# Wagner–Meerwein Rearrangements in the Solvolyses of Benzobicyclo[2.2.2]octenyl and -octadienyl Brosylates and Nuclear Magnetic Resonance Spectra of the Benzobicyclo[3.2.1]octadiene and Benzo[3,4]tricyclo[3.2.1.0^{2,7}]octene Systems

Hiroshi Tanida, Kazuo Tori, and Keizo Kitahonoki

Contribution from Shionogi Research Laboratory, Shionogi and Company, Ltd., Fukushima-ku, Osaka, Japan. Received January 20, 1967

Abstract: Rate constants and products in the acetolyses of *endo-* and *exo*-benzobicyclo[2.2.2]octen-2-yl (I-OBs and II-OBs) and -octa-5,7-dien-2-yl brosylates (III-OBs and IV-OBs) were determined. The rates of I-OBs, II-OBs, III-OBs, and IV-OBs at 25° relative to that of bicyclo[2.2.2]octan-2-yl brosylate were 0.92, 2.6, 11, and 2.9, respectively. The reaction with I-OBs proceeds with complete rearrangement forming quantitatively a mixture of axial and equatorial benzo[3,4]bicyclo[3.2.1]octen-2-ol acetates. The product from II-OBs is an 83:17 mixture of benzobicyclo[2.2.2]octen-2-ol acetate and rearranged benzo[6,7]bicyclo[3.2.1]octen-2(axial)-ol acetate. Only in this case is the reaction stereospecific. In the acetolysis of III-OBs, the major products are axial and equatorial benzo[3,4]bicyclo[3.2.1]octa-3,6-dien-2-ol acetates, and the minor products are *exo-* and *endo*-benzo[3,4]tricyclo[3.2.1.0^{2,7}]octen-6-ol acetates. The acetolysis of IV-OBs yields a mixture of axial and equatorial benzo[6,7]bicyclo[3.2.1]octa3,6-dien-2-ol acetates with complete rearrangement. The nmr spectra of the newly formed benzobicyclo[3.2.1]octadienyl and benzotricyclo[3.2.1.0^{2,7}]octenyl derivatives were examined for structural elucidation. Several long-range spin couplings found in these systems are described.

The chemistry of bridged benzocyclenes is one of the research interests in our laboratory. Synthesis of the smallest bridged benzocyclene ever known, benzobicyclo[2.1.1]hexene, was recently achieved.[1] Some reported parts of our studies of carbonium ion reactions in the benzonorbornenyl system demonstrated the advantage of discussing the participation effect and the structure of the transition state involved in reactions of this kind.[2] Along this line, this paper reports a comprehensive study of the rates and Wagner–Meerwein rearrangements in the acetolyses of benzobicyclo[2.2.2]octen-2-yl and -octa-5,7-dien-2-yl brosylates. Rearrangements in the dienyl derivatives produced compounds having new bridged unsaturated systems. The structure elucidation of these compounds leaned heavily on their nmr spectra, and the proton spin-decoupling experiments (nmdr and nmtr spectroscopy) performed here are considered to be a model technique for the structure determination of molecules of these kinds.

I and II   III and IV
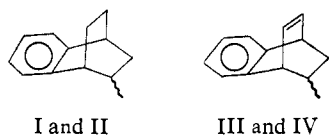
Preparations. Syntheses and properties of *endo-* and *exo*-benzobicyclo[2.2.2]octen-2-ols (I-OH and II-OH) used in this study are already known.[3–5] Lithium aluminum hydride reduction of benzobicyclo[2.2.2]octa-5,7-dien-2-one[3] led to a mixture of the *endo-*

and *exo*-dienols, III-OH and IV-OH, each of which was isolated in the pure state by elution chromatography. The brosylates of these four alcohols were prepared by standard procedures. The brosylates, III-OBs and IV-OBs, were rather unstable and could be stored for a few days in a dry ether solution at 0°.

Solvolysis Rates. The rates of acetolyses were carried out in glacial acetic acid containing equivalent sodium acetate by the standard procedure.[2b,6] In each experiment the reaction was followed to at least 80% completion. Good first-order kinetics were observed in the reactions of all the brosylates, and the infinity titers corresponded to theory. The solvolysis rates are summarized in Table I, together with the derived activation parameters and the data of relevant compounds. For comparison, the rate constants at 25.0° were calculated from Arrhenius plots. The relative rates are determined taking that of the parent bicyclo[2.2.2]octyl brosylate (V-OBs) as unity. Table I also lists, for discussion, the *exo*:*endo* rate ratios in the bicyclo[2.2.2]octenyl, benzobicyclo[2.2.2]octenyl, and benzobicyclo[2.2.2]octadienyl series.
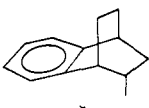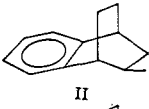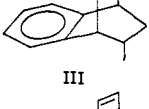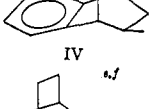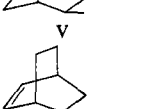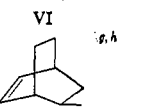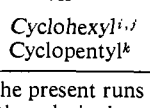
Ethanolyses of I-OBs and II-OBs also followed good first-order kinetics and the rate constants are presented in footnotes to Table I.

Solvolysis Products. For product determination, the acetolyses were carried out under the same conditions used for the rate studies. In all cases, the brosylates quantitatively produced mixtures of acetates. The product composition was examined by vpc analysis of the acetate mixtures and, in addition, of the alcohol mixtures derived therefrom by lithium aluminum hydride reduction. Each component of the acetate mixtures was isolated by preparative vpc. The yields of products were determined by vpc with the isolated pure

(1) H. Tanida and Y. Hata, *J. Am. Chem. Soc.*, **88**, 4289 (1966).

(2) (a) H. Tanida, *ibid.*, **85**, 1703 (1967); (b) H. Tanida, T. Tsuji, and H. Ishitobi, *ibid.*, **86**, 4904 (1964); (c) H. Tanida and H. Ishitobi, *ibid.*, **88**, 3663 (1966).

(3) K. Kitahonoki and Y. Takano, *Tetrahedron Letters*, 1597 (1963).

(4) The terms axial and equatorial in this paper are abridged as ax and eq. The *endo* and *exo* are defined as follows: substituents on the side of the benzene ring are *endo* and those on the other side are *exo*.

(5) The numbering used in this paper is shown in the charts.

(6) *E.g.*, S. Winstein, C. Hanson, and E. Grunwald, *J. Am. Chem. Soc.*, **70**, 812 (1948); S. Winstein, E. Grunwald, and L. L. Ingraham, *ibid.*, **70**, 821 (1948).

Table I. Acetolyses of Bicyclo[2.2.2]octyl Brosylates[a]

R–OBs	Temp, °C[b]	k_1, sec^{-1}	Calcd at 25.0°				
			ΔH‡, kcal	ΔS‡, cal/deg	k_1, sec^{-1}	Rate rel to bicyclo-[2.2.2]octyl	exo:endo ratio
I [c]	34.97 / 54.94	3.12 × 10⁻⁵ / 3.45 × 10⁻⁴	23.5	−2.9	8.38 × 10⁻⁶	0.92	2.8
II [d]	34.97 / 54.94	8.94 × 10⁻⁵ / 1.00 × 10⁻³	23.7	−0.1	2.37 × 10⁻⁵	2.6	
III	24.97 / 25.06	9.60 × 10⁻⁵ / 1.03 × 10⁻⁴			1.01 × 10⁻⁴	11	0.26
IV	25.03 / 35.02 / 54.93	2.68 × 10⁻⁵ / 1.04 × 10⁻⁴ / 1.11 × 10⁻³	24.8	3.7	2.61 × 10⁻⁵	2.9	
V [e,f]	25.00 / 50.97	9.07 × 10⁻⁶ / 2.61 × 10⁻⁴	24.6	1.2	9.07 × 10⁻⁶	1	
VI	30.07 / 42.06	2.97 × 10⁻⁵ l / 1.32 × 10⁻⁴ l	23.0 l	−3.3 l	4.57 × 10⁻⁵ m	5.0	52
VII [g,h]	25.00	2.40 × 10⁻³			2.40 × 10⁻³	260	
Cyclohexyl[i,j]			26.8	0.6	1.84 × 10⁻⁷	0.02	
Cyclopentyl[k]			22.7	−6.3	6.28 × 10⁻⁶	0.69	

[a] The present runs were conducted in glacial acetic acid containing equivalent sodium acetate. [b] Controlled to 0.02° in the present work. [c] In ethanolysis, k_1 at 35.02° was 6.40 × 10⁻⁶ sec⁻¹. [d] In ethanolysis, k_1 at 35.02° was 3.44 × 10⁻⁵ sec⁻¹. Thus the exo:endo ratio was 5.4. [e] Reference 19a. [f] For the tosylate, Goering, and Sloan[20b] reported the values of 6.8 × 10⁻⁶ sec⁻¹ at 30.07° and 7.4 × 10⁻⁵ at 49.03°. Extrapolation gave k_1 (25°) = 3.41 × 10⁻⁶, ΔH‡ = 23.9 kcal, and ΔS‡ = −3.9 cal/deg. [g] Reference 21. [h] The rates of tosylate were reported as 6.1 × 10⁻⁴ sec⁻¹ at 25.0 (see ref 21) and 2.4 × 10⁻⁴ sec⁻¹ at 18.2° in ref 22. [i] Extrapolated from the data for other temperatures taken from H. C. Brown and G. Ham, J. Am. Chem. Soc., 78, 2735 (1956). [j] S. Winstein, et al., ibid., 74, 1127 (1952), reported the values of 1.71 × 10⁻⁷ sec⁻¹ at 25.0°, ΔH‡ = 26.6 kcal, and ΔS‡ = −0.3 cal/deg. [k] The observed value in footnote i. [l] Data of the tosylate cited from ref 20b. [m] Calculated from the rate of tosylate with ROBs/ROTs = 3.

acetates and a proper compound being used as an internal reference. The estimated error in the yields is ±2%. For discussion, it was considered important to check, in all the acetolyses, the products of retention of configuration and those of inversion. These experiments were also performed by vpc. Demonstration of the absence of such a compound means that it was not formed in amounts greater than 0.5% yield. The product mixtures contained derivatives of benzyl acetate and cyclopropylcarbinyl acetate. They are anticipated to undergo acid-catalyzed isomerization in the acetolysis medium. Therefore, in order to verify that the products and their ratios were, in fact, those of kinetically controlled solvolyses, those isolated pure were treated with acetic acid and acetic acid–sodium acetate under the same conditions used for the product studies (actually for more than the corresponding ten half-lives). The products were recovered unchanged.[7]

(7) It seems likely that such epimerization requires much more severe conditions. For example, treatment of VIII-axOAc in the acetolysis solvent at 150° for 3 hr led to a mixture consisting of 85% VIII-axOAc and 15% VIII-eqOAc. A related example, the epimerization and rearrangement of dibenzobicyclo[3.2.1]octadien-2-ol acetate studied by Cristol, et al.,[8] required such a strong condition at HClO₄–CH₃COOH.

