Proton Magnetic Resonance Spectra of Selected 2-Norcarene Derivatives

LEO A. PAQUETTE* AND STANLEY E. WILSON[1]

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

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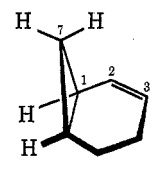
Proton magnetic resonance spectra are given for seven 2-norcarene derivatives. Analyses of these spectra permit one to deduce the syn or anti configuration of a 7-methyl substituent (if present) and the site (C-2 or C-3) of alkyl bonding to the double bond (if relevant). The data given herein should provide useful starting points for configurational and positional assignments to a broad range of 2-norcarene derivatives.

Recently there have been reports from this laboratory describing the isomerization of certain tricyclo[4.1.0.0^{2,7}]heptane derivatives to various methyl-substituted 2-norcarenes under conditions of Ag^+ catalysis.[2,3] Interest arose immediately in the possibility of making structural assignments to these hydrocarbons by means of pmr methods. In particular, the capability for unambiguous assignment of stereochemistry (syn or anti) at C-7 (see **1**) and for distinction between alkyl substitution at C-2 and C-3 was of principal concern. 2-Carenes and related sesquiterpenoids such as sirenin (**2**)[4] and sesquicarene (**3**)[5] are available from natural souces, but the extent



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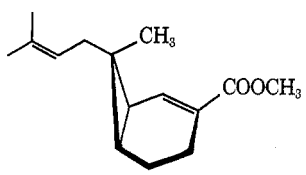

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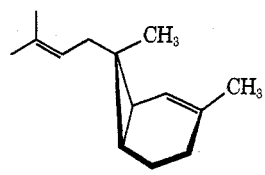

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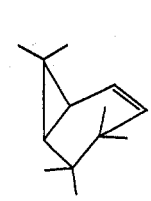
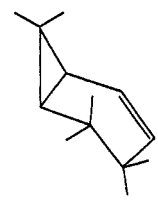
of substitution in such molecules, particularly at C-7, does not lend itself readily to analysis of simpler systems. Also, although 2-norcarene (**1**) has been known for over a decade,[6,7] no detailed consideration appears to have been given its pmr spectrum. The limited number of known monofunctionalized congeners of **1**[8] have likewise been incompletely studied.

Our interest in the foregoing pmr assignment questions encouraged the preparation of several methylated 2-norcarene derivatives. The selected hydrocarbons which were synthesized attest rather convincingly to the fact that the various isomeric possibilities can be distinguished by pmr spectroscopy.

The 60-MHz pmr spectrum of 2-norcarene (**1**) shown in Figure 1 consists of two low-field multiplets centered approximately at δ 6.04 and 5.42 which correspond to the nonequivalent pair of olefinic protons, and a series of three high-field multiplets at *ca.* δ 1.80, 1.23, and 0.68 of relative area 4, 2, and 2, respectively. Of the two conformations available to **1**,[8e,9] pseudo-boat conformation A enjoys a diminished level of non-



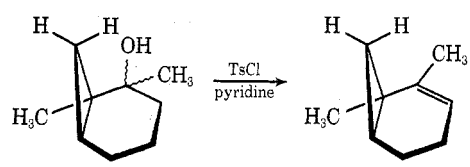
A



B

bonded interaction and allows for greater overlap of of the 1,6 and 1,7 bonds with the p orbital at C-2; consequently, it is favored over the pseudo-chair form (B). In B, the plane of the cyclopropane ring is somewhat tilted away from the double bond, with the result that endo H-7 falls in the shielding cone of the double bond. As will be seen, the adoption by a given 2-norcarene derivative of the pseudo-chair conformation for steric reasons engenders pronounced changes in the chemical shifts of the cyclopropyl and olefinic protons.

