such that 1-naphthol, 2-naphthol, or 6-bromo-2-naphthol was readily nitrosated, **4** was unreactive, just as 1-chloro-2-naphthol or 1-bromo-2-naphthol. Also, with 1 equiv of Br_2 in HOAc containing NaOAc, followed by quenching with ice and extraction with $HCCl_3$, **4** gave a solution that exhibited strong absorption at 5.89 μ and that liberated iodine from aqueous KI. This behavior was the same as that of 1-chloro-2-naphthol or 1-bromo-2-naphthol, and quite different from that of 2-naphthol. Oxidation of **4** with alkaline $KMnO_4$ led to 4-nitrophthalic acid, identified by melting point and mixture melting point.

Intramolecularity of the Rearrangement.—1-Chloro-2-naphthol (320 mg) in 3 ml of $HCCl_3$ was added to a solution of 120 mg of urea, 0.2 ml of H_2SO_4, and 0.11 ml of 70% HNO_3 in 4 ml of Ac_2O and 2 ml of AcOH. The mixture was allowed to stand at 60° for 3 hr and was then treated as above. Tlc of the hydrolyzate showed only 1-chloro-2-naphthol.

Reaction of 1-Bromo-1-nitro-2-keto-1,2-dihydronaphthalene (2, X = Br).—A fresh $HCCl_3$ solution of this material, prepared by nitration of 1.00 g of 1-bromo-2-naphthol, was filtered through Na_2SO_4 into a cooled, stirred solution of 0.6 g of urea, 1 ml of concentrated H_2SO_4, 10 ml of redistilled Ac_2O, and 5 ml of AcOH. Work-up as for the chloro analog gave 480 mg of crude acetate, which was hydrolyzed to 320 mg of brown solid. Recrystallization of this material from $HCCl_3$ gave orange crystals of 1-nitro-2-naphthol, identified by melting point and mixture melting point. Tlc of the crude material indicated that 1-nitro-2-naphthol was the principal product. No 1-bromo-2-naphthol could be detected, but tlc indicated the presence of a small amount of another substance, presumably 6-bromo-1-nitro-2-naphthol, which was not investigated. Acidification of the NaOH extract led to 130 mg of brown solid containing chiefly 2-hydroxy-1,4-naphthoquinone.

Registry No.—2, X = Br, 26885-81-4; 2, X = Cl, 26885-82-5; **4**, 26885-83-6.

Acknowledgments.—We are indebted to Dr. F. Thomas Bond for helpful suggestions and to Mr. Jerome F. Keeton for some preliminary experiments.

Substituent Effects on Solvolyses of 1,4-Ethano-1,2,3,4-tetrahydronaphthalen-2(*exo* and *endo*)-yl (Benzobicyclo[2.2.2]octen-2(*exo* and *endo*)-yl) Derivatives[1,2]