The acetolysis of I-OBs for ten half-lives produced in quantitative yield a mixture consisting of 98% of benzo-[3,4]bicyclo[3.2.1]octen-axial-2-ol acetate (VII-axOAc) and 2% of its epimer VIII-eqOAc. The retained product I-OAc and the inverted product II-OAc were absent. Hydrolysis of both acetates with lithium aluminum hydride, followed by Oppenauer oxidation, afforded the same reported benzo[3,4]bicyclo[3.2.1]-

I-OBs → VIII-ax OAc + VIII-eq OAc
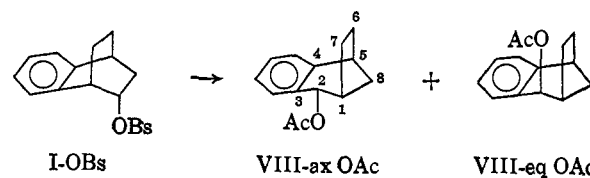
octen-2-one, the semicarbazone of which was identified by comparison with an authentic sample.[9] This fact proves the ring system of both acetates. It has been reported in nmr studies of bicyclo[3.2.1]oct-3-en-2-yl,

(8) S. J. Cristol, F. P. Parungo, D. E. Plorde, and K. Schwarzenbach, J. Am. Chem. Soc., 87, 2879 (1965).
(9) We thank Professor W. Baker for providing the sample. Refer to W. Baker and W. G. Leeds, J. Chem. Soc., 974 (1948).

benzo[3,4]bicyclo[3.2.1]octen-2-yl, and dibenzobicyclo-[3.2.1]octadien-2-yl derivatives that the eqH$_2$ shows a coupling constant of 1.4–2.9 Hz with the bridgehead H$_1$, whereas the corresponding coupling constant of the axH$_2$ is 4.3–5.4 Hz.[10-12] Thus the coupling constants, 2.8 and 4.6 Hz, observed for VIII-axOH and VIII-eqOH, respectively, confirmed the configuration of the hydroxyl groups.

Acetolysis of II-OBs led to a nearly quantitative yield of an acetate mixture containing 83% of the retained II-OAc and 17% of the rearranged IX-axOAc.

II-OBs → II-OAc + IX-ax OAc
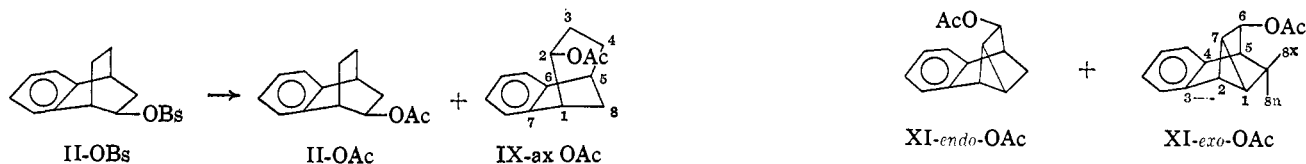
Vpc demonstrated the absence of the inverted acetate I-OAc and IX-eqOAc. The structure of IX-axOAc was identified with an authentic sample which was prepared, as shown in the following chart, by the *exo* addition of dichlorocarbene (prepared from chloroform and potassium *t*-butoxide) to benzonorbornene, followed by hydrolysis and then hydrogenation. Substantially the same reaction route has been reported by several workers for the synthesis of bicyclo[3.2.1]oct-3-en-2-yl derivatives.[10,12,13] Hydrolysis of the intermediate XIII was indicated by nmr spectroscopy to yield predominantly the ax-allylic alcohol XIV, in which $J_{1,2}$

XIII --CCl$_2$→ [intermediate] →

XIII --H$_2$O→ XIV → IX-ax OH
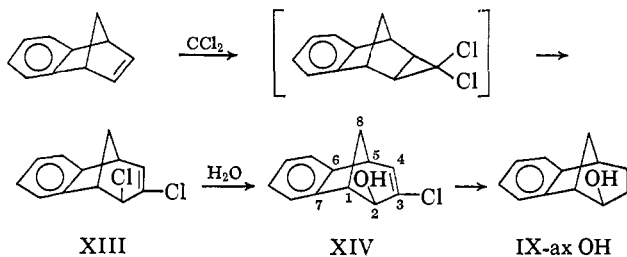
is 2.2 Hz. This stereospecific result was similarly observed in the hydrolysis of ax-2,3-dichlorobicyclo[3.2.1]-oct-3-ene.[10b,12-15] An authentic sample of IX-eqOAc was prepared by Oppenauer oxidation of IX-axOH, followed by lithium aluminum hydride reduction[17] and then acetylation.

Acetolysis of III-OBs resulted in a mixture consisting of the four compounds, ax- and eq-benzo[3,4]bicyclo-[3.2.1]octa-3,6-dien-2-ol acetates (X-axOAc and -eq-OAc) and *exo*- and *endo*-benzo[3,4]tricyclo[3.2.1.0^{2,7}]-octen-6-ol acetates[18] (XI-*exo*-OAc and -*endo*-OAc).

(10) (a) W. R. Moore, W. R. Moser, and J. E. LaPrade, *J. Org. Chem.*, 28, 2200 (1963); (b) R. C. DeSelms and C. M. Combs, *ibid.*, 28, 2206 (1963).
(11) A. R. Katritzky and B. Wallis, *Chem. Ind.* (London), 2025 (1964).
(12) C. W. Jefford, S. Mahajan, J. Waslyn, and B. Waegell, *J. Am. Chem. Soc.*, 87, 2183 (1965).
(13) (a) E. Bergman, *J. Org. Chem.*, 28, 2210 (1963); (b) C. W. Jefford and R. Medary, *Tetrahedron Letters*, 2069 (1966).
(14) A related result has been reported by Cristol in the reaction of dibenzobicyclo[3.2.1]octadien-2-yl cation which reacts from the *exo* (quasi-ax) side reversibly most rapidly to give (generally) the *exo* product as that of kinetic control.[8]
(15) Results of this kind are reasonable since in allylic cyclohexenyl systems formation and cleavage of quasi-ax bonds is stereoelectronically favored over formation and cleavage of quasi-eq bonds.[16]
(16) (a) H. L. Goering and E. F. Silversmith, *J. Am. Chem. Soc.*, 79, 348 (1957), and also (b) H. L. Goering and D. L. Towns, *ibid.*, 85, 2295 (1963).
(17) The reduction gave IX-eqOH and IX-axOH in a ratio of 3:2.

At ten half-lives, the relative peak areas of X-axOAc, X-eqOAc, XI-*endo*-OAc, and XI-*exo*-OAc on vpc analysis were 72, 11, 7, and 10, respectively. However,

III-OBs → X-ax OAc + X-eq OAc + XI-*endo*-OAc + XI-*exo*-OAc
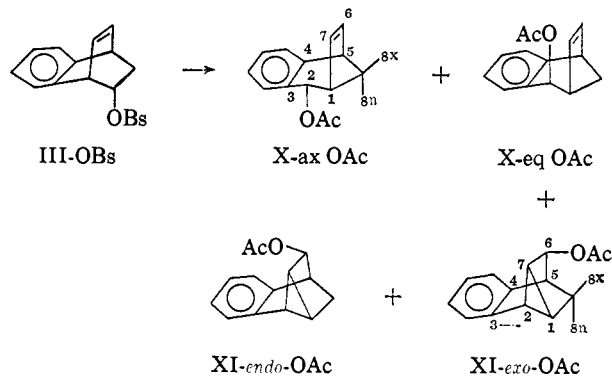
because only a capillary vpc column could separate X-eqOAc and XI-*endo*-OAc, the errors in these product ratios will be approximately twice as large as those in the other cases. Confirmatory evidence for the indicated structures was provided by detailed examination of their nmr spectra, as described in the following section. In addition, the main products from catalytic reductions of X-axOAc and X-eqOAc over PtO$_2$ were VIII-axOAc and VIII-eqOAc, respectively. These results chemically confirmed structures of the X derivatives.

Complete rearrangement to the benzo[6,7]bicyclo-[3.2.1]octa-3,6-dien-2-yl system XII was observed in the acetolysis of IV-OBs. The product for ten half-lives was an 83:17 mixture of XII-axOAc and XII-eqOAc. The structures of the products were convincingly established by the nmr spectra, mentioned below. The structure of XII-axOAc was also chemically confirmed

IV-OBs → XII-ax OAc + XII-eq OAc
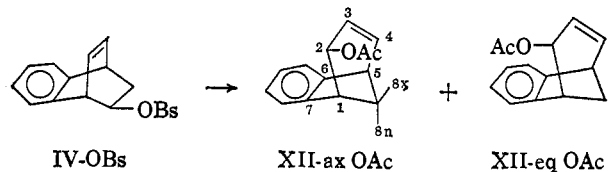
by the predominant formation of IX-axOAc on catalytic reduction over PtO$_2$.

It is particularly significant that careful search by vpc demonstrated the absence of the retained and inverted products in the acetolysis mixtures of III-OBs and IV-OBs.

Discussion of Solvolysis Results. Relevant solvolytic studies have been reported by Walborsky, *et al.*,[19] and Goering, *et al.*,[16b,20] for the bicyclo[2.2.2]octyl system V, by Goering, *et al.*, for the *endo*-2-bicyclo[2.2.2]octenyl system VI, by LeBel, *et al.*,[21] and Fraser, *et al.*,[22] for the *exo*-2-bicyclo[2.2.2]octenyl system VII, and by Cristol and his co-workers[23] for the dibenzo[2.2.2]octadienyl system. With these available data, the present results build up an almost complete set of

(18) The IUPAC name is used according to the suggestion in J. Meinwald and J. K. Crandall, *J. Am. Chem. Soc.*, 88, 1292 (1966).
(19) (a) H. M. Walborsky, M. E. Baum, and A. A. Youssef, *ibid.*, 83, 988 (1961); (b) H. M. Walborsky, J. Webb, and C. C. Pitt, *J. Org. Chem.*, 28, 3214 (1963).
(20) (a) H. L. Goering and M. F. Sloan, *J. Am. Chem. Soc.*, 83, 1397 (1961); (b) *ibid.*, 83, 1992 (1961).
(21) N. A. LeBel and J. E. Huber, *ibid.*, 83, 3193 (1963).
(22) R. R. Fraser and S. O'Farrell, *Tetrahedron Letters*, 1143 (1962).
(23) Reference 8 and references cited therein.

the solvolytic behavior of bicyclo[2.2.2]octyl and its unsaturated derivatives. The ratios k_{AcOH}/k_{EtOH} = 4.9 and 2.6 at 35° in the solvolyses of I-OBs and II-OBs, respectively (footnotes in Table I), suggest that nucleophilic participation by solvent is not important; in other words, acetolysis[24] (probably also ethanolysis) involves carbonium ion intermediates.[25]

The rates in acetolyses of dehydronorborn- and benzonorbornen-2(endo)-yl brosylates drop to 0.022 and 0.002 that of norborn-2(endo)-yl brosylate.[26–28] In contrast, the rates of VI-OBs and I-OBs were five times greater than and nearly equal (a factor of 0.92) to that of V-OBs, respectively. This indicates that the unsaturation affects the endo-norbornenyl and -octenyl systems differently. However, the fact that their ratios, 0.022:0.002 and 5.0:0.92, are in the same order of magnitude means that the relative effect of a double bond and a benzene ring is almost the same in each of the systems.[29]

The products in the acetolysis of I-OBs, 98% VIII-axOAc and 2% VIII-eqOAc, are comparable with those in the acetolysis of VI-OBs.[16b] Thus, the combined kinetic and stereochemical results are consistent with direct formation of the carbonium ion A stabilized by benzylic resonance, as discussed in the case of VI-OBs. The stereospecific conversion of A to VIII-axOAc would be explained as in similar cases;[8,15,16b] that is, A stereoelectronically favors formation of quasi-ax over quasi-eq bonds. Lithium aluminum hydride reduction of the corresponding 2-one leads to an 8:2 mixture of VIII-axOH and VIII-eqOH. Since the stereochemical results for the reduction of bridged cyclic ketones by complex hydrides are controlled by "steric approach control,"[30,31] the major formation of VIII-axOH may

suggest that the ax side is sterically more hindered. It is indicated, therefore, that collapse of the ion A to products is predominantly taking place from the sterically unfavorable direction.

The 2.6-fold increase in the rate of II-OBs (relative to V-OBs) and the small exo:endo rate ratio (a factor of 2.8) are insufficient values to propose a homobenzylic ion B as an intermediate, in which anchimeric assistance from π electrons in the benzene ring is significantly provided. Similarly, by such a small value as the 2.9-fold increase in the case of IV-OBs, assistance from the benzene ring cannot be considered. The exo:endo rate ratios in the norbornen-2-yl and benzonorbornen-2-yl arenesulfonates are both in the same order of magnitude (at 25°, 7000[26] and 15,000,[27] respectively). Thus, the nonclassical ion C analogous to B has been suggested for the solvolysis of benzonorbornen-2-yl arenesulfonate.[27,32] The rate-increasing effect of the double bond in VII-OBs has been reported as a factor of 260 and the exo:endo rate ratio thus obtained is 52, so that considerable anchimeric assistance by the double bond is demonstrated.[21] Therefore, the present results are in striking contrast.

