over magnesium sulfate, and filtered. The ether was removed by means of a rotary evaporator. The remaining oil (2.46 g) was sublimed and yielded oxime **29**, mp 54–57.5° (2.21 g, 95%). The infrared spectrum (CCl_4) showed absorption maxima at 3.0–3.2, 3.4, 5.88, 7.80, 8.05, 8.29, 8.97, 9.16, 10.6, 10.8, and 11.05 μ.

Anal. Calcd for $C_8H_{11}NO$: C, 70.04; H, 8.08; N, 10.21. Found: C, 70.25; H, 7.98; N, 10.08.

If the starting material were not pure ketone **10** but a mixture of ketone **10** and acetate **11**, then the best method for the purification of the oxime was recrystallization from pentane. The impure oxime was dissolved in *ca.* 15 times its volume of pentane and cooled to −40°. An oil separated after 1 hr; the pentane was decanted from this oil and the pentane cooled to −40° for an additional 12 hr. The pentane was decanted from the crystalline oxime and the oxime was blown free of pentane by a stream of nitrogen. The yield was *ca.* 70%.

3-Tricyclo[3.3.0.0^{2,6}]octylamine (30). A solution of oxime **29** (8.1 g, 0.059 mole) in anhydrous tetrahydrofuran (100 ml) was added dropwise to a stirred suspension of lithium aluminum hydride (6.0 g) in tetrahydrofuran (300 ml). The reaction mixture was refluxed for 2 days. After cooling, the suspension was hydrolyzed by the dropwise addition of water (25 ml), followed by stirring for an additional 30 min. The solution was filtered, and the precipitated inorganic salts were extracted by ether in a Soxhlet apparatus for 1 day. The combined tetrahydrofuran and ether solutions were dried over molecular sieves (Fisher Type 4A) and filtered, and the solvent was distilled off through a Podbielniak-type column. The residue was distilled and yielded amine **30** (6.0 g, 82%), bp 83° (32 mm). The infrared spectrum (neat) showed absorption maxima at 2.95, 3.0, 3.40, 3.47, 6.2, 6.81, 6.90, 7.22, 7.40, 7.80, 9.13, and 11.1 μ. The nmr spectrum showed a complex one-proton doublet (J = *ca.* 8 cps) at τ 6.68 (HCN), and a complex series of peaks, characteristic of the 3-substituted derivatives of the tricyclooctane nucleus, from τ 7.7 to 9.0.

A phenylthiourea, mp 134–143°, was prepared from **30**. Repeated recrystallizations from ethanol and acetone–pentane gave a sample which was analyzed, despite its broad melting range (134–143°).

Anal. Calcd for $C_{15}H_{18}N_2S$: C, 69.74; H, 7.02. Found: C, 69.72; H, 7.12.

3-N,N-Dimethylaminotricyclo[3.3.0.0.^{2,6}]octane (32). To amine **30** (3.0 g, 0.024 mole) was added, with cooling, formic acid (5.0 g) and formaldehyde (5.5 g of a 33% solution). The reaction mixture was heated on a steam bath for several hours, cooled, and acidified with 6 *N* hydrochloric acid. All volatile material was removed under reduced pressure, and the remaining oil made basic with aqueous sodium hydroxide. The aqueous mixture was extracted with ether and dried over magnesium sulfate and the ether removed using a rotary evaporator. The remaining colorless oil was distilled and yielded amine **32** (3.0 g, 80%), bp 74° (15 mm). The infrared spectrum showed absorption maxima at 3.55 and 3.61 μ, characteristic of the N,N-dimethyl grouping.

A picrate, mp 178–178.5°, was prepared from **32** and recrystallized for analysis from ethanol.

Anal. Calcd for $C_{16}H_{20}N_4O_7$: C, 50.53; H, 5.30; N, 14.73. Found: C, 50.72; H, 5.33; N, 14.63.