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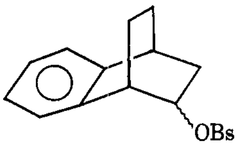
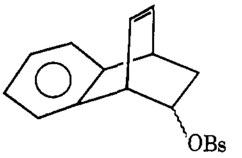
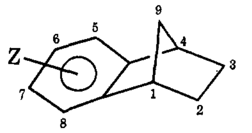
Series of aromatic-substituted 1,4-ethano-1,2,3,4-tetrahydronaphthalen-2(*exo*)-yl *p*-bromobenzenesulfonates (Z-**A**-OBs) or chlorides and the corresponding endo epimers (Z-**B**-OBs) were prepared and the solvolysis reactions studied. In the exo series, the relative rates of acetolysis of 6-CH_3O, H, 7-CH_3O, 7-NO_2, 6-NO_2, and 6,7-$(NO_2)_2$ derivatives at 77.6° were 224, 1, 0.58, 3.4×10^{-3}, 2.4×10^{-3}, and 2.1×10^{-4}, respectively. The solvolyses of 6-CH_3O, H, and 7-CH_3O lead to products entirely controlled by the neighboring aryl group, **A** alcohols (or esters) of retained configuration, and 1,5-methanobenzocyclohepten-2(ax)-ols (or esters) (Z-**C**-X) by rearrangement. In contrast, the acetolysis of deactivated 7-NO_2-**A**-OBs gave, besides **A** and **C** derivatives, the inverted 7-NO_2-**B**-OAc, 7-nitro-1,4-methanobenzocyclohepten-5(ax and eq)-yl acetates (7-NO_2-**D**-OAc), and minor hydrocarbons. Also, the **A**-OAc:**C**-OAc product ratio for the 7-NO_2 compound was different from the constant ratio obtained from the 6-CH_3O, H, and 7-CH_3O compounds. From the 6,7-$(NO_2)_2$ brosylate, **B** and **D** derivatives and hydrocarbons were obtained, but not **A** and **C** derivatives. The results from the 7-NO_2 compound are interpreted in terms of concurrence of the aryl-assisted path (k_Δ) and the solvent-assisted path (k_s); those from the 6,7-$(NO_2)_2$ compound suggest no participation and the products are explained in terms of a k_s process and its leakage. The rates of the 6-CH_3O, H, 7-CH_3O, 7-NO_2, and 6-NO_2 brosylates are well correlated with σ^+ constants, yielding a ρ of -3.25, but that of the 6,7-$(NO_2)_2$ brosylate is not. The relative rates in acetolysis of the endo brosylates were 0.34 for H, 2.7×10^{-2} for 7-NO_2, 2.4×10^{-2} for 6-NO_2, and 2.0×10^{-3} for 6,7-$(NO_2)_2$. No notable substituent effect on the distribution of products was observed. The predominant products in these cases were **D** acetates. The ρ–σ treatment of the endo rates yields a straight line with a ρ of -1.50. The apparent exo:endo rate ratios decrease from 2.9 for the H compounds to 0.13 for the 7-NO_2 compounds, but those for the 7-NO_2, 6-NO_2, and 6,7-$(NO_2)_2$ compounds are essentially constant at ~0.1.

In a previous paper solvolyses of the parent 1,4-ethano-1,2,3,4-tetrahydronaphthalen-2(*exo* and *endo*)-yl brosylates and of 1,4-ethano-1,4-dihydronaphthalen-9-(*exo* and *endo*)-yl (benzobicyclo[2.2.2]octadien-2(*exo* and *endo*)-yl) brosylates were reported.[3] Since our initial work on the benzonorbornen-9-yl system,[4] interest in substituent effects on the solvolysis of this ring system has remained at a high level.[5-8] The study of cationic intermediates of bicyclo[2.2.2]octyl







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[1] The terms 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. Axial and equatorial indicate the configuration of a substituent on the cyclohexane moiety and are abridged as ax and eq, respectively.

[2] The numbering used in this paper is shown in the charts.

(3) H. Tanida, K. Tori, and K. Kitahonoki, *J. Amer. Chem. Soc.*, **89**, 3212 (1967).

(4) H. Tanida, *ibid.*, **85**, 1703 (1963); H. Tanida, Y. Hata, S. Ikegami, and H. Ishitobi, *ibid.*, **89**, 2928 (1967), and a series of our papers cited therein.

(5) (a) H. C. Brown and G. L. Tritle, *ibid.*, **88**, 1320 (1966); (b) **90**, 2689 (1968); (c) H. C. Brown and K.-T. Liu, *ibid.*, **91**, 5909 (1969); (d) H. C. Brown, S. Ikegami, and K.-T. Liu, *ibid.*, **91**, 5911 (1969).

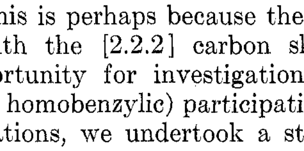
(6) (a) D. V. Braddon, G. A. Wiley, J. Dirlam, and S. Winstein, *ibid.*, **90**, 1901 (1968); (b) J. P. Dirlam and S. Winstein, *ibid.*, **91**, 5905 (1969); (c) *ibid.*, **91**, 5907 (1969).