The kinetic results and the stereochemical findings (the lack of I-OAc and IX-eqOAc) in the acetolysis of II-OBs could be rationalized by postulating either a nonclassical cation D which may involve participation of the $C_{1,6}$-methylene bond, but not that of the benzene π electrons, or a rapidly equilibrating set of classical ions E and F which simulate D. A windshield-

(24) S. Winstein, et al., J. Am. Chem. Soc., 79, 4146 (1957); 75, 147 (1953); 73, 2700 (1951).

(25) It has been shown that internal return may be an important factor in acetolysis. See S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck, and G. C. Robinson, ibid., 78, 328 (1956). However, any ion-pair return that might be involved in the acetolysis of I-OBs, III-OBs, and IV-OBs would not affect the solvolysis rate (i.e., in these cases the solvolysis rate corresponds to the ionization rate). This is because the expected products of ion-pair return, that is, VIII-axOBs for I-OBs, X-axOBs and XI-exo-OBs for III-OBs, and XII-axOBs for IV-OBs, would solvolyze very rapidly. For a similar situation, see A. H. Fainberg and S. Winstein, ibid., 78, 2767 (1956); footnote 23 in ref 20b; footnote 16 in ref 21; footnote 12 in S. J. Cristol, W. K. Seifert, D. W. Johnson, and J. B. Jurale, J. Am. Chem. Soc., 84, 3918 (1962). In the remaining case, that is, in the acetolysis of II-OBs, ion-pair return would conceivably give rise to the starting II-OBs and IX-axOBs. IX-axOBs might be expected to solvolyze more slowly than II-OBs. However, careful first-order plots gave no evidence for this expectation.

(26) S. Winstein, H. M. Walborsky, and K. Schreiber, ibid., 72, 5795 (1950).

(27) P. D. Bartlett and W. P. Giddings, ibid., 82, 1240 (1960). The rate constant at 25° originally reported in this paper was 1×10^{-9} sec^{−1}. However, the recalculation by H. C. Brown and G. L. Tritle corrected it to 5.1×10^{-10} sec^{−1} (a private communication from Professor Brown). We confirmed the recalculation. Therefore, the factor 0.004 reported widely in reviews is corrected to 0.002, and also the exo: endo rate ratio in the acetolysis of benzonorbornen-2-yl brosylates is corrected to 15,000 from 7500.
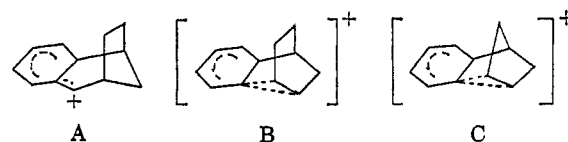
(28) (a) For a review, see J. A. Berson in "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 193; (b) for summarized data, see ref 2b.

(29) From this consideration and the rate constant for IV-OBs, we can derive the rate constant of $\sim 4 \times 10^{-6}$ sec[−1] at 25° for the acetolysis of dibenzobicyclo[2.2.2]octadien-2-ol brosylate. This value is compatible with that obtained by Cristol and Mohrig. According to a private communication from Professor S. J. Cristol, they obtained an approximate rate constant of 2×10^{-6} sec^{−1} for the corresponding tosylate at 25° in a water–acetic acid (3.6:96.4 mole %) solvent (Ph.D. Dissertation of J. R. Mohrig, University of Colorado, 1963).

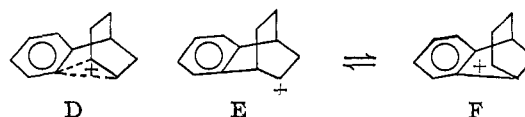(30) W. G. Dauben, D. G. Fonker, and D. S. Noyce, J. Am. Chem. Soc., 78, 2579 (1956).

(31) H. C. Brown and J. Muzzio, ibid., 88, 2811 (1966).

wiper effect in this equilibrating set can be invoked in order to explain the observed stereochemistry.[33] It should be noted that the results in the lithium aluminum hydride reduction of the 2-one[17] indicate little difference in the steric factors between ax and eq approach to the open C_2 carbonium ion, if formed.[34]

In contrast to the acetolyses of the octenyl derivatives, no stereospecific result was obtained in the reactions of the octadienyl derivatives. From the kinetic data, especially from the small rate ratio $k_{III-OBs}/k_{IV-OBs} = 3.8$, it can be argued that little, if any, participation by the double bond is being exerted in the acetolysis of III-OBs. Stereochemical results preclude the participation of the classical [2.2.2]dienyl ion G as an intermediate. Absence of products having the [2.2.2] skeleton and lack of stereospecificity also make nonclassical intermediates such as H, I, and J or a rapid and reversible equilibrium between classical ions K and L unsatisfactory. The

(32) W. P. Giddings and J. Dirlam, ibid., 85, 3900 (1963).

(33) H. C. Brown, "The Transition State," Special Publication No. 16, The Chemical Society, London, 1962, pp 140–158, 174–178.

(34) It has been reported by A. A. Yousef, M. E. Baum, and H. M. Walborsky, J. Am. Chem. Soc., 81, 4709 (1959), that LiAlH4 reduction of bicyclo[3.2.1]octan-2-one give the corresponding eq- and ax-2-ols in a ratio of 9:1 and the eq is thermodynamically more stable than the ax.

Table II.   Nmr Spectral Data on Some Benzobicyclo[3.2.1]octadienes and Benzotricyclo[3.2.1.0²,⁷]octenes

| Compd		Chemical shift, τ^a	Coupling constant, J, Hz^b (dihedral angle, θ, deg)^c		
X-axOAc	H_1	7.11m(7.11m)	1,2eq = 2.0 (76)	6,7 = 5.8	2eq,8x = 0.8
	H_{2eq}	4.38d(4.10d)	1,8x = 4.7 (40)	5,8x = 4.7 (40)	6,8n ≤ 0.2
	H_5	6.66m(6.93m)	1,8n = 0.5 (80)	5,8n = 0.5 (80)	7,8n ≤ 0.2
	H_6	3.53q(3.77q)	1,7 = 2.7	5,6 = 3.1	
	H_7	4.10q(4.35q)	8x,8n = 10.0		
	H_{8x}	~7.8m(8.00d-t-d)			
	H_{8n}	~7.8m(7.78d)			
	OAc	7.96s(8.27s)			
X-eqOAc	H_1	6.75t-d(6.78t-d)	1,2ax = 5.4 (44)	6,7 = 5.8	2ax,7 ≈ 0.3
	H_{2ax}	4.04d(3.86d)	1,8x = 5.0 (40)	5,8x = 4.7 (40)	6,8n ≤ 0.1
	H_5	6.77q(7.03q)	1,8n ≈ 0.5 (80)	5,8n ≈ 0.5 (80)	7,8n ≤ 0.1
	H_6	3.60q(3.73q)	1,7 = 2.8	5,6 = 2.9	
	H_7	4.29q(4.27q)	8x,8n = 10.3		
	H_{8x}	7.74d-t(7.96d-t)			
	H_{8n}	7.95d(8.26d)			
	OAc	7.96s(8.25s)			
XII-axOAc	H_1	6.76m(6.69m)	1,2eq = 2.0 (76)	3,4 = 9.4	2eq, 4 = 1.0
	H_{2eq}	4.99q-d(4.71q-d)	1,8x = 0.9 (80)	5,8x = 0.9 (80)	2eq,8n ≤ 0.3
	H_3	4.80d-q(4.75d-q)	1,8n = 4.6 (40)	5,8n = 4.2 (40)	1,3 = 1.8
	H_4	3.60q(3.78q)	2eq,3 = 3.6	4,5 = 6.6	4,8n = 1.0
	H_5	6.75m(6.97q-m)	8x,8n = 10.1		
	H_{8x}	~7.8m(7.75d-t)			
	H_{8n}	~7.8m(7.94d-t-d)			
	OAc	7.97s(8.25s)			
XII-eqOAc	H_1	6.40t-m(6.49t-m)	1,2ax = 5.5 (44)	3,4 = 9.5	2ax,4 = 2.3
	H_{2ax}	4.50t-d-d(4.39t-d-d)	1,8x = 1.0 (80)	5,8x = 1.0 (80)	1,3 = 1.8
	H_3	4.93d-q-d(4.92d-q-d)	1,8n = 4.7 (40)	5,8n = 4.2 (40)	4,8n = 1.2
	H_4	3.70q-t(3.94q-t)	2ax,3 = 2.7	4,5 = 6.2	
	H_5	6.80q-m(7.16q-m)	8x,8n = 10.0		
	H_{8x}	7.75d-t(8.08d-t)			
	H_{8n}	7.62d-t-d(7.90d-t-d)			
	OAc	8.05s(8.37s)			
XI-exo-OAc	H_1	8.28d-m(8.50q-m)	5,6n = 0.7 (81)	6n,7 = 1.0 (75)	1,5 = 1.0
	H_2	7.80t(8.10t)	1,8x = 2.8 (45)	5,8x = 4.9 (39)	7,5 = 1.0
	H_5	7.00d-m(7.02d-m)	1,8n = 0.6 (75)	5,8n = 0.3 (81)	1,6n = 0.4
	H_{6n}	5.55s(5.35t)	1,2 = 7.0	2,7 = 7.0	7,8n ≈ 0
	H_7	8.28d-m(8.38q-t)	1,7 = 5.0	8x,8n = 11.6	2,8x ≤ 0.2
	H_{8x}	7.80m(7.85d-q)			6n,8x ≤ 0.2
	H_{8n}	8.96d(9.06d)			
	OAc	8.00s(8.30s)			
XI-endo-OAc	H_1	~8.25m(8.77m)	5,6x = 5.0 (39)	6x,7 = 3.0 (45)	1,5^d
	H_2	7.78t(8.03t)	1,8x = 2.8 (45)	5,8x = 5.0 (39)	5,7 = 0.7
	H_5	6.65t(6.70t)	1,8n = 1.0 (75)	5,8n = 0.3 (81)	7,8n^d
	H_{6x}	4.95q(4.87q)	1,2 = 7.0	2,7 = 7.0	2,6x = 0.4
	H_7	8.32m(8.36m)	1,7 = 5.5	8x,8n = 11.8	2,8x ≤ 0.2
	H_{8x}	7.95d-q(8.33d-q)			6x,8n ≤ 0.2
	H_{8n}	8.96d(9.20d)			
	OAc	8.38s(8.63s)			

^{a} Obtained in CCl_4.   Values in parentheses are data obtained in C_6D_6.   Peak multiplicities are represented by s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). ^{b} Absolute values. ^{c} Obtained from Dreiding models.   Accuracies are ±2°. ^{d} Obscured.

combination of kinetic and stereochemical behavior can be accommodated by the direct formation of an equilibrium mixture containing the benzylic cation M and the
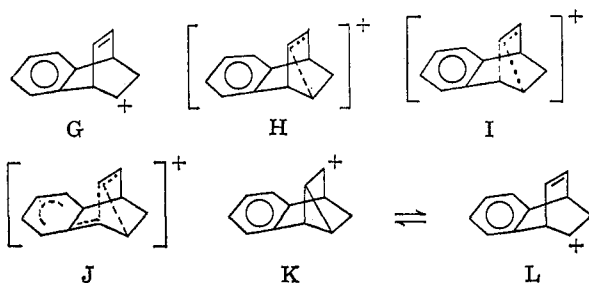
cyclopropylcarbinyl cation N. The predominant formation of X-axOAc would be accounted for with a stereoelectronic factor as in the above-mentioned case.