The spectrum (Figure 2) of 1,2-dimethyl-2-norcarene (**5**), available by dehydration of alcohol **4** with *p*-



4 **5**

toluenesulfonyl chloride in pyridine,[3] is somewhat simpler than that of **1**. In this instance, the low-field multiplet must correspond to H-3; this indicates that the H-2 absorption in those 2-norcarenes which adopt conformation A appears downfield from that due to H-3. In general, the $\Delta\delta$ of these absorptions is of the order of 0.3–0.6 ppm.[8a,e] The geminal pair of protons at C-7 appear as a multiplet centered at δ 0.6; the

(1) National Institutes of Health Postdoctoral Fellow, 1970–1971; National Science Foundation Postdoctoral Fellow, 1971–1972.

(2) L. A. Paquette, R. P. Henzel, and S. E. Wilson, *J. Amer. Chem. Soc.*, **93**, 2335 (1971).

(3) L. A. Paquette, S. E. Wilson, R. P. Henzel, and G. R. Allen, Jr., *ibid.*, **94**, 7761 (1972).

(4) (a) E. J. Corey, K. Achiwa, and J. A. Katzenellenbogen, *ibid.*, **91**, 4318 (1969); (b) J. J. Plattner, V. T. Bhalerao, and H. Rapoport, *ibid.*, **91**, 4933 (1969); (c) E. J. Corey and K. Achiwa, *Tetrahedron Lett.*, 2245 (1970); (d) V. T. Bhalerao, J. J. Plattner, and H. Rapoport, *J. Amer. Chem. Soc.*, **92**, 3429 (1970); (e) J. J. Plattner and H. Rapoport, *ibid.*, **93**, 1758 (1971).

(5) (a) Y. Ohta and Y. Hirose, *Tetrahedron Lett.*, 1251 (1968); (b) E. J. Corey and K. Achiwa, *ibid.*, 1837 (1969).

(6) W. R. Moore, H. R. Ward, and R. F. Merritt, *J. Amer. Chem. Soc.*, **83**, 2019 (1961).

(7) For more recent syntheses of **1**, consult (a) G. Wittig and F. Wingler, *Chem. Ber.*, **97**, 2146 (1964); (b) C. L. Osborn, T. C. Shields, B. A. Shoulders, J. F. Krause, H. V. Cortez, and P. D. Gardner, *J. Amer. Chem. Soc.*, **87**, 3158 (1965); (c) M. Rey, R. Begrich, W. Kirmse, and A. S. Dreiding, *Helv. Chim. Acta*, **51**, 1002 (1968).

(8) (a) J. J. Sims, *J. Amer. Chem. Soc.*, **87**, 3511 (1965); (b) I. A. D'yakonov, T. V. Domareva-Mandel'shtam, and I. Z. Egenburg, *Zh. Org. Khim.*, **3**, 1441 (1967); *Chem. Abstr.*, **68**, 59166r (1968); (c) B. Besinet, R. Fraisse, R. Jacquier, and P. Viallefont, *Bull. Soc. Chim. Fr.*, 1377 (1960); (d) D. L. Garin and K. O. Henderson, *Tetrahedron Lett.*, 2009 (1970); (e) W. R. Moore and B. J. King, *J. Org. Chem.*, **36**, 1882 (1971).

(9) S. P. Acharya, *Tetrahedron Lett.*, 4117 (1966).

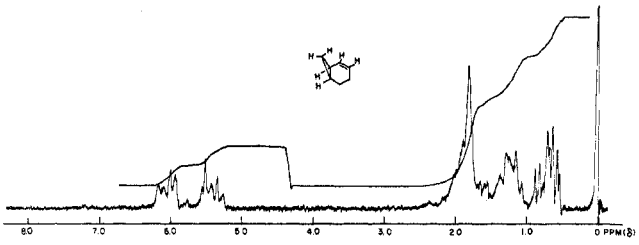


Figure 1.—Pmr spectrum (60 MHz) of **1** in $CDCl_3$ solution.

