the deaminative ring expansion of 2-aminomethylbicyclo[2.2.1]-oct-5-en-2-ol.

Registry No.—**2**, 34956-61-1; **3**, 34956-62-2; **3** MeI, 34956-63-3; **4**, 34956-64-4; **5**, 34956-65-5; **6**, 34956-66-6; **7**, 34956-67-7; **8**, 34956-68-8; **8** 2,4-DNP, 34956-69-9; 3-cyclohexen-1-acetaldehyde, 24480-99-7.

Reactions of Bicyclo[3.2.1]octan-8-ylidene and Bicyclo[3.2.1]oct-2-en-8-ylidene

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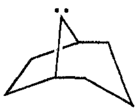
The "nonclassical" stabilization of singlet carbenes by olefinic bonds has been suggested by Hoffmann and Gleiter[1] for systems in which the molecule is constrained in such a way that addition to the double bond cannot occur. This has been termed a "foiled methylene" and is commonly referred to as a nonclassical carbene. Fisch and Pierce[2] and Moss, Dolling, and Whittle[3] have recently described such potential cases with the bicyclo[3.3.1]non-2-en-9-ylidene[2] and 7-norbornenylidene[3] systems. We would like to report work on some related carbenes, bicyclo[3.2.1]-octan-8-ylidene (**1**) and bicyclo[3.2.1]oct-2-en-8-ylidene (**2**), the latter providing an excellent example of the foiled methylene reaction.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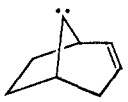
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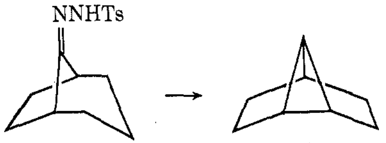
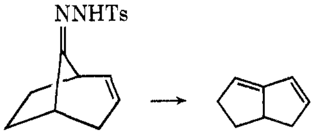
Carbenes **1** and **2** were generated by the sodium methoxide catalyzed decomposition of the corresponding tosylhydrazones **3** and **4** at 150° in dry diglyme. Hydrocarbon products were isolated in 80-90% yield by pentane extraction of the water-diluted reaction mixture and analyzed by capillary gas chromatography (gc). Decompositions were carried out using both 2 and 4 equiv of base with no significant effect on product composition.[4]

The two carbenes follow strikingly different reaction paths. **1** gave a product mixture containing three components in the relative amounts of 1.5, 98, and *ca.* 0.5% (in order of elution from the gc column). The major product was identified as tricyclo[3.3.0.0^{2,8}]-octane (**5**), the result of a 1,3-insertion reaction, by a comparison of its gc retention time and ir and nmr spectra with those of an authentic sample of the known hydrocarbon.[5,6] The unsaturated carbene **2** gave two products in the relative amounts of 3 and 97%. The major product is an unstable, colorless liquid and is assigned the structure of the 1,2-rearrangement product, bicyclo[3.3.0]octa-1,7-diene (**6**), on the basis of



3 **5**



4 **6**

its hydrogenation to bicyclo[3.3.0]octane and the following spectral data: nmr (CCl_4) δ 5.23 (m, 1 H, vinyl), 6.16 (AB, 2 H, $J = 7$ Hz, five-membered ring vinyl[7]), 3.0 (m, broad, 1 H, bridgehead), 1.2–2.8 (6 H, envelope of peaks); uv (pentane) λ_{max} 247 nm (heteroannular conjugated diene)[8]; ir (CCl_4) 3110 and 3050 (vinyl CH), 1648 (C═C), 720 cm^{-1} (out of plane CH bend for cis alkene); mass spectrum (70 eV) M^+ 106. No attempt was made to identify the minor products of these reactions.

The contrasting behavior of carbenes **1** and **2**—insertion *vs.* rearrangement—is similar to but far more dramatic than that found for the related C_7 and C_9 carbenes.[2,9] Apparently the saturated carbene **1** has the carbenoid center well situated for insertion into the axial C_2–H bond. It shows a much greater propensity for insertion compared to rearrangement (98%) than the homologous carbenes, norbornan-7-ylidene (12%)[9] and bicyclo[3.3.1]nonan-9-ylidene (80%).[2]

The preference for rearrangement in the unsaturated carbene **2** can be explained in several ways. Since models indicate that the axial hydrogen in **2** is farther away from the carbenoid center than it is in **1**, it is possible that the insertion reaction is simply less favorable than rearrangement in this case. Alternatively, the difference in behavior can be rationalized very nicely in terms of a "foiled methylene." A stabilizing interaction of the carbenoid center with the double bond would further discourage the insertion reaction, because it tends to twist the axial hydrogen even farther away from the reacting center. Since addition to the double bond is also discouraged by the nature of the strained tetracyclic hydrocarbon **7**[10] which would result, the most favorable reaction of the nonclassical carbene becomes the 1,2 rearrangement to the diene **6**. Presumably, double-bond interaction in the stab-

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[1] R. Gleiter and R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 5457 (1968).

[2] M. H. Fisch and H. D. Pierce, Jr., *Chem. Commun.*, 503 (1970).