As in the case of I-OBs, the direct formation of the classical cation O, stabilized by allylic resonance and not involving participation from the benzene ring, can accommodate all results from IV-OBs.
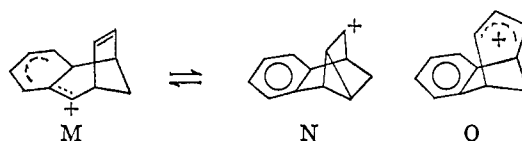
A summary of related data shows that the relative rates at 25° in acetolyses are for norbornyl, dehydronorbornyl, and benzonorbornenyl exo-2-brosylates, 1, 0.5, and 0.08; for V-OBs, VII-OBs, and II-OBs, 1, 260, and 2.6; for I-OBs, III-OBs, and dibenzobicyclo-[2.2.2]octadienyl-OBs, 1, 12, and ~0.5.²⁹ In each series, ratios of relative rates for the dehydro and the benzo derivatives (0.5:0.08 = 6, 260:2.6 = 100, and 12:0.5 = 24) express the relative effectiveness of double
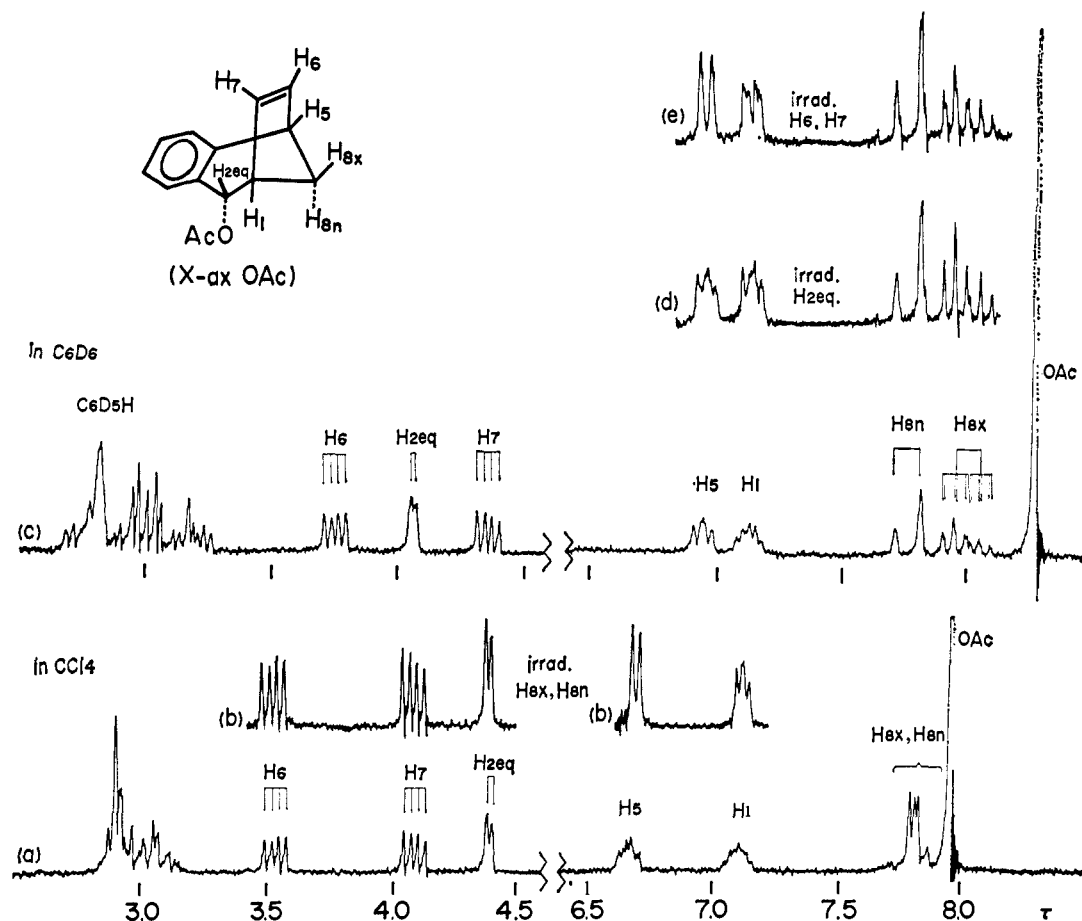
Figure 1. Nmr, nmdr, and nmtr spectra of X-axOAc in CCl₄ and C₆D₆ at 100 MHz. (Spectra shown in b, d, and e were run at increased gains).

bonds vs. benzene rings for participation. Thus, it is clear that the most flexible [2.2.2]octenyl system can achieve the most favorable conformation for participation (the factor of 100). The least participation (the factor of 6) is indicated in the rigid norbornenyl system. However, the present study cannot rationalize the origin of the rate of V-OBs which is 49 times faster than that of cyclohexyl brosylates.

Nmr Spectra of Benzo[3,4]bicyclo[3.2.1]octa-3,6-dien-2-yl (X), Benzo[6,7]bicyclo[3.2.1]octa-3,6-dien-2-yl (XII), and Benzo[3,4]tricyclo[3.2.1.0²,⁷]octen-6-yl (XI) Derivatives. Investigations of the nmr spectra of the six products X–XII by using double and triple resonance (nmdr and nmtr) techniques and the solvent effect of benzene[35] at 100 MHz provided evidence for their structures. The nmr spectra with some spin-decoupling experiments are shown in Figures 1–6. In Table II are listed the chemical shifts and the coupling constants (absolute values) obtained. The procedure for the spectral assignments of these compounds is described in the Experimental Section.

The fact that the two bridgeheads H_1 and H_5 are vicinally coupled to the olefinic H_6 and H_7 in the two compounds X indicates that these compounds belong to the

benzo[3,4]bicyclo[3.2.1]octa-3,6-diene system. Applying the Karplus correlation[37] to the obtained $J_{1,2}$ values,[10-12] we confirmed that the acetoxyl at C_2 in X-axOAc and X-eqOAc has an ax and an eq configuration, respectively. Among long-range spin couplings expected by analogy with bicyclo[2.2.1]heptenes,[38] a $J_{ax,7}$ of about 0.3 Hz and very small $J_{6,8n}$ and $J_{7,8n}$ were only observed. The overlapping of the back-side lobe of the σ orbital of H_{8n} with π orbitals of the double bond[38] might be slight in this system. A long-range $J_{2eq,8x}$ of 0.8 Hz was, however, clearly established, as expected from the "W-letter" rule.[38]

Decoupling experiments on the two compounds XII showed that only one bridgehead H_5 is vicinally coupled to the one olefinic H_4. This fact implies that these compounds belong to the benzo[6,7]bicyclo[3.2.1]octa-3,6-diene system. The observed $J_{1,2}$ likewise determined the configurations of the acetoxyls at C_2 in XII-axOAc and XII-eqOAc as ax and eq, respectively. The allylic $J_{2ax,4}$ (2.3 Hz) in XII-eqOAc was greater than $J_{2eq,4}$ (1.0 Hz) in XII-axOAc. This indicates that, as suggested by the molecular models, H_{2ax} has more ax character than H_{2eq}.[38] Jefford, et al.,[39] reported that similar allylic $J_{2,4}$ cannot be observed in several exo-

(35) Since all the compounds examined here contain an acetoxyl group, their nmr spectra are expected to be fairly changed with an alteration of the solvent from CCl₄ to hexadeuteriobenzene (C₆D₆).[36]

(36) N. S. Bhacca and D. H. Williams, Tetrahedron Letters, 3127 (1964); D. H. Williams and N. S. Bhacca, Tetrahedron, 21, 1641, 2021 (1965); J. D. Connolly and R. McCrindle, Chem. Ind. (London), 379, 2066 (1965); C. J. Timmons, Chem. Commun., 576 (1965).

(37) M. Karplus, J. Chem. Phys., 30, 11 (1959); M. Karplus, J. Am. Chem. Soc., 85, 2870 (1963).

(38) S. Sternhell, Rev. Pure Appl. Chem., 14, 15 (1964); A. Rassat, C. W. Jefford, J. M. Lehn, and B. Waegell, Tetrahedron Letters, 233 (1964); E. W. Garbisch, Jr., Chem. Ind. (London), 1715 (1964); M. Barfield, J. Chem. Phys., 41, 3825 (1964), and references cited therein.

(39) C. W. Jefford, B. Waegell, and K. Ramey, J. Am. Chem. Soc., 87, 2191 (1965).

H6
H7
H5
OAc
H8x
H8n
H1
H2ax

(X-eq OAc)

in C6D6

C6D6H

H2ax

H6

H7

H1

H5

H8x

H8n

OAc

irrad. (f)
H2ax

irrad.
H2ax

(e)

(e)

in CCl4

OAc

Irrad. (b)
H1,H5

Irrad.
H7 (d)

H6

H2ax

H7

irrad.
H6 (c)

H1, H5

H8x

H8n

(d)

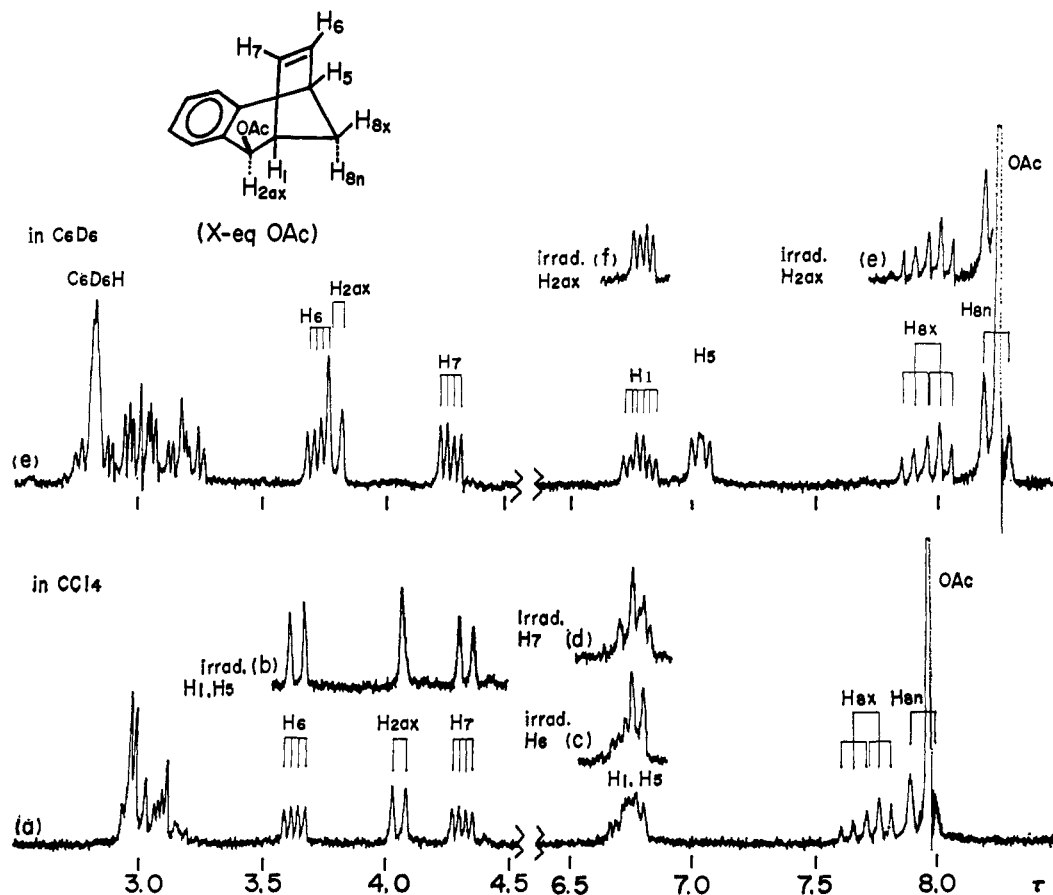3.0   3.5   4.0   4.5   6.5   7.0   7.5   8.0   τ

Figure 2. Nmr, nmdr, and nmtr spectra of X-eqOAc in CCl_4 and C_6D_6 at 100 MHz.