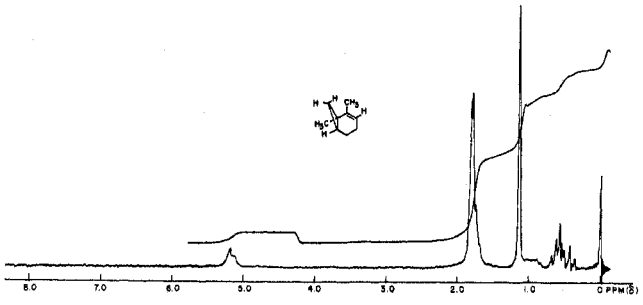
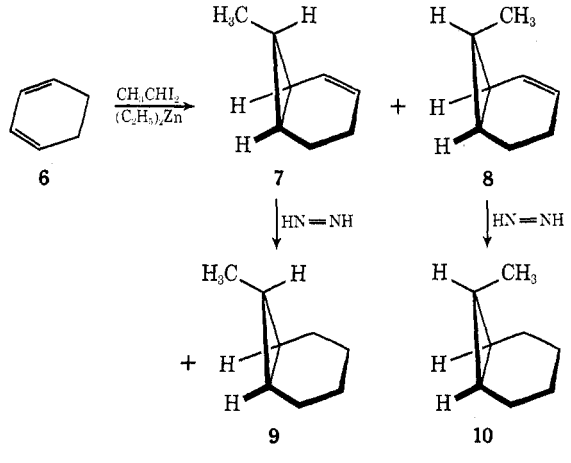


Figure 2.—Pmr spectrum (60 MHz) of **5** in $CDCl_3$ solution.



6 7 8 9 10

remaining cyclopropyl hydrogen (H-6) is seen as a very broad absorption at *ca.* δ 1.0.

To arrive at the epimeric 7-methyl derivatives **7** and **8**, 1,3-cyclohexadiene (**6**) was cyclopropanated with 1,1-diiodoethane and diethylzinc according to established procedures.[10] In agreement with earlier observations which denoted preferential formation of the endo epimer under these conditions, **8** dominated the product distribution by a factor of 4.5:1. The isomers were separated by preparative scale gas chromatography and the assigned stereochemistry in each case was established by diimide reduction to the known 7-methylbicyclo[4.1.0]heptanes **9** and **10**.[10,11]

The olefinic hydrogens of exo isomer **7** are again characterized by distinctively different chemical shifts (Figure 3). The magnitude of $\Delta\delta$ in this derivative is approximately 0.7. Introduction of the anti 7-methyl group appears to alter the preferred conformation of the norcarene nucleus only slightly. Though the cyclopropyl protons are somewhat downfield shifted, the

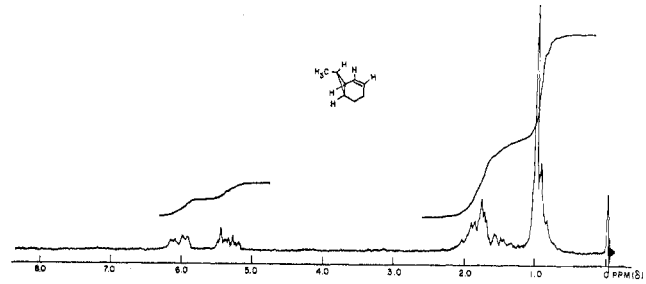


Figure 3.—Pmr spectrum (60 MHz) of **7** in $CDCl_3$ solution.

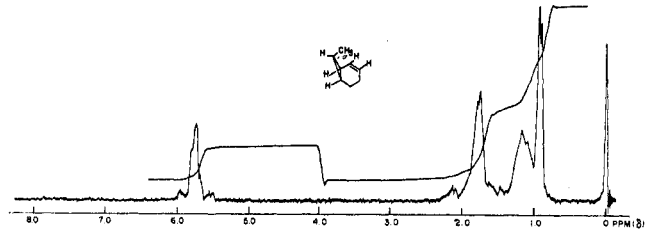


Figure 4.—Pmr spectrum (60 MHz) of **8** in $CDCl_3$ solution.

magnitude of this change may be rationalized in terms of the conventional consequence of alkyl substitution. The effect does not appear to be sufficiently large as to suggest that more substantive conformational alterations have taken place.