3-Tricyclo[3.3.0.0^{2,6}]octyltrimethylammonium Iodide (33a). A. To **32** (1.08 g, 0.0071 mole) in ether (20 ml) was added methyl iodide (2 ml) and potassium carbonate (0.25 g). The reaction mixture started to turn cloudy almost immediately and was let stand at room temperature overnight. The precipitate that had formed was filtered, washed with ether, and recrystallized from ethanol–ether, yielding **33a** (2.02 g, 95%), mp 234–243°. A sample, mp 245–247° dec, was recrystallized for analysis from ethanol–ether.

Anal. Calcd for $C_{11}H_{20}NI$: C, 45.23; H, 6.85; N, 4.76; I, 43.12. Found: C, 44.99; H, 6.70; N, 4.82; I, 43.18.

B. Oxime **29** (12.0 g, 0.0879 mole) in tetrahydrofuran (100 ml) was added to a stirred slurry of lithium aluminum hydride (10 g) in tetrahydrofuran (500 ml, freshly distilled from lithium aluminum hydride). The reaction mixture was refluxed for 2 days and cooled, and water (40 ml) was carefully added. The reaction mixture, after stirring for an additional hour, was filtered, and the precipitated inorganic salts were extracted by ether in a Soxhlet apparatus for 1 day. The combined tetrahydrofuran and ether solutions were dried over molecular sieves (Fisher Type 4A). The solution was decanted from the molecular sieves, and methyl iodide (8.1 ml, 0.088 mole) was added to the solution and let stand overnight. The solvent was distilled off through a Podbielniak-type column. The residue was transferred to a small flask and methanol (100 ml), methyl iodide (35 ml), and sodium carbonate (30 g) were added; the reaction mixture was then refluxed for 2 days. The methanol and methyl iodide were removed by means of a rotary evaporator and the remaining salts extracted four times with boiling chloroform (100-ml portions). The chloroform was removed by rotary evaporation, and the residue was recrystallized from ethanol–ether, yielding crystalline **33a** (22.9 g, 83%).

Tricyclo[3.3.0.0^{2,6}]octene-3 (4). Trimethylammonium iodide **33a** (12.5 g, 0.040 mole) was dissolved in a solution of methanol (100 ml) and water (50 ml). To this solution was added freshly prepared silver oxide (0.050 mole), and the reaction mixture was stirred for 2 days at 35°. The reaction mixture was then filtered, and the silver salts were washed with three portions of methanol (20 ml). The combined filtrate and washings were distilled, in a nitrogen atmosphere, under reduced pressure. When the solvent had been removed, the syrupy residue was heated. Decomposition commenced at 95° (12 mm) and was complete at 120° (12 mm). To the products, which were collected in a flask cooled in a Dry Ice bath, was added pentane (5 ml). The reaction mixture was cooled in a freezer. After the water had frozen, the organic layer was decanted and the ice washed with pentane (5 ml). The combined pentane solution was dried over sodium sulfate. The solution was then distilled through an 8-in., spinning-band column and was cut into six fractions: (1) 0.0547 g, bp 63° (130 mm); (2) 0.616 g, bp 58° (110 mm); (3) 0.232 g, bp 86–108° (100 mm); (4) 1.15 g, bp 108–118° (100 mm); (5) 1.01 g, bp 118° (100 mm); (6) 0.807 g, bp 118° (100 mm). Fractions 1 and 2 were shown to be **4** (29% yield from **33a**; 60% based on unrecovered amine **32**) and fractions 3–6 were shown to be **32**. The infrared spectrum of **4** showed absorption at 3.24, 3.37, 3.48, 6.44, 6.82, 7.65, 8.02, 8.3, 8.57, 11.15, and 14.7 μ. The infrared absorption band at 6.44 μ is tentatively assigned to the C=C stretching frequency.[44] The nmr spectrum (CCl_4) showed a two-proton triplet (J = 2 cps) at τ 3.93, a 2-proton pentuplet (J = 0.7 cps) at τ 6.53, a two-proton triplet (J = 2 cps) of pentuplets (J = 0.4 cps) at τ 8.15, and a complex four-proton band centered at τ 8.27. A sample of fraction 1 was analyzed.