(7) (a) H. Tanida, H. Ishitobi, T. Irie, and T. Tsushima, *ibid.*, **91**, 4512 (1969); (b) H. Tanida, T. Irie, and T. Tsushima, *ibid.*, **92**, 3404 (1970), and a series of our papers cited therein.

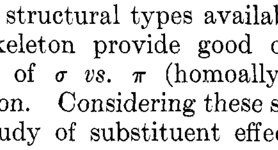
(8) A systematic study on the solvolysis of benzonorbornenyl derivatives was recently reported by J. W. Witt and P. J. Chenier, *J. Org. Chem.*, **35**, 1562, 1571 (1970).

and its unsaturated derivatives is also very active.[9-15] This is perhaps because the structural types available with the [2.2.2] carbon skeleton provide good opportunity for investigation of σ *vs.* π (homoallylic or homobenzylic) participation. Considering these situations, we undertook a study of substituent effects on the solvolysis of 1,4-ethano-1,2,3,4-tetrahydronaphthalen-2(*exo* and *endo*)-yl systems, which was based principally on the same ideas as applied to the benzonorbornenyl system.[7] The results are discussed in comparison with those from the benzonorbornenyl system.

To economically describe the compounds used, the following symbols are used: for 1,4-ethano-1,2,3,4-tetrahydronaphthalen-2(*exo*)-yl derivatives and their endo epimers, **A** and **B**; for 1,5-methanobenzocyclohepten-2(ax)-yl (benzo[6,7]bicyclo[3.2.1]octen-2(ax)-yl) derivatives, **C**; 1,4-methanobenzocyclohepten-5(ax and eq)-yl [benzo[3,4]bicyclo[3.2.1]octen-2(ax and eq)-yl] derivatives, **D** (ax and eq); for 1,4-ethano-1,4-dihydronaphthalene (benzobicyclo[2.2.2]octadiene) derivatives, **E**; and for 1,4-ethano-2-oxo-1,2,3,4-tetrahydronaphthalene (benzobicyclo[2.2.2]octen-2-one) derivatives, **F**.



Z-A-X



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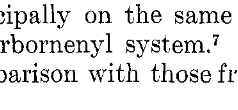
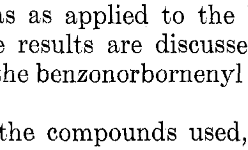
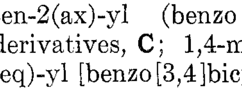


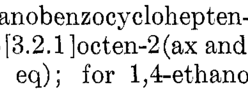
Z-C-X



Z-D(ax or eq)-X



Z-E



Z-F

Z = CH_3O, H, NO_2, $(NO_2)_2$; X = OH, OAc, OBs, Cl

Results

Preparations.—A facile synthetic method for the parent aromatic-unsubstituted **E** was recently reported,[16a] and the exo and endo alcohols **A**-OH and **B**-OH are already known.[16b] In this study these alcohols were prepared by the addition of diborane to **E** followed by oxidation with alkaline hydrogen peroxide, which gave a mixture showing an **A**:**B** ratio of 3:7 (separable by elution chromatography). Intramolecular hydrogen bonding between the hydroxyl group and the benzene ring is detected in **B**-OH, but not in **A**-OH. Nmr signals of the proton α to the hydroxy group (or its ester, or the chloro group) in the **A** system appear as a complicated multiplet, while those in **B** appear simply as a doublet of triplets. Nmr data of these protons and the bridgehead protons characteristic of the ring systems **A**–**D** are summarized in Table IV in the Experimental Section. On the basis of one or both of the ir and nmr spectral features, the orientation (exo or endo) of substituents at C_2 was determined in all [2.2.2] derivatives prepared in the present study. Electrophilic aromatic substitution reactions of the [2.2.2] system show an unusually strong β orientation.[17] Thus, nitration of a mixture of the acetates, **A**-OAc and **B**-OAc, with fuming nitric acid in acetic anhydride yields almost exclusively the 6- or 7-mononitro acetates (in total, four kinds of isomers), which were hydrolyzed into alcohols and oxidized with chromic anhydride–pyridine complex to a mixture of the nitro ketones, 6-NO_2**F** and 7-NO_2**F**, and separated by preparative layer chromatography (eq 1). Similarly to previous cases,[7] the analysis of nmr patterns of aromatic protons in the nitro ketones (AMX type, in acetone-d_6 at 100 MHz) produces evidence for the homo-para and homo-meta assignments. Lithium borohydride reductions of these ketones followed by separation of exo and endo epimers gave pure samples of 6-NO_2-**A**-OH, 6-NO_2-**B**-OH, 7-NO_2-**A**-OH, and 7-NO_2-**B**-OH.