In contrast, the olefinic proton absorptions in related endo isomer **8** are seen to have merged into a multiplet of rather narrow width at a field position (δ 5.78) intermediate between the two extremes present in **7** (Figure 4). Additionally, all three cyclopropyl protons in **8** experience deshielding relative to their counterparts in **7**. In terms of the currently accepted ring current model for cyclopropane, protons in or near the plane of the ring should experience deshielding and those above the ring shielding.[12,13] Additionally, the anisotropic effects of the double bond are such[14] that hydrogen atoms lying in the positive cone are diamagnetically shifted upfield and those lying in the negative cone are shifted downfield. The magnitude of these shifts is recognized to vary with proximity to the symmetrical axis of the π bond. An examination of Prentice–Hall molecular models reveals that the steric bulk of the endo 7-methyl group is such as to cause steric compression with the axially disposed C-4 hydrogen in conformer A. To relieve this intramolecular crowding, conformation B is presumably adopted. Accordingly, the varied shielding and deshielding effects of the constituent protons are the consequence of changes in bond and strained ring anisotropies at each of the sites. The observed spectral alterations are of sufficient magnitude to support the concept of conformational crossover.

Scrutiny of the spectrum (Figure 5) of **12**, the 2-norcarene produced exclusively upon treatment of 2-methyl-1,3-cyclohexadiene (**11**) with 1,1-diiodoethane and diethylzinc, likewise revealed the presence of a narrow two-proton olefinic absorption at δ 5.63. The environment of the sp^2 C-bonded hydrogens in **12** must

(10) J. Furukawa, N. Kawabata, and J. Nishimura, *Tetrahedron Lett.*, 3495 (1968); J. Nishimura, N. Kawabata, and J. Furukawa, *Tetrahedron*, **25**, 2647 (1969).

(11) (a) H. E. Simmons, E. P. Blanchard, and R. D. Smith, *J. Amer. Chem. Soc.*, **86**, 1347 (1964); (b) G. Wittig and M. Jautelat, *Justus Liebigs Ann. Chem.*, **702**, 24 (1967); (c) W. L. Dilling and F. Y. Edamura, *Chem. Commun.*, 183 (1967); (d) R. M. Magid and J. G. Welch, *ibid.*, 518 (1967).

(12) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, London, 1969, pp 98–101, and references cited therein.

(13) F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy," Academic Press, New York, N. Y., 1969, p 71.

(14) See ref 12, pp 83–88.

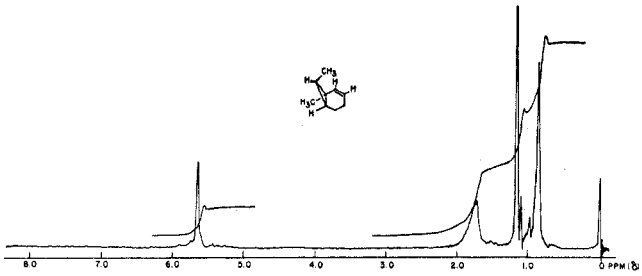


Figure 5.—Pmr spectrum (60 MHz) of **12** in $CDCl_3$ solution.

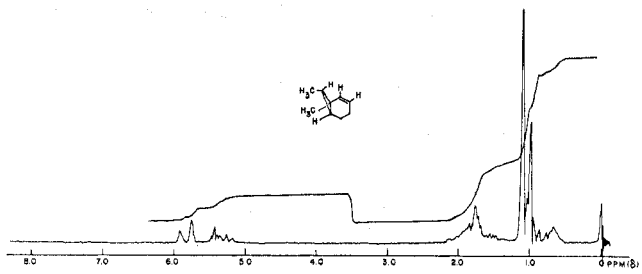


Figure 6.—Pmr spectrum (60 MHz) of **14** in $CDCl_3$ solution.

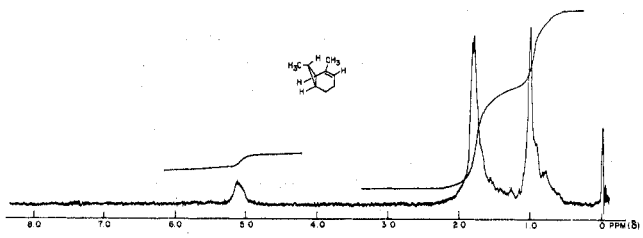
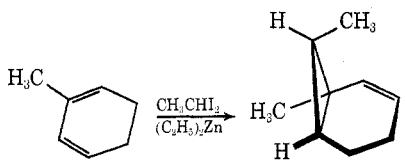