Anal. Calcd for C_8H_{10}: C, 90.51; H, 9.49. Found: C, 90.35; H, 9.50.

A small sample of **4** was hydrogenated over prereduced Adams catalyst in methanol. The methanol solution was extracted with water and pentane. The pentane layer was dried over magnesium sulfate. The pentane was distilled off and the residue was separated, by preparative glpc (30% TCEP), from the remaining solvent and shown to be tricyclo[3.3.0.0^{2,6}]octane by glpc and infrared and nmr spectral comparisons.

The ultraviolet spectrum of **4** showed an absorption maximum at *ca.* 215 mμ (in isooctane) with an extinction coefficient of 2640; at 230 mμ, the extinction coefficient was 1730; at 240 mμ, it was 700; at 250 mμ, it was 150. The O–O band is centered at 250 mμ in this solvent. A spectrum was also run in the vapor phase. A very small drop of **4** was spaced in a 1-cm liquid cell and a spectrum of the vapor was taken. Vibrational fine structure could be seen on the electronic absorption envelope at 251, 246, 239, 237, 232, 227, 223, 220, 219, 215, 213.5, 212.2, 211.2, and 211.0 mμ. The extinction coefficients were not determined in the vapor phase spectrum.

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[44] For a discussion of the relationship between C=C stretching frequencies and bond angles, see C. F. Wilcox and R. R. Craig, *J. Am. Chem. Soc.*, **83**, 3866 (1961).

The mass spectrum of **4** determined on a CEC 21-130A instrument at 70 ev showed a parent peak at *m/e* 106, a base peak at 78, and other intense peaks at 91, 39, and 105.

3-N,N-Dimethyltricyclo[3.3.0,0^{2,6}]octylamino Oxide (34). To a 50-ml flask was added **32** (0.718 g, 4.75 mmoles), methanol (2 ml), and hydrogen peroxide (30%, 2 ml), and the reaction mixture was let stand at room temperature for 2 days. A small amount of platinum black was added to destroy any remaining hydrogen peroxide. The solvent was removed under reduced pressure, leaving a white solid (0.86 g). The amine oxide was recrystallized from tetrahydrofuran to yield crystalline **34** (0.76 g, 95%), mp 104–106°, no dec.

Pyrolysis of Amine Oxide 34. Pyrolysis of the amine oxide **34** was accomplished by heating in a round-bottomed flask equipped with a capillary nitrogen inlet and connected through a short column to two traps in series, cooled in Dry Ice. The nitrogen pressure was reduced to 10 mm, and most of the amine oxide decomposition took place between 180 and 210°. An nmr spectrum of the crude volatile products showed that only about 5% was the hoped for tricyclooctene **4**, while the rest seemed to be aromatic.

Aromatic Azapentalenes. I. Dibenzo-1,3a,4,6a-tetraazapentalene and Dibenzo-1,3a,6,6a-tetraazapentalene.[1] New Heteroaromatic Systems

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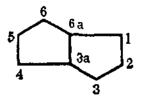
Abstract: The new heteroaromatic compounds, dibenzo-1,3a,6,6a-tetraazapentalene (III) and -1,3a,4,6a-tetraazapentalene (II), have been prepared in good yield by the thermal and photochemical decompositions of the *o*-azido phenyl derivatives of 1H- and 2H-benzotriazoles, respectively. The physical and spectral properties of these unusually stable pentalene analogs are described, as well as their structure determination. The mode of formation of the tetraazapentalene and the role of the annular nitrogen atoms in providing a $4n + 2$ π electron system are discussed.