[3] R. A. Moss, U.-H. Dolling, and J. R. Whittle, *Tetrahedron Lett.*, 931 (1971).

[4] Variation in the number of equivalents of base present has been observed to strongly affect product composition. See R. H. Shapiro, J. H. Duncan, and J. C. Clopton, *J. Amer. Chem. Soc.*, **89**, 1442 (1967).

[5] M. Schwarz, A. Besold, and E. R. Nelson, *J. Org. Chem.*, **30**, 2425 (1965).

[6] The decomposition of **3** serves as an excellent synthetic route to **5**.

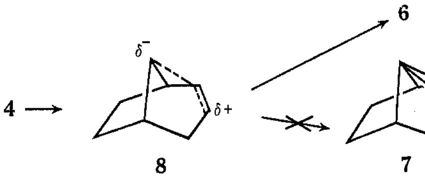
[7] (a) O. L. Chapman, *J. Amer. Chem. Soc.*, **85**, 2014 (1963); (b) G. V. Smith and H. Kriloff, *ibid.*, **85**, 2016 (1963); (c) P. Laszlo and P. v. R. Schleyer, *ibid.*, **85**, 2017 (1963).

[8] The λ_{max} calculated for compound **6** using Woodward's rules is 234 nm. The discrepancy between the calculated value and the observed value (bathochromic shift) can be attributed to the strain of the double bond at the ring juncture. Consider, for example, $\Delta^{3,5}$-*B*-norcholestadiene: ψ_{max}^{calcd} 234 nm, λ_{max}^{obsd} 245 nm. L. F. Fieser, *J. Amer. Chem. Soc.*, **75**, 4386 (1953). Bicyclo[3.2.0]hepta-1,6-diene: λ_{max}^{calcd} 234 nm, λ_{max}^{obsd} 255 nm.[3]

[9] R. A. Moss and J. R. Whittle, *Chem. Commun.*, 341 (1969).

[10] This hydrocarbon would contain a carbon atom having all four bonds on one side of a plane. For the synthesis and properties of such compounds, see, for example, K. B. Wiberg, *et al.*, *J. Amer. Chem. Soc.*, **93**, 246 (1971); **91**, 3372 (1969); *Tetrahedron Lett.*, 5855 (1968); 317 (1969). For theoretical discussions see M. D. Newton and J. M. Schulman, *J. Amer. Chem. Soc.*, **94**, 773 (1972), and W.-D. Stohrer and R. Hoffmann, *ibid.*, **94**, 779 (1972).

ilized carbene would be of the unsymmetrical homoallylic type indicated in **8**, as has been suggested for the



related carbonium ion.[11] Although the nonclassical carbene rationalization is an attractive one for explaining the chemistry of **2**, present results do not allow a decision between it and alternative mechanisms. We plan to pursue experiments which will help to distinguish between possible mechanisms.

Experimental Section[12]

Bicyclo[3.2.1]oct-2-en-8-one was prepared by the method of Foote and Woodward,[13] except that dioxane was used in place of methanol for cleavage of the ethylene ketal. This gave the ketone with only a trace of the ketal (by gc), boiling at 74–75° (8 mm) [lit. bp 130° (25 mm),[13] 69–70° (5 mm)[11]].

Bicyclo[3.2.1]octan-8-one was prepared from the bicyclo-[3.2.1]oct-2-en-8-one described above by hydrogenation over platinum oxide in methanol.[13] This produced a mixture containing 40% ketone and 60% of a higher boiling material presumed to be the corresponding dimethyl ketal. Treatment of the mixture under the cleavage conditions mentioned above gave the ketone in 73% yield after sublimation (90°, aspirator pressure) as a white, waxy solid melting at 141–144.8° (st, lit.[13] mp 140–141°).

Bicyclo[3.2.1]octan-8-one Tosylhydrazone (3).—Bicyclo-[3.2.1]octan-8-one (1.24 g, 0.01 mol) in 5 ml of methanol was added all at once to a gently refluxing solution of 1.96 g (0.0105 mol) of *p*-toluenesulfonylhydrazine[14] in 10 ml of methanol. More methanol (5 ml) was added and the solution was allowed to reflux for 20 min. An equal volume of hot water was added and the tosylhydrazone was allowed to crystallize. Collection of the solid and recrystallization from methanol–water gave 2.64 g (90% yield) of white, crystalline **3** melting at 182.5–184° dec.

Anal. Calcd for $C_{15}H_{20}N_2O_2S$: C, 61.62; H, 6.90. Found: C, 61.48; H, 6.86.

Bicyclo[3.2.1]oct-2-en-8-one Tosylhydrazone (4).—Bicyclo-[3.2.1]oct-2-en-8-one was converted to the crystalline tosylhydrazone in 98% yield by the same procedure as described above for **3**, mp 182.5–183.5° dec.

Anal. Calcd for $C_{15}H_{18}N_2O_2S$: C, 62.04; H, 6.25. Found: C, 62.28; H, 6.13.