2-substituted 3-bromobicyclo[3.2.1]oct-3-enes. The negligibly small $J_{2,4}$ in their compounds appears due to electronegativity of the bromine atom at C_3. The relatively stronger long-range $J_{1,3}$ of 1.8 Hz can be

in X, and $J_{3,5}$ in XII), benzylic,[40] homoallylic[28] ($J_{1,5}$ in X and $J_{2,5}$ in XII), and homobenzylic couplings[40] ($J_{2,5}$ in X and $J_{1,5}$ in XII). This substantiates the fact that the $\sigma-\pi$ overlapping necessary for these couplings[38]

Table III. Properties and Analyses of Benzobicyclooctene Derivatives

Ring system	Subst	Mp[b] or bp,[c] °C (mm)/nD (°C)	Formula	Carbon % Calcd	Carbon % Found	Hydrogen % Calcd	Hydrogen % Found
I	OBs	[91–92]	$C_{18}H_{17}BrO_3S$	54.97	55.18	4.36	4.53
II	OBs	[109–110]	$C_{18}H_{17}BrO_3S$	54.97	55.00	4.36	4.20
	OAc	120(1)/1.5389(24)	$C_{14}H_{16}O_2$	77.95	77.79	7.46	7.58
III	OH	[103.5–104.5]	$C_{12}H_{12}O$	83.69	83.46	7.02	7.31
	OBs	d	$C_{18}H_{15}BrO_3S$	55.25	55.15	3.86	4.05
IV	OH	[96.5–97.5]	$C_{12}H_{12}O$	83.69	83.63	7.02	7.03
	OBs	d	$C_{18}H_{15}BrO_3S$	55.25	55.34	3.86	4.00
VIII	axOH	[83.5–84.5]	$C_{12}H_{14}O$	82.72	82.72	8.10	8.09
	eqONB[a]	[112–113]	$C_{19}H_{17}NO_4$	70.57	70.50	5.30	5.46
IX	axOH	[72.5–73.5]	$C_{12}H_{14}O$	82.72	82.56	8.26	8.26
	axOAc	125(5)	$C_{14}H_{16}O_2$	77.76	77.66	7.46	7.43
X	axOAc	125(3)/1.5457(27)	$C_{14}H_{14}O_2$	78.48	78.37	6.59	6.74
	eqOAc	125(3)/1.5445(26)	$C_{14}H_{14}O_2$	78.48	78.59	6.59	6.98
XI	exo-OAc	[75.5–76.5]	$C_{14}H_{14}O_2$	78.48	78.54	6.59	6.57
	endo-OAc	126–128(1)/1.5530(25)	$C_{14}H_{14}O_2$	78.48	78.53	6.59	6.70
XII	axOAc	125–128(4)/1.5431(28)	$C_{14}H_{14}O_2$	78.48	78.78	6.59	6.75
	eqOAc	123–126(2)/1.5421(28)	$C_{14}H_{14}O_2$	78.48	78.22	6.59	6.81

[a] p-Nitrobenzoate. [b] Melting points are presented in brackets. [c] Indicated as bath temperature when boiling. [d] Gradually decompose, not indicating clear melting points.

ascribed to the "W-letter" rule.[38] Long-range $J_{4,8n}$ and $J_{2eq,3n}$ in XII-axOAc and $J_{4,8n}$ in XII-eqOAc were also observed.[39]

The present experiments on X and XII indicated negligibly small magnitudes for allylic ($J_{1,6}$ and $J_{5,7}$

is minimized. It should be further noted that $J_{3,4}$ (9.5 Hz) and $J_{4,5}$ (ca. 6.5 Hz) in XII are greater than $J_{6,7}$ (5.8 Hz) and $J_{1,7}$ or $J_{5,6}$ (ca. 2.9 Hz) in X, respec-

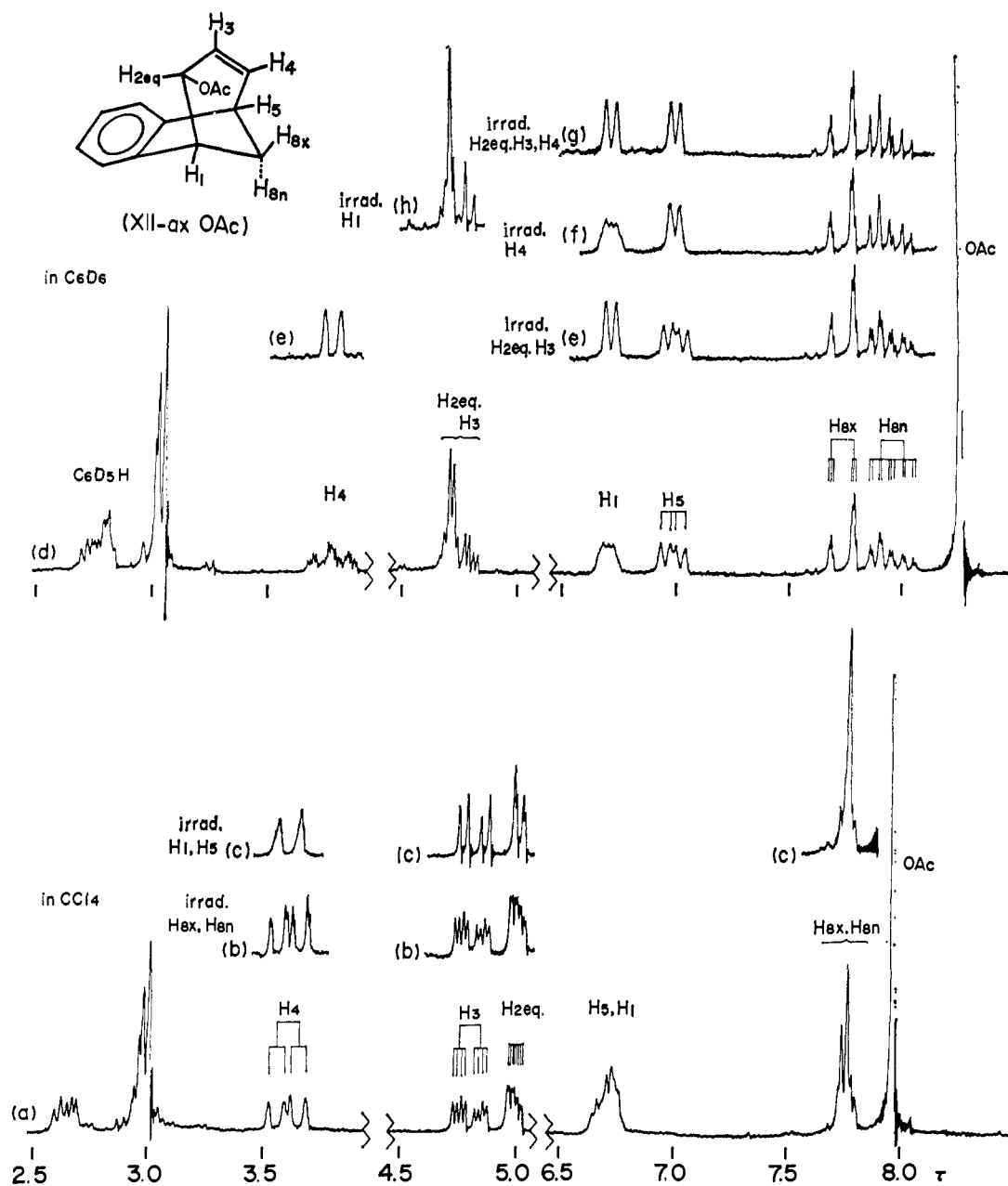(40) F. P. Johnson, A. Melera, and S. Sternhell, Australian J. Chem., 19, 1523 (1966).

Figure 3. Nmr, nmdr, and nmtr spectra of XII-axOAc in CCl₄ and C₆D₆ at 100 MHz.

tively, and that $|J_{8x,8n}|$ ($ca.$ ∓10 Hz) is not so small. The former fact can be derived and explained by the difference in the ring size;[41] the latter fact implies that the methylene bridges in X and XII are relatively less strained than in the case of bicyclo[2.2.1]heptenes, in which J values between the two bridge methylene protons are about ∓8.5 Hz.[42]

For the structures of the two remaining products XI, it is possible to assume the alternative ring systems, benzo[3,4]tricyclo[3.2.1.0²,⁷]octene (XI) and benzo[3,4]-tricyclo[3.1.1.1²,⁶]octene (XV). Although the spectrum of XI-exo-OAc in CCl₄ (see Figure 5a) shows very complicated signals at τ 7.8 and 8.0, in C₆D₆ the signals appear

fairly separated. The spectrum showed only one signal, assignable to one bridgehead proton; this is inconsistent with XV having two bridgehead protons on the benzylic
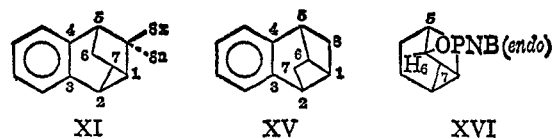
carbons. On the other hand, H₂ in XI is benzylic and also cyclopropyl; therefore it can be anticipated to appear at a higher field than at an ordinary position. Further, LeBel and Huber[21] have reported that H₆ in tricyclo[3.2.1.0²,⁷]octan-6($endo$)-ol p-nitrobenzoate (XVI) ($endo$ is for cyclopropyl) appears as a singlet because both the dihedral angles between H₆ₓ and H₅, H₇ protons are close to 80°. The broad singlet signal in XI-exo-OAc at τ 5.55 in CCl₄ (at τ 5.35 in C₆D₆)

(41) O. L. Chapman, *J. Am. Chem. Soc.*, **85**, 2014 (1963); G. V. Smith and H. Kriloff, *ibid.*, **85**, 2016 (1963); P. Laszlo and P. von R. Schleyer, *ibid.*, **85**, 2017 (1963); K. Tori, R. Muneyuki, and H. Tanida, *Can. J. Chem.*, **41**, 3142 (1963).

(42) K. Tori, K. Aono, Y. Hata, R. Muneyuki, T. Tsuji, and H. Tanida, *Tetrahedron Letters*, 9 (1966), and references therein.
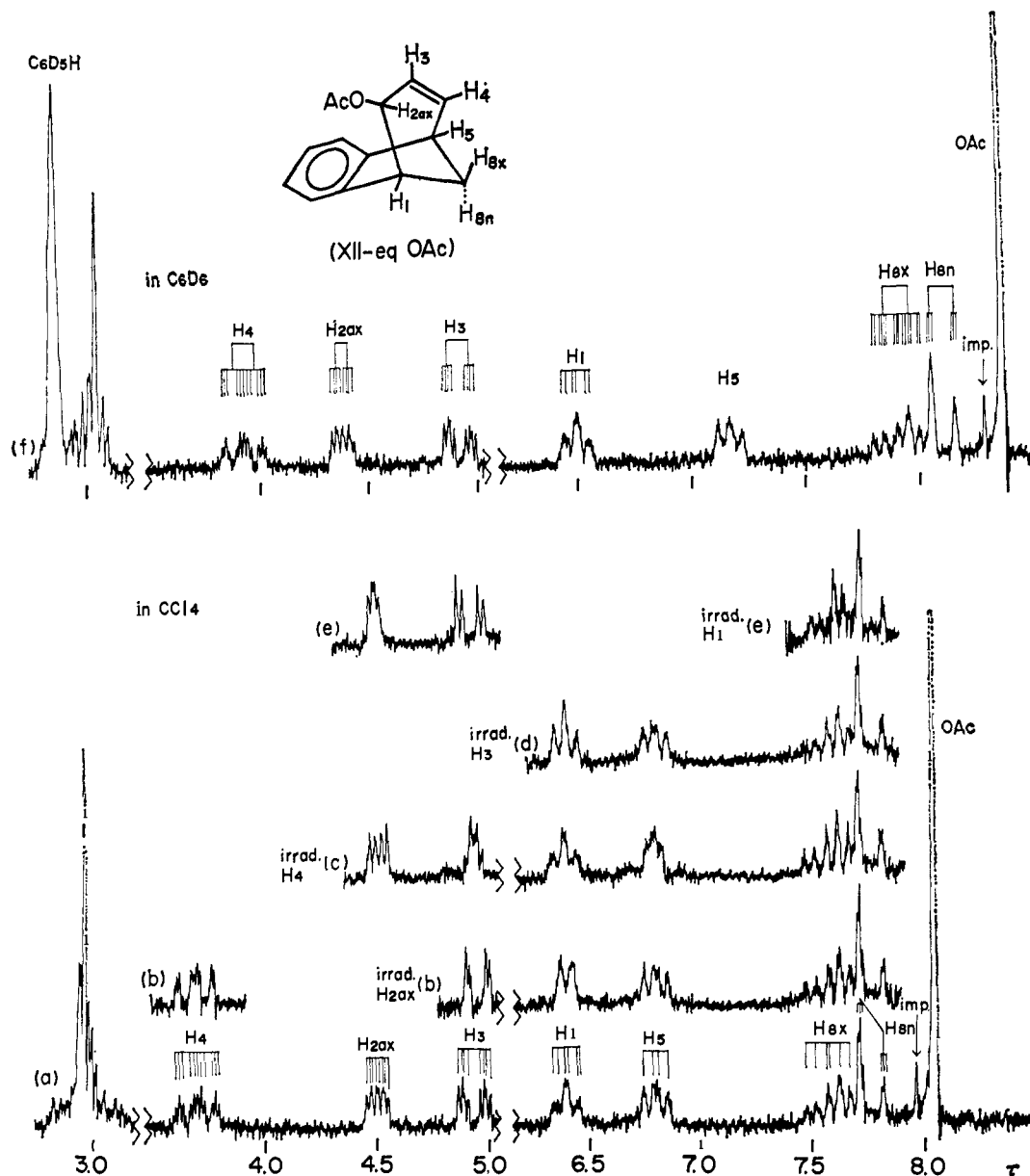
Figure 4. Nmr and nmdr spectra of XII-eqOAc in CCl_4 and C_6D_6 at 100 MHz.