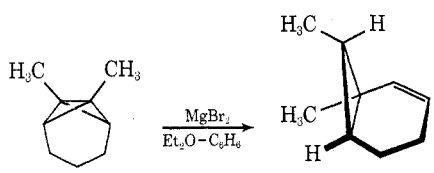
Figure 7.—Pmr spectrum (60 MHz) of **16** in $CDCl_3$ solution.

therefore resemble closely that of the corresponding protons in **8**. It follows that **12** is the endo 7-methyl isomer, an assignment which receives further support at the mechanistic level.[10]



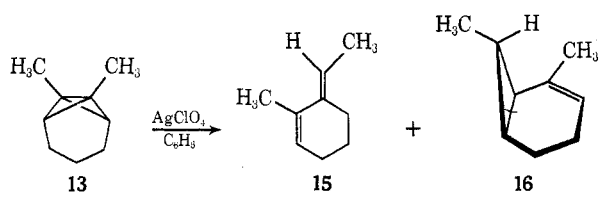
11 **12**

At this stage it was decided that the stereochemical outcome of the anhydrous magnesium bromide promoted rearrangement of 1,7-dimethyltricyclo[4.1.0.$0^{2,7}$]heptane (**13**) should be capable of analysis. To this end, a dry benzene solution of **13** was treated with a freshly prepared solution of $MgBr_2$ in anhydrous ether for 2.5 hr at 50°. A single 2-norcarene was obtained, the pmr spectrum of which (Figure 6) clearly differs from that of **12**. In particular, the H-2 and H-3 absorptions are distinctly separated and H-7 now appears at higher field than the methyl peaks. The exo placement of the 7-methyl group is therby revealed. Since the appearance of H-2 as a doublet (J = 10 Hz) requires methyl substitution at C-1, the hydrocarbon produced in this rearrangement (**14**) must be epimeric with **12**. Therefore, the isomerization of tricycloheptane **13** to **14** under these conditions proceeds with retention of configuration at C-7.



13 **14**

The silver ion catalyzed rearrangement of **13**,[2,3] on the other hand, has been found to give rise to ethylidenecyclohexene (**15**) (80%) and to a 2-norcarene (20%) which proved to be isomeric with **5**, **12**, and **14**, yet distinctly different from these structures.[15] The position of the trigonally bound methyl group can be assigned with certainty at C-2 in view of the absence of the low-field olefinic absorption (Figure 7). Furthermore, because this multiplet appears at δ 5.00–5.23 and not further downfield, this molecule must reside chiefly in conformation A. Mechanistic reasoning[2,3] places the second methyl group at C-7, and the pmr spectrum indicates that this substituent must be exo oriented as in **16**.



13 **15** **16**

With these data, chemical shifts and coupling constants necessary for positional and configurational assignment to substituents at positions 1, 2, 3, and 7 in a 2-norcarene are available. We anticipate that these spectral features will prove general in scope and permit structural distinction in a broad range of derivatives.

Experimental Section[11]

Syntheses of a number of hydrocarbons were achieved according to literature directions. 2-Norcarene (**1**) was prepared by $MgBr_2$-catalyzed isomerization of tricyclo[4.1.0.$0^{2,7}$]heptane,[6] 1,2-dimethyl-2-norcarene (**5**) by dehydration of **4**,[3] and 1,7-dimethyltricyclo[4.1.0.$0^{2,7}$]heptane (**13**) by dimethylation of the parent hydrocarbon.[16] Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. Proton magnetic resonance spectra were obtained with a Varian A-60A spectrometer.