Decomposition of Tosylhydrazone 3.—**3** (294 mg, 1 mmol) and 112 mg (2 mmol) of sodium methoxide were slurried in 5 ml of dry diglyme in a single-necked flask fitted with a condenser, and the mixture was heated at 145–150° with magnetic stirring for 1 hr. Rapid evolution of nitrogen was over in about 10 min. The reaction mixture was allowed to cool, and then poured into 50 ml of water. The aqueous solution was extracted with five 10-ml portions of pentane and the combined pentane extracts were washed with eight 10-ml portions of water and dried ($MgSO_4$). The pentane solution was concentrated by distillation (glass helicies column) to about 1 ml and analyzed by gas chromatography on a 150 ft × 0.01 in. stainless steel capillary column coated with tris-β-cyanoethoxypropane (TCEP) and operated at 58° and 25 psi nitrogen pressure. The analysis showed peaks at 5.4, 6.4, and 9.2 min in the respective relative amounts of 1.5, 98, and *ca.* 0.5%. A duplicate experiment using 4 equiv of base gave the same product composition within experimental error. The major product has the same gc retention time and ir and nmr spectra as an authentic sample of tricyclo[3.3.0.0^{2,8}]-octane (**5**) prepared by the method of Schwarz, *et al.*[5]

In a larger scale experiment[15] 3.62 g (0.0124 mol) of **3** was decomposed in 25 ml of diglyme with 2.98 g (0.0552 mol) of sodium methoxide. The crude product (1.20 g, 90% yield) was distilled at 131–136° (647 mm) [lit.[5] bp 68–72° (45 mm)] to give 0.916 g of a colorless oil (69% overall yield). The tricyclooctane was 95% pure by gc analysis.

Decomposition of Tosylhydrazone 4.—Decomposition of **4** and analysis of the products were carried out as described above for **3**. With 2 equiv of base, gc analysis showed peaks at 6.3 and 9.1 min in the relative amounts of 2 and 98%, respectively. With 4 equiv of base 4% of the minor component was observed. The major product is a colorless liquid which appears to polymerize readily. Pure compound was isolated by preparative gas chromatography on a 6 ft × 0.25 in. column packed with 10% FFAP[16] on Chromosorb W, operating temperature 72°, helium flow 50 ml/min. Spectral data for the compound are listed in the text above and are consistent with bicyclo[3.3.0]octa-1,7-diene (**6**) as the structure.

Hydrogenation of the decomposition product over platinum oxide in pentane gave a colorless liquid which was shown to be identical with a sample of bicyclo[3.3.0]octane by a comparison of their gc retention times and nmr spectra. The nmr spectrum (CCl_4) consists of a broad singlet at δ 2.48 (2 H, bridge) and a highly symmetrical complex multiplet centered at δ 1.5 (12 H). The authentic sample of bicyclo[3.3.0]octane was prepared by the thermal decomposition of bicyclo[3.3.0]octan-2-one[17] semicarbazone, mp 183–184° dec (lit.[18] mp 180° dec), with potassium hydroxide as described by Cook and Linstead.[18] The hydrogenation product was also compared with a sample of bicyclo-[4.2.0]octane prepared by hydrogenation over platinum oxide in pentane of the photolysis product of 1,3-cyclooctadiene.[19] The two had different gc retention times on the 150-ft capillary column at 58° and different nmr spectra. The nmr spectrum (neat) of bicyclo[4.2.0]octane consists of a broad singlet at δ 2.28 (2 H, bridge), a complex multiplet centered at δ 1.78 (4 H, C_7, C_8), and a singlet at δ 1.48 (8 H, C_2, C_3, C_4, C_5).

Registry No.—**1**, 34952-71-1; **2**, 34952-72-2; **3**, 34956-57-5; **4**, 34956-58-6; **5**, 2401-89-0; **6**, 34956-60-0.

Acknowledgment.—We wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Graduate School of the University of Nevada, Reno, for support of this research.

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[12] Melting points and boiling points are uncorrected. Nmr spectra were recorded on a Varian Associates A-60 spectrometer, using tetramethylsilane as an internal standard.

[13] C. S. Foote and R. B. Woodward, *Tetrahedron*, **20**, 687 (1964).

[14] L. Friedman, R. L. Little, and W. R. Reichle, *Org. Syn.*, **40**, 93 (1960).

[15] Data of Dean Evans, University of Nevada.

[16] FFAP is a modified Carbowax 20M stationary phase available from Varian Aerograph, Walnut Creek, Calif.

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

[18] A. H. Cook and R. P. Linstead, *J. Chem. Soc.*, 946 (1934).

[19] (a) R. S. H. Liu, *J. Amer. Chem. Soc.*, **89**, 112 (1967); (b) W. J. Nebe and G. J. Fonken, *ibid.*, **91**, 1249 (1969).

The Dienone–Phenol Rearrangement. The So-Called Medium Effect[1]

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Among the acid-catalyzed rearrangements of dienones to phenols[3–6] are found examples in which the course of

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[1] Supported by a grant from the Robert A. Welch Foundation.

[2] Postdoctoral Fellow, 1969–1971.

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