suggests an *exo* configuration for the acetoxyl. The nmdr and nmtr experiments (see Figure 5 and Experimental Section) confirmed the structure of XI-*exo*-OAc from various approaches. The fact that $J_{8x,8n}$ (∓ 11.6 Hz) falls in a range of magnitudes expected from geminal couplings between methylene protons on a normal sp^3 carbon indicates, in accord with the above assignment, that the C_8 orbital is not highly strained.

Similarly, the nmdr and nmtr experiments on XI-*endo*-OAc (see Figure 6 and Experimental Section) led us to conclude that this compound is an epimer of XI-*exo*-OAc. An important change in the spectrum of this compound from that of XI-*exo*-OAc is the appearance of a broad quartet due to H_{6x} ($J = 5.0$ and 3.0 Hz),[21] instead of the broad singlet due to H_{6n} (see the dihedral angles in Table II).

Except $J_{7,8n}$ and $J_{6n,8n}$, many long-range couplings were observed, as expected from the ring system of XI according to "W-letter rule."[38] Besides the expectation, $J_{6n,8x}$ and $J_{6x,8n}$ were obtained, though less than or

equal to 0.2 Hz. It is interesting to note that $J_{1,2}$ and $J_{2,7}$ (7.0 Hz) are not equal to $J_{1,7}$ (5 Hz). This finding may suggest that the strain at C_1 and C_7 is different from that at C_2.

Experimental Section[43]

Properties and analyses of the new compounds prepared in the present study are summarized in Table III.

Materials. For the preparation of III-OH and IV-OH the reduction of benzobicyclo[2.2.2]octadien-2-one[3] was carried out with 4 equiv of lithium aluminum hydride in anhydrous tetrahydrofuran. The usual work-up, followed by separation using elution chromatography over silica gel (Woelm neutral, added with 5% of H_2O), gave pure samples of III-OH and IV-OH in a ratio of 7:3.

Kinetic Measurements. The kinetic procedure for the acetolysis studies was essentially the same as that employed previously.[2b,6] In all cases the initial concentration of brosylate was approximately 0.03 M. The reactions were carried out in glacial acetic acid

(43) Melting points were taken by capillary and are corrected. Boiling points are uncorrected. Ultraviolet spectra were recorded on a Beckman DK-2 spectrometer.
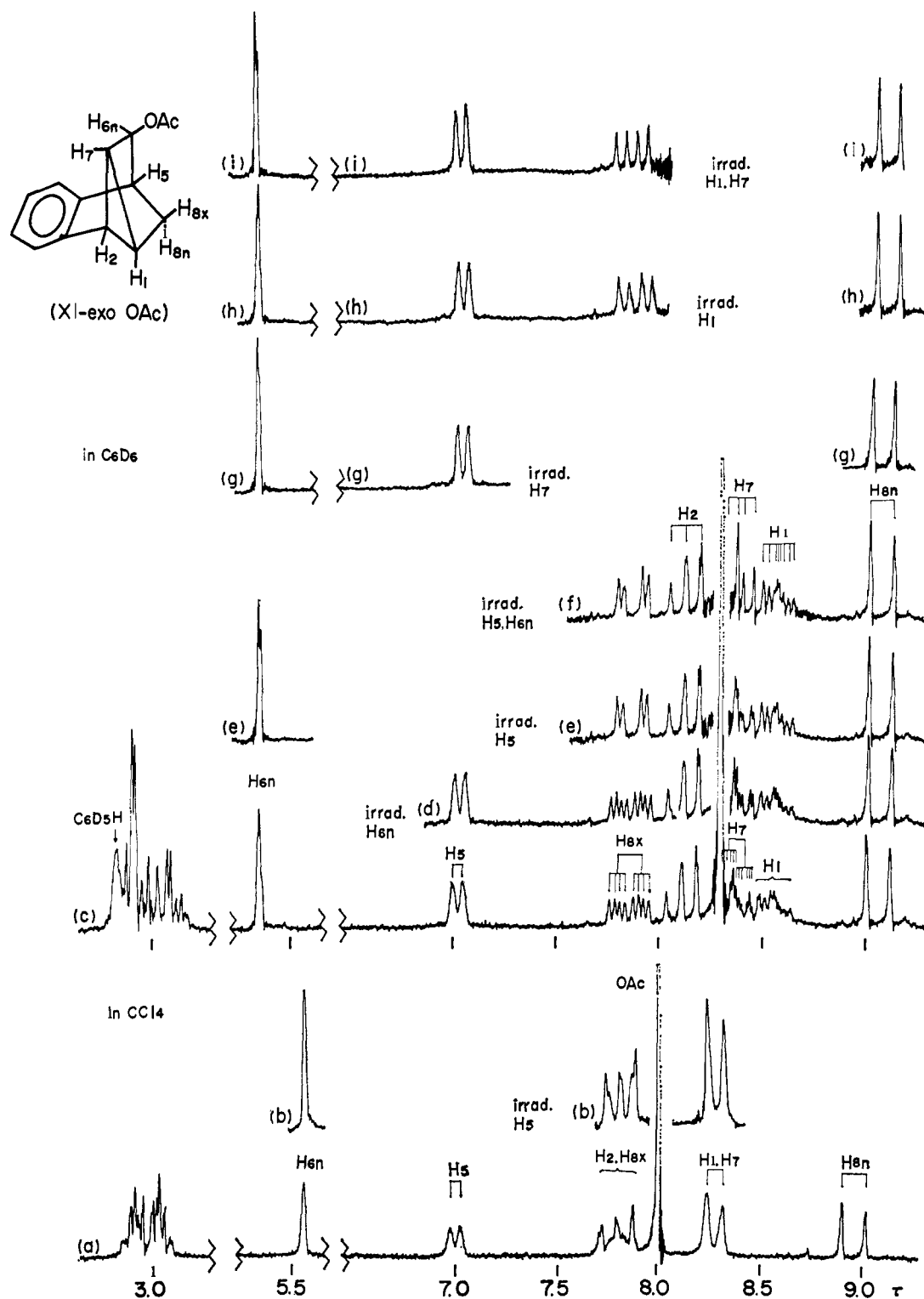
Figure 5. Nmr, nmdr, and nmtr spectra of XI-*exo*-OAc in CCl$_4$ and C$_6$D$_6$ at 100 MHz.

containing an equivalent of sodium acetate and 1 wt % of acetic anhydride. Rate constants were determined by the infinity titer method. Usually, ten aliquots, 2 ml in volume, were periodically withdrawn, run into 20 ml of cooled dioxane, and titrated immediately with 0.06 M standard perchloric acid solution. Infinity titers were obtained after at least ten half-lives. In all cases observed infinity titers were within ±2% of the calculated values.

The ethanolyses were carried out in anhydrous ethanol. They were followed by titrating usually ten aliquots, 2 ml in volume, which were quenched by adding to 20 ml of ice-cold acetone, with a standard solution of 0.006 M sodium methoxide in mixed benzene and methanol (1:3). A methanol solution of methyl red and bromocresol green was used as the indicator.

Isolation of Acetolysis Products. The acetolysis solution was allowed to remain in a constant temperature bath for ten half-lives of each of the brosylates, concentrated by distilling the acetic acid, treated with ice-water, and extracted four times with pentane. The pentane solution was washed with aqueous sodium carbonate and dried. After removal of the solvent, the residue was subjected to analytical and preparative vpc.

Analytical Vapor Phase Chromatography. A standard column, 2 m × 6 mm, of stainless-steel tubing was employed with helium as a carrier gas in a Hitachi gas chromatograph Model F-6. The column was packed with 10 wt % diethylene glycol succinate polymer on 30–60 mesh Chromosorb W. The retention times of I-OAc, II-OAc, VIII-axOAc, VIII-eqOAc, and IX-axOAc were 16.5,
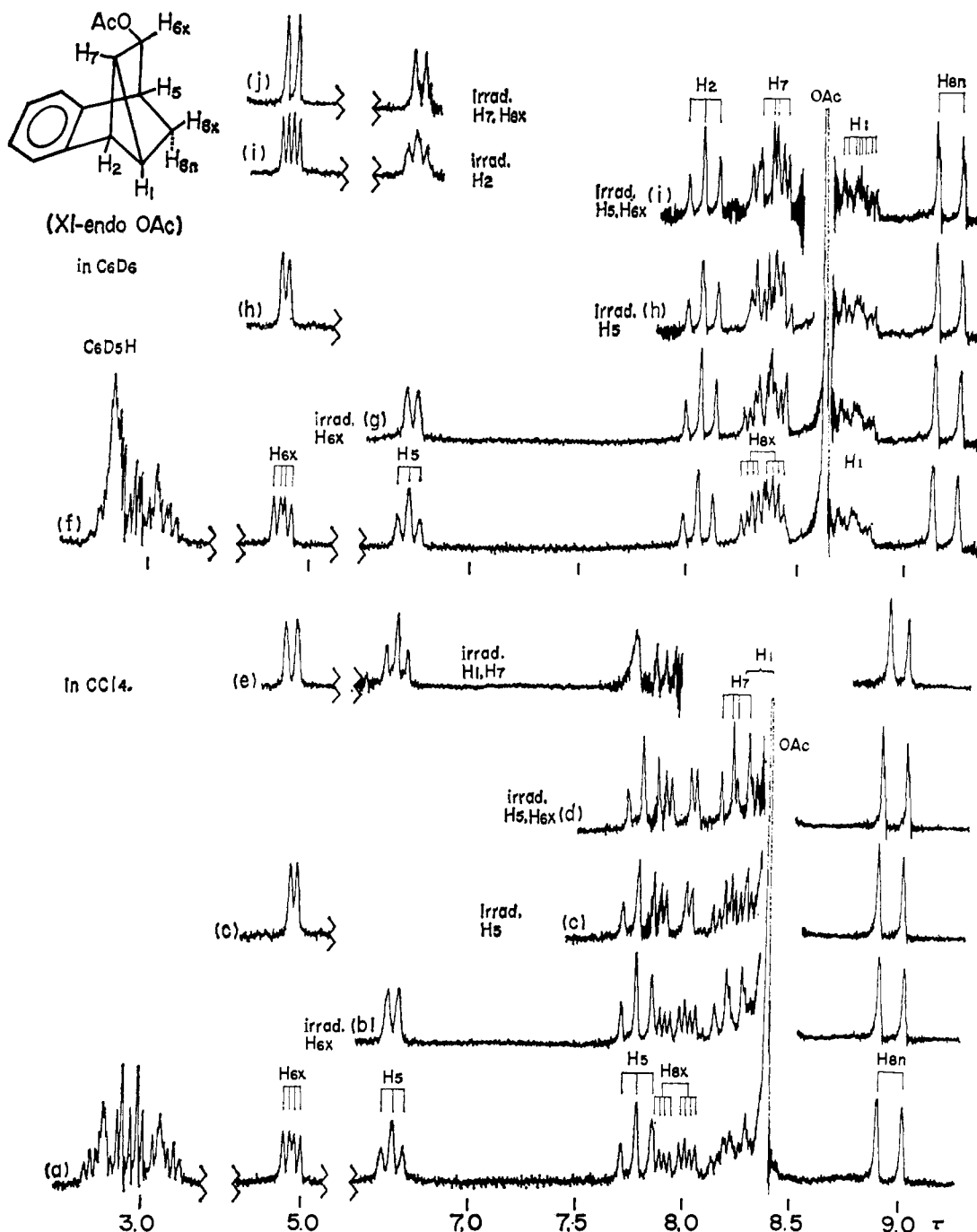
Figure 6. Nmr, nmdr, and nmtr spectra of XI-*endo*-OAc in CCl$_4$ and C$_6$D$_6$ at 100 MHz.