endo- and *exo*-**7-Methylbicyclo[4.1.0]hept-2-ene (7 and 8).**—The apparatus consisted of a 50-ml flask with reflux condenser, nitrogen inlet, and two pressure-equalizing addition funnels. A diethylzinc cylinder was attached to the top of one addition funnel. The system was evacuated three times by means of a vacuum pump followed by admission of dry nitrogen gas. 1,3-Cyclohexadiene (**6**, 6.0 g, 75 mmol) and diethylzinc (3.7 g, 30 mmol) were introduced into 20 ml of dry pentane, and a solution of 10.30 g (36.5 mmol) of 1,1-diiodoethane in 10 ml of pentane was added dropwise during 1 hr at room temperature. The reaction mixture was allowed to stand overnight and poured into 50 ml of cold dilute hydrochloric acid. When the somewhat vigorous reaction had subsided, 50 ml of pentane was added and the organic phase was washed with saturated aqueous sodium bicarbonate and sodium chloride solutions. The pentane solution was dried and solvent together with unreacted **6** was removed by distillation through a short Vigreux column at atmospheric pressure. The remaining material was distilled at

(15) Masamune and coworkers have erroneously assigned structure **14** to this product: M. Sakai, H. H. Westberg, H. Yamaguchi, and S. Masamune, *J. Amer. Chem. Soc.*, **93**, 4611 (1971).

(16) G. L. Closs and L. E. Closs, *ibid.*, **85**, 2022 (1963).

60° (bath temperature) (10 mm) and the distillate was collected at −78°. Gas chromatographic analysis and separation on a 10 ft × 0.25 in. 5% OV-17 column at 110° showed **7** and **8** to be present in a ratio of 1:4.5. There was collected 90 mg of **7** and 410 mg of **8**.

For **7**: *Anal.* Calcd for C_8H_{12}: C, 88.81; H, 11.19. Found: C, 88.52; H, 11.29. For **8**: Found: C, 88.70; H, 11.45.

Reduction of 7.—A vigorously stirred solution of 54 mg (0.50 mmol) of **7** and 3.88 g (20 mmol) of dipotassium azodicarboxylate in 6 ml of methanol was treated dropwise during 30 min with 3.0 g (50 mmol) of acetic acid. Stirring was continued until the yellow color had faded, and the reaction mixture was poured onto 25 ml of water and 25 ml of pentane. The water layer was extracted with pentane (10 ml) and the combined organic phases were shaken with saturated sodium bicarbonate solution and dried. The majority of the solvent was removed by careful distillation at atmospheric pressure, and the product (10 mg) was collected on the OV-17 column at 110°. The nmr sample of the hydrocarbon was identical with that of an authentic sample of *exo*-7-methylbicyclo[4.1.0]heptane (**9**).[10,11,17]

Reduction of 8.—Like treatment of **8** resulted in the formation of *endo*-7-methylbicyclo[4.1.0]heptane (**10**), whose pmr spectrum was identical in all respects with that of an authentic sample.[17]

***endo*-1,7-Dimethylbicyclo[4.1.0]hept-2-ene (12).**—When a solution of 1.0 g (10.6 mmol) of 2-methyl-1,3-cyclohexadiene (**11**) and 1.6 ml (15 mmol) of diethylzinc in 5 ml of dry pentane was treated dropwise under nitrogen with 5.65 g (20 mmol) of 1,1-diiodoethane dissolved in 3 ml of pentane in the predescribed manner, there was produced a single substance (190 mg isolated after preparative vpc purification on the OV-17 column at 110°) identified as **12**.

Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.46; H, 11.55.

Magnesium Bromide Catalyzed Isomerization of 13.—To a solution of freshly prepared magnesium bromide in anhydrous ether [2 ml of a solution (bottom layer) prepared from magnesium turnings (excess) and 1,2-dibromoethane (18.8 g, 0.10 mol) in 100 ml of ether] diluted with 6 ml of dry benzene was added 0.44 g (3.6 mmol) of **13**. After 2.5 hr at 50°, the reaction mixture was cooled in ice water and 10 ml of water was cautiously introduced. The organic layer was removed and the aqueous phase was extracted with pentane. The combined organic phases were dried and carefully concentrated at atmospheric pressure. The remaining material was distilled at 60° (bath temperature) (1 mm) and the volatiles were collected at −78°. The lone product was purified by preparative vpc on the OV-17 column at 110° and identified as **14** (21 mg).

Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.25; H, 11.71.