Further nitration of the mononitro mixture, NO_2-**A**-OAc plus NO_2-**B**-OAc, with fuming nitric acid and concentrated sulfuric acid yielded predominantly a mixture of the 6,7-dinitro derivatives, $(NO_2)_2$-**A**-OAc and $(NO_2)_2$-**B**-OAc (eq 2). After hydrolysis, $(NO_2)_2$-**A**-OH and $(NO_2)_2$-**B**-OH were isolated by elution chromatography. Esterification with *p*-bromobenzenesulfonyl chloride in pyridine gave brosylates for solvolytic studies from the endo and exo epimers of the parent, the homo-para nitro, the homo-meta nitro, and the dinitro alcohols.

Oxidation of dicyclohexadiene (**1**)[16a,18] at the secondary allylic carbon by allowing it to stand with chromic anhydride in pyridine afforded the enone **2**, but not the isomer **3**, accompanying a double-bond migration. The structure of **2** was assigned by nmr. Treatment of **2** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in anhydrous dioxane containing 1% hydrochloric acid yielded the phenol HO-**E** in a crude state, the product to be expected from the dienone–phenol rearrangement of the cross dienone **4**. This phenol was, without purification, methylated to give 6-methoxy-1,4-ethano-1,4-dihydronaphthalene (CH_3O-**E**, homogeneous on vpc) in 20% yield from **2** (eq 3), the structure of which was confirmed by an independent synthesis which is shown in eq 3. The Friedel–Crafts acylation of 1,4-ethano-1,2,3,4-tetrahydronaphthalene afforded the β-acyl derivative **5**.[17] Oxidation of **5** with *m*-chloroperbenzoic acid to the

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[9] H. M. Walborsky, J. Webb, and C. C. Pitt, *J. Org. Chem.*, **28**, 3214 (1963), and other papers by this group.

[10] H. L. Goering and G. N. Fickes, *J. Amer. Chem. Soc.*, **90**, 2848, 2856, 2862 (1968), and other papers in that series.

[11] (a) N. A. LeBel and J. E. Huber, *ibid.*, **85**, 3193 (1963); (b) N. A. LeBel and R. J. Maxwell, *ibid.*, **91**, 2307 (1969).

[12] J. A. Berson, J. J. Gajewski, and D. S. Donald, *ibid.*, **91**, 5550 (1969), and references cited therein.

[13] H. Kwart and J. L. Irvine, *ibid.*, **91**, 5541 (1969).