18.5, 19.2, 17.5, and 13.5 min, respectively, at 200° with 1.5 kg/cm^2 of He. Those of X-axOAc, X-eqOAc, XI-*endo*-OAc, and XI-*exo*-OAc were 15.0, 18.0, 18.0 (overlapped), and 25.0 min, respectively, at 190° with 1.5 kg/cm^2 of He. Capillary vpc on a 45-m Golay Z-45 at 125° with 1.0 kg/cm^2 of He showed separated peaks at the retention time of 10.5 for X-eqOAc and 11.0 for XI-*endo*-OAc. The retention times of III-OAc, IV-OAc, XII-axOAc, and XII-eqOAc were 15.2, 18.3, 16.0, and 18.0 min, respectively, at 190° with 1.5 kg/cm^2.

Preparative vapor phase chromatography was carried out (a) on a Hitachi gas chromatograph Model F-6, equipped with a 2 m × 21 mm stainless-steel tubing column packed with 10 wt % of diethylene glycol succinate polymer on 30–60 mesh Chromosorb W (column A); (b) on a Yanagimoto gas chromatograph Model GCG-3D, equipped with a 5 m × 14 mm stainless-steel tubing column packed with 5 wt % diethylene glycol succinate polymer on the same support (column B). The retention times were 15.2 and 13.0 min, respectively (200° of column B and 300 cc/min of He),

for II-OAc and IX-axOAc; 19.5, 23.5, 23.5 (overlapped), and 32.0 min, respectively (210° of column A and 600 cc/min of He), for X-axOAc, X-eqOAc, XI-*endo*-OAc, and XI-*exo*-OAc; 20.5 and 22.5 min, respectively (210° of column A and 500 cc/min of He), for XII-axOAc and XII-eqOAc.

Benzo[3,4]bicyclo[3.2.1]octen-2-one. A solution of 72 mg of VIII-axOH, 53.6 mg of benzoquinone, and 203.6 mg of aluminum *t*-butoxide in 7 ml of benzene was refluxed overnight. The mixture was washed with dilute sulfuric acid and then with aqueous sodium hydroxide until the inorganic layer was colorless. The benzene solution was dried and evaporated, and the residue was distilled to give 59 mg of the ketone at 132–135° (5 mm), n^{24}D 1.5684 [lit.[9] bp 162–163° (23 mm), n^{25}D 1.577), $\lambda_{max}^{95\% \ EtOH}$ 249 mμ (ϵ 11,600) and 293 (2310).

Anal. Calcd for C$_{12}$H$_{12}$O: C, 83.69; H, 7.02. Found: C, 83.59; H, 7.14.

Axial 2,3-Dichlorobenzo[6,7]bicyclo[3.2.1]octa-3,6-diene (XIII). To a stirred solution of 121 g of benzonorbornene in 500 g of dry

chloroform, maintained at 0° under nitrogen, was added 175 g of potassium t-butoxide during 6 hr. The mixture was added to water and neutralized with hydrochloric acid. The organic layer was dried and distilled to remove t-butyl alcohol, chloroform, and most of the unchanged benzonorbornene. Further distillation under reduced pressure, followed by elution chromatography, gave 10 g of XIII, bp 124–125° (2 mm), n^{23}D 1.5963, nmr in CCl_4: four aromatic H at τ 2.6–3.0 (m), one vinyl H at 3.61 (d), one C_2 $endo$-H at 5.74 (d), one C_1 bridgehead H at ~6.35 (m), one C_5 bridgehead H at ~6.60 (m), two C_8 H at 7.4–8.0 (m), $J_{1,2}$ = 2.1 and $J_{4,5}$ = 6.8 Hz.

Anal. Calcd for $C_{12}H_{10}Cl_2$: C, 64.02; H, 4.48. Found: C, 64.32; H, 4.64.

3-Chloro-2(axial)-hydroxybenzo[6,7]bicyclo[3.2.1]octa-3,6-diene (XIV). A suspension of 2.7 g of XIII, 4.0 g of calcium carbonate, 20 ml of tetrahydrofuran, and 40 ml of water was refluxed under nitrogen for 51 hr. The mixture was extracted with ether. Evaporation of the ether gave 2.2 g of XIV, mp 119–120°; nmr in CCl_4: four aromatic H at τ 2.6–3.0 (m), one vinyl H at 3.64 (d), one C_2 $endo$-H at 6.11 (d), two $C_{1,5}$ bridgehead H at ~6.5 (m), two C_8 H at ~7.7 (m), $J_{1,2}$ = 2.2 and $J_{4,5}$ = 7.2 Hz.

Anal. Calcd for $C_{12}H_{11}ClO$: C, 69.74; H, 5.37; Cl, 17.15. Found: C, 70.09; H, 5.76; Cl, 17.32.

Hydrogenation of XIV. A solution of 127 mg of XIV in 3 ml of tetrahydrofuran and 0.7 ml of 1.0 N sodium hydroxide was hydrogenated over palladium–charcoal. The hydrogen uptake was 29.0 ml. The usual work-up left 98 mg of crude IX-axOH. Purification was performed by preparative vpc: 10% diethylene glycol succinate polymer on Chromosorb W, column temperature 185°, He 600 cc/min, retention time 18.5 min, nmr in CCl_4: four aromatic H at τ ~2.9 (m), one CHOH at 6.13 (m), two bridgehead H at ~6.9 (m), six H at 7.5–9.0; nmr of the acetate (IX-axOAc) in CCl_4: four aromatic H at τ ~2.9 (m), one CHOAc at 5.17 (m), two bridgehead H at ~6.8 (m), six H at 7.6–9.1, three CH_3CO at 7.97.

Nmr Measurements. Nmr spectra were taken with a Varian A-60A spectrometer (60 MHz), calibration of which was checked by the usual side-band method, and/or a Varian HA-100 spectrometer operating at a 100-MHz field in the frequency-swept and tetramethylsilane (TMS) locked mode. The calibration of 100-MHz spectra was made by using a Hewlett-Packard HP-5212A electronic counter. Accuracies of chemical shifts and coupling constants are within τ ±0.01 and ±0.1 Hz, respectively. The spectra were measured by using about 2–5% (w/v) solutions of samples in CCl_4 and/or C_6D_6 containing TMS as an internal reference Nmdr and nmtr experiments were made by using the HA-100 spectrometer and two Hewlett-Packard HP-200ABR audio-oscillators in the frequency-swept operation.

Procedure for the Nmr Spectral Assignments of Benzobicyclo-[3.2.1]octadiene Derivatives X and XII. The spectrum of X-axOAc in CCl_4 (Figure 1a) shows a singlet at τ 7.96 due to the acetoxyl, multiplets at about τ 7.8 assignable to the bridge methylene H_{8x} and H_{8n}, two multiplets at τ 7.11 and 6.66 due to the bridgehead H_1 and H_5, two quartets at τ 4.10 and 3.53 arising from the olefinic H_6 and H_7, a doublet at τ 4.38 corresponding to H_2, and complex multiplets at lower fields due to benzene ring protons. In this spectrum, the signal positions of H_{8x} and H_{8n} are so close that their assignments are difficult and the signals of H_1 and H_5 appear as second-order patterns. Double irradiation at the center of resonance frequencies of H_{8x} and H_{8n} (Figure 1b) made the two quartets at τ 3.53 (J = 5.8 and 3.1 Hz) and 4.10 (J = 5.8 and 2.7 Hz) and the doublet at τ 4.38 (J = 2.0 Hz) relatively sharper, showing the presence of weak long-range couplings, and changed the multiplet at τ 7.11 into a quartet (J = 2.7 and 2.0 Hz), which was assignable to H_1, and the multiplet at τ 6.66 into a doublet (J = 3.1 Hz), which might be due to H_5. On double irradiation on H_5, one olefinic proton signal at τ 3.53 collapsed to a doublet (J = 5.8 Hz), which was therefore assigned to H_6. Decoupling of H_1 resulted in changes of the H_7 signal at τ 4.10 into a doublet (J = 5.8 Hz) and of the doublet at τ 4.38 into a somewhat broad singlet, assignable to H_{2eq} on the basis of its $J_{1,2}$ value.[10–12] These experiments showed that no appreciable $J_{1,6}$, $J_{5,7}$, and benzylic couplings[38,42] are discernible. The spectrum in C_6D_6 (Figure 1c) shows the signals of H_{8x} and H_{8n} separately as a doublet of triplets (J = 10.0 and 4.7 Hz) and a doublet (J = 10.0 Hz), respectively, as expected from the effect of benzene.[35,36] These assignments were made according to the Karplus correlation[33] (see the dihedral angles in Table II). Double irradiation on H_{2eq} (τ 4.10) made each H_{8x} signal peak very sharp (Figure 1d). On triple irradiation on H_6 and H_7 (Figure 1e), each H_{8x} peak clearly appeared as a doublet (J = 0.8 Hz), and each

H_{8n} peak changed into a clear triplet (J = 0.5 Hz). This irradiation also collapsed the H_1 and H_5 signals into a doublet of quartets (J = 4.7, 2.0, and 0.5 Hz) and a quartet (J = 4.7 and 0.5 Hz), respectively. These nmdr and nmtr spectra proved the presence of a long-range $J_{2eq,8x}$ of 0.8 Hz.[38,39]

The spectrum of X-eqOAc in CCl_4 (Figure 2a) shows overlapping multiplets at about τ 6.8 due to H_1 and H_5. Double irradiation at τ 6.8 changed two quartets at τ 3.60 and 4.29 due to the two olefinic protons into two doublets (J = 5.8 Hz) which are coupled to each other, the doublet at τ 4.04 (J = 5.4 Hz) due to H_{2ax} into a singlet,[10–12] a doublet of triplets at τ 7.74 into a doublet (J = 10.3 Hz), and a doublet at τ 7.95 (J = 10.3 Hz) into a somewhat sharper signal. This irradiation (Figure 2b) also revealed the presence of a weak long-range coupling between H_2 and one olefinic proton which gave the quartet at τ 4.29. On each double irradiation on an olefinic proton at τ 3.60 and the other one at τ 4.29 (Figures 2c and 2d), a doublet (J = 5.0 Hz) and a quartet (J = 5.4 and 5.0 Hz) clearly arose from the overlapping multiplets at about τ 6.8, respectively. Triple irradiation on the two olefinic protons resulted in the multiplets changing to the doublet due to H_5 and the quartet due to H_1 simultaneously. This irradiation also made some change in the signals arising from H_{8x} and H_{8n}. Therefore, the quartets at τ 3.60 and 4.29 were assigned to H_6 and H_7, respectively. These observations provided evidence for the structure of X-eqOAc. Applying the Karplus correlation,[37] we reached the assignments such that the doublet of triplets (J = 10.3 and 5.0 Hz) at τ 7.74 and the doublet further weakly split into triplets (J = 10.3 and *ca.* 0.5 Hz) at τ 7.95 arise from H_{8x} and H_{8n}, respectively, from the dihedral angles listed in Table II. Similar nmdr and nmtr experiments on X-eqOAc in C_6D_6 were made to obtain the same conclusion. As shown in Figure 2e, the signals of H_1 at τ 6.78 and H_5 at τ 7.03 are well separated and supported the above assignments. $J_{1,6}$ and $J_{5,7}$ are too small to be determined from these examinations. In addition, the long-range $J_{2eq,7}$, $J_{6,8n}$, and $J_{7,8n}$ in X-axOAc and X-eqOAc were found to be weak up to the extent of 0.3 Hz.