In recent years, there has been great interest in formulating and demonstrating aromatic character for a variety of carbocyclic and heterocyclic systems.[2] Aromatic stability has been demonstrated in cyclopropenium, cyclopentadienide, benzene, tropylium, and cyclononatetraenide, as well as in nonalternant and hetero systems, such as ferrocene, tropolone, and azulene.[3] All of these compounds contain 2, 6, 10, etc., π electrons and illustrate an extension of Hückel's argument that cyclic molecules having $4n + 2$ π electrons possess closed shells of electrons and large delocalization energies.[4]

The hydrocarbon pentalene, an 8 π electron system, has never been synthesized despite repeated efforts.[5] Condensed pentalenes have been prepared and found to possess no special stability; for example, dibenzopentalene is reported to exhibit olefinic properties around the central pentalene nucleus, which undergoes polymerization, addition of bromine, etc.[5b]

The azapentalenes are of special interest since their properties are governed to a striking extent by the orientation of the hetero atoms. Thus, azapentalenes with pyridine-type nitrogens at the nonfused positions (*e.g.*, 1–6 of compound I) in either or both rings contain 8 π electrons and are expected to be nonaromatic.



I

Paul and Weise found that both 2,3-benzo-1-azapentalene and 5,6-benzo-1-azapentalene are brown, unstable materials which could not be isolated pure.[6]

Kato and Ohta[8] were unsuccessful in an attempt to prepare the 8 π electron dibenzo-1,4-diazapentalene from diindole. Treibs[9] reported the preparation of this derivative through dehydrogenation of diindole; however, this work was recently reported[10] to be erroneous.

The preparation of the highly stable, heteroaromatic compound, dibenzo-1,3a,4,6a-tetraazapentalene (II), was described earlier.[11a] Recently, we have synthe-

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(1) These compounds may be named as 5,11-dehydro-5H,11H-benzotriazolo[2,1-*a*]- and 5,7-dehydro-5H,7H-benzotriazolo[1,2-*a*]-benzotriazole, respectively. The trivial name of azapentalenes is employed in this and subsequent papers in order to call attention to the central rings, to which these systems owe so much of their properties.

(2) Excellent reviews of these topics have appeared recently. See, for instance: (a) "Non-Benzenoid Aromatic Compounds," D. Ginsberg, Ed., Interscience Publishers, Inc., New York, N. Y., 1959; (b) M. E. Vol'pin, *Russ. Chem. Rev.*, 29, 129 (1960).

(3) Leading references to recent works appear in E. A. LaLancette and R. E. Benson, *J. Am. Chem. Soc.*, 87, 1941 (1965).

(4) E. Hückel, *Z. Physik.*, 70, 204 (1931).

(5) (a) J. W. Barrett and R. P. Linstead, *J. Chem. Soc.*, 611 (1936); (b) C. T. Blood and R. P. Linstead, *ibid.*, 2255, 2263 (1952); C. C. Chuen and S. W. Fenten, *J. Org. Chem.*, 23, 1538 (1958); (c) J. D. Roberts and W. F. Gorham, *J. Am. Chem. Soc.*, 74, 2278 (1952); (d) M. Gates and S. P. Malchick, *ibid.*, 79, 5546 (1957).

(6) H. Paul and A. Weise, *Tetrahedron Letters*, 163 (1963). These authors dispute an earlier report of the synthesis of 2,3-benzo-1-azapentalene.[7]

(7) W. Treibs, *Naturwissenschaften*, 46, 170 (1959).

(8) H. Kato and M. Ohta, *Bull. Chem. Soc. Japan*, 34, 357 (1961).

(9) W. Treibs, *Naturwissenschaften*, 48, 130 (1961).

(10) H. Paul and A. Weise, *Z. Chem.*, 4, 147 (1964).

(11) (a) R. A. Carboni and J. E. Castle, *J. Am. Chem. Soc.*, 84, 2453 (1962). Since this report, several other examples of aromatic azapentalenes have appeared; *e.g.*, (b) T. W. G. Solomons and F. W. Fowler, *Chem. Ind.* (London), 1462 (1963); (c) T. W. G. Solomons, F. W. Fow-