Registry No.—**1**, 2566-57-6; **5**, 36601-89-5; **7**, 36601-90-8; **8**, 36601-91-9; **12**, 36601-92-0; **14**, 36601-93-1; **16**, 33375-20-1.

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(17) We thank Professor R. M. Magid for kindly providing us with the requisite pmr spectra.

Rearrangements Attending Attempts to Form the 1-Dibenzosemibullvalenylcarbinyl (1-Dibenzotricyclo[3.3.0.0^{2,8}]octadienylcarbinyl) Cation[1]

STANLEY J. CRISTOL,*[2] GEORGE C. SCHLOEMER,[2] DONALD R. JAMES,[3] AND LEO A. PAQUETTE[3]

Departments of Chemistry, University of Colorado, Boulder, Colorado 80302, and The Ohio State University, Columbus, Ohio 43210

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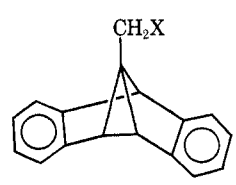
Silver acetate promoted acetolysis of 1-bromomethyl-3,6-dibenzotricyclo[3.3.0.0^{2,8}]octadiene (**1**-Br) and deamination of 1-aminomethyl-3,6-dibenzotricyclo[3.3.0.0^{2,8}]octadiene (**1**-NH_2) have been studied. Solvolysis leads only to the rearranged acetates **2**, **3**, **4**, and **5**, along with benzofluorene **6**; "normal" deamination in acetic acid gives, besides **6**, unrearranged acetate **1**-OAc and alcohol **1**-OH and exo products **2** (acetate and alcohol); and "aprotic" deamination gives **6**, **1**-OAc, and **2**-OAc. Mechanistic rationalizations of these differing sets of results are offered.

Each of our groups has developed interest in carbonium-ion rearrangements in bridged polycyclic compounds and, in particular, in the question of multiplicity of carbonium-ion intermediates, as well as in the study of dibenzosemibullvalene and its derivatives.[4] These interests overlapped in work on the rearrangements attending treatment of 1-bromomethyl-3,6-dibenzotricyclo[3.3.0.0^{2,8}]octadiene (1-bromomethyldibenzosemibullvalene, **1**-Br) with silver acetate in acetic acid (Colorado group) and of the corresponding deamination of **1**-NH_2 (Ohio State group). This paper describes the results of those experiments.

When **1**-Br was treated in acetic acid with silver acetate, either at room temperature or at approximately 100°, ready reaction occurred with the formation of four acetate products (**2**-OAc, **3**-OAc, **4**-OAc, and **5**-OAc) and one hydrocarbon, 3,4-benzofluorene (**6**). Pmr analysis indicated that the reaction mixture comprised 30% **2**-OAc, 6% **3**-OAc, 24% **4**-OAc, 23% **5**-OAc, and 16% **6**. No unrearranged **1**-OAc was detectible in the reaction mixture, nor was there any evidence for ring opening to the benzohydryl acetate **7**. That the reaction mixture is the result of kinetic, rather than thermodynamic, control was demonstrated by treatment of a mixture of the four acetates with 0.5 *M* $HClO_4$ in acetic acid at room temperature. The mixture was converted cleanly to **4**-OAc. Treatment with 0.02 *M* $HClO_4$ demonstrated that *endo*-**3**-OAc was more



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(1) Paper LXXIV in series Bridged Polycyclic Compounds of the University of Colorado group. Paper LXIII: S. J. Cristol, J. R. Mohrig, and G. T. Tiedeman, *J. Org. Chem.*, **37**, 3239 (1972).

(2) University of Colorado. G. C. S. gratefully acknowledges support *via* a NASA fellowship.

(3) The Ohio State University.

(4) See, for example, (a) S. J. Cristol, R. M. Sequeira, and G. O. Mayo, *J. Amer. Chem. Soc.*, **90**, 5564 (1968); (b) S. J. Cristol, W. Y. Lim, and A. R. Dahl, *ibid.*, **92**, 4013 (1970); (c) L. A. Paquette and G. H. Birnberg, *ibid.*, **94**, 164 (1972); (d) L. A. Paquette and G. V. Meehan, *ibid.*, **92**, 3039 (1970).