The spectrum of XII-axOAc in CCl_4 (Figure 3a) exhibits well-unresolved signals because the differences between the chemical shifts of H_1 and H_5 and of H_{8x} and H_{8n} are very small. The nmdr spectrum irradiated simultaneously on H_{8x} and H_{8n} (Figure 3b) showed a distinct octet at τ 3.60 (J = 9.6, 6.6, and 1.0 Hz) due to one olefinic proton. On double irradiation at the resonance frequency of the center of the two overlapping multiplets due to H_1 and H_5 (Figure 3c), the signal at τ 3.60 collapsed to a doublet of triplets (J = 9.6 and 1.0 Hz), a doublet of quartets at τ 4.80 (J = 9.6, 3.6, and 1.8 Hz) to a quartet (J = 9.6 and 3.6 Hz) which was therefore assignable to the other olefinic proton signal, a quartet of doublets at τ 4.99 (J = 3.6, 2.0, and 1.0 Hz) to a quartet (J = 3.6 and 1.0 Hz), and the signals due to H_{8x} and H_{8n} to a broad singlet, which implies the difference between their chemical shifts are small. From these results, we can assign the signals at τ 3.60, 4.80, and 4.99 to H_4, H_3, and H_{2eq}, respectively, and, accordingly, XII-axOAc belongs to the benzo[6,7]bicyclo[3.2.1]octa-3,6-diene, and conclude from $J_{1,2}$ of 2.0 Hz that the acetoxyl has an ax configuration.[11–12,39] Long-range J's were determined by nmdr and nmtr experiments in C_6D_6, in which the signals of H_{8x} and H_{8n} as well as those of H_1 and H_5 were well separated, as shown in Figure 3d. A doublet of triplets at τ 7.75 (J = 10.1 and 0.9 Hz) and a doublet of triplets of doublets at τ 7.94 (J = 10.1, *ca.* 4.5, and 1.0 Hz) were respectively assigned to H_{8x} and H_{8n} from their coupling constants to the bridgehead protons because the models showed that the acute dihedral angle between $H_1(H_5)$ and H_{8x} is larger than that between $H_1(H_5)$ and H_{8n} (Table II). The nmdr spectrum irradiated at the resonance frequency of the center of the H_{2eq} and H_3 signals (Figure 3e) showed a doublet (J = 4.6 Hz) at τ 6.69, a doublet at τ 3.60 (J = 6.6 Hz), an unchanged quartet of multiplets at τ 6.97 (J = 6.6 and 4.2 Hz), and the H_{8x} and H_{8n} signals. Decoupling of H_4 (Figure 3f) resulted in the signal at τ 6.97 changing into a doublet (J = 4.2 Hz) which can be assigned to H_5, and each peak of the H_{8n} signal changing into single sharp one. Thus, the long-range $J_{4,8n}$ of 1.0 Hz was confirmed.[39] Triple irradiation on H_{2eq}, H_3, and H_4 that changed the H_1 (τ 6.69) and H_5 (τ 6.97) signals into two doublets made it possible to determine $J_{1,8x}$ (4.6 Hz) and $J_{5,8x}$ (4.2 Hz) (Figure 3g). While double irradiation on H_5 did not cause any changes in the signals of H_{2eq} and H_3, a coupling (J = 1.8 Hz) in the signal of H_3 disappeared in the spectrum irradiated on H_1 (Figure 3h). These experiments provided evidence for the long-range $J_{1,3}$ (1.8 Hz). The second-order patterns of the signals of H_1 and H_4 are due to the close positions of the signals of H_{2eq} and H_3.

The nmr spectra of XII-eqOAc in CCl₄ and C₆D₆ are essentially the same except for the signal positions (Figures 4a and 4f). Decoupling experiments similar to the above revealed signal assignments and all J's (Figures 4b–e). These results are consistent with the structure of XII-eqOAc. Long-range J's in these compounds are listed in Table II.

Procedure for the Nmr Spectral Assignments of Benzo[3,4]tricyclo-[3.2.1.0²,⁷]octene Deriatives XI. The spectrum of XI-*exo*-OAc in CCl₄ (Figure 5a) shows complicated signals due to two protons at about τ 7.8 and a broad doublet due to two protons at about τ 8.28, so that the signal assignment was difficult. Moreover, the nmdr spectrum irradiated at τ 7.00 (a broad doublet signal) also gave no insight, as shown in Figure 5b. However, the appearance of only one signal at τ 7.00 assignable to the bridgehead proton can exclude the XV structure. Further, a singlet at τ 5.55 indicates a C₆ *exo*-acetoxyl²¹ in the benzo[3,4]tricyclo[3.2.1.0²,⁷]oct-3-ene system. The spectrum in C₆D₆ (Figure 5c) shows all proton signals separated. Double irradiation on a thin triplet at τ 5.35 assignable to H₆ₙ (Figure 5d) made each peak of a doublet at τ 7.02 due to the bridgehead H₅ and a multiplet around τ 8.5 fairly sharp, and caused a quartet of triplets at τ 8.38 (J = 7.0, 5.0, and 1.0 Hz) to collapse into a quartet of doublets (J = 7.0, 5.0, and 1.0 Hz). On double irradiation at τ 5.55 (H₅) (Figure 5e), a doublet of quartets at τ 7.85 (J = 11.6, 4.9, and 2.8 Hz), the quartet of triplets at τ 8.38, the multiplet at about τ 8.5, a doublet at τ 9.06 having some broadening (J = 11.6 Hz), and the thin triplet at τ 5.35 due to H₆ₙ were changed into a doublet of doublets (J = 11.6 and 2.8 Hz), a quartet of doublets (J = 7.0, 5.0, and 1.0 Hz), a sharper signal, a doublet of doublets (J = 11.6 and 0.6 Hz), and a thin doublet (J = 1.0 Hz), respectively. Triple irradiation on H₅ and H₆ₙ (Figure 5f) gave important changes in the two signals at τ 8.38 and 8.5; the former collapsed to a distinct quartet (J = 7.0 and 5.0 Hz), the lowest field peak of which is overlapped with the acetoxyl signal, whereas the latter multiplet collapsed to a doublet of quartets further split into thin doublets (J = 7.0, 5.0, 2.8, and 0.6 Hz). These decoupling experiments confirmed the assignments given in Figure 5 and determined J's in Table II. Dreiding models suggest that several long-range J's should be found in this ring system, besides $J_{1,5}$ and $J_{5,7}$ (1.0 Hz) already obtained, according

to the "W-letter rule."³⁸ The absence of $J_{6n,8n}$ was indicated by no change in the signal shape of H₆ₙ suffered from double irradiation on H₈ₙ. Double and triple irradiation on H₇ and H₁ resulted in changes of the signals of H₆ₙ, H₅, H₈ₓ, and H₈ₙ (Figures 5g–i), and showed the presence of $J_{1,6n}$ (0.4 Hz) and the absence of $J_{7,8n}$. Although we failed to determine the magnitudes of $J_{2,8x}$ and $J_{6n,8x}$, they may be up to the extent of 0.2 Hz.

The spectra of XI-*endo*-OAc in CCl₄ and C₆D₆ (Figures 6a and 6f) show features similar to that of XI-*exo*-OAc in C₆D₆. However, in XI-*endo*-OAc the signals of H₆ₓ and H₅ appear as a quartet having some broadening (J = 5.0 and 3.0 Hz) and as a triplet further split into multiplets (J = 5.0 Hz). Decoupling experiments in CCl₄ (Figures 5b–e) confirmed assignments of the signals and determined the J's in Table II. In this case, the signals of H₁ and H₇ overlapped. However, triple irradiation on H₅ and H₆ₓ revealed the H₇ signal. The values of $J_{5,6x}$ (5.0 Hz) and $J_{6x,7}$ (5.0 Hz) indicate an *endo* configuration²¹ for the acetoxyl (see the dihedral angles in Table II). Similar nmdr and nmtr experiments in C₆D₆ (Figures 5g–j) also confirmed the assignments and J's. Here, the signals of H₇ and H₈ₓ overlapped. Double irradiation on H₂ and on H₇ and H₈ₓ, respectively, indicated the presence of $J_{2,6x}$ (0.4 Hz) and $J_{6x,8n}$ ($\leq$ 0.2 Hz). However, we could not determine the magnitudes of $J_{1,5}$ and $J_{7,8n}$.

Nmr of Benzo[3,4]bicyclo[3.2.1]octene Derivatives in CCl₄. The spectrum of VIII-axOH showed four aromatic H at τ 2.6–3.0 (m), one C*H*OH at 5.73 (d), two bridgehead H at 6.94 (m) and 7.47 (m), eight H at 7.9–9.1, and $J_{1,2}$ = 2.8 Hz. The spectrum of VIII-eqOH showed four aromatic H at τ 2.7–3.4 (m), one C*H*OH at 5.24 (d), two bridgehead H at 7.12 (m) and 7.55 (m), eight H at 8.0–8.8, and $J_{1,2}$ = 4.6 Hz. The C*H*OAc in VIII-axOAc appeared at τ 4.46 ($J_{1,2}$ = 2.5 Hz), and that in VIII-eqOAc appeared at 3.93 ($J_{1,2}$ = 4.6 Hz).

Arylation by Aromatic Nitro Compounds at High Temperatures. II. Nitrobenzene Alone and with Benzene and Benzene-d_6

Ellis K. Fields[1a] and Seymour Meyerson[1b]

Contribution from the Research and Development Department, Amoco Chemicals Corporation, Whiting, Indiana, and the Research and Development Department, American Oil Company, Whiting, Indiana 46394. Received February 13, 1967

Abstract: The nitroarene bond in nitrobenzene and other aromatic nitro compounds breaks above 400°; this provides an easy means of generating phenyl and a great many other aromatic radicals. The decomposition of nitrobenzene alone at 600° seems to parallel rather closely its decomposition under electron impact in the mass spectrometer. With benzene and benzene-d_6, nitrobenzene yields mainly biphenyl and terphenyl and their deuterated analogs, respectively. Higher yields than calculated on the basis of only one radical indicate the involvement of the NO₂ portion of the original nitrobenzene.

Although nitrobenzene has been known for over 130 years² and has been the subject of innumerable investigations as well as the source of many useful chemicals, its thermal decomposition products have never been adequately described. Smith³ studied the kinetics of its decomposition at 455–515° and 17–92 min in Pyrex, and concluded that the reaction was largely homogeneous, between first and second order,

with an activation energy of 51 kcal/mole. Maksimov⁴ determined the first-order rate constant for nitrobenzene decomposition at 395–445°, and confirmed Smith's value for the activation energy. Neither author proposed a mechanism or determined any nongaseous products.

The discovery that the nitroarene bond in nitrobenzene and other aromatic nitro compounds breaks above 400° made possible the easy generation of phenyl and

(1) (a) Amoco Chemicals Corp. (b) American Oil Co.
(2) E. A. Mitscherlich, *Ann. Physik*, **31**, 625 (1834).
(3) R. E. Smith, *Trans. Faraday Soc.*, **36**, 985 (1940).

(4) Y. Y. Maksimov, *Teoriya Vzryvchatykh Veshchestv, Sb. Statei*, 338 (1963); *Chem. Abstr.*, **59**, 15137a (1963).