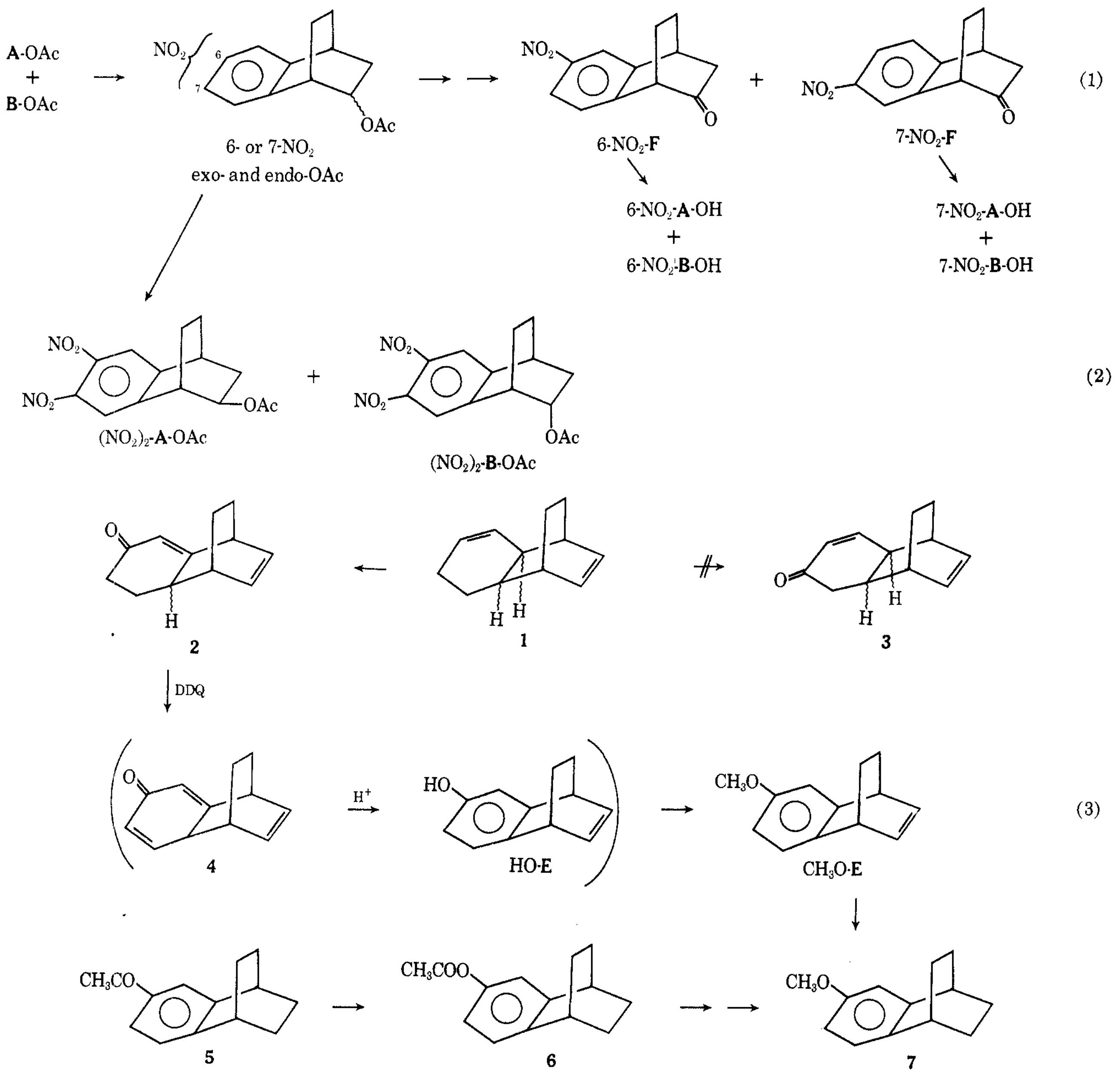
[14] S. J. Cristol, F. P. Parungo, D. E. Plorde, and K. Schwarzenbach, *ibid.*, **87**, 2879 (1965).

[15] E. Ciorănescu, A. Mihai, G. Mihai, M. Elian, and C. D. Nenitzescu, *Rev. Roum. Chim.*, **10**, 149 (1965).

[16] (a) K. Kitahonoki and Y. Takano, *Tetrahedron*, **25**, 2417 (1969); (b) *Tetrahedron Lett.*, 1597 (1963).

[17] H. Tanida and R. Muneyuki, *J. Amer. Chem. Soc.*, **87**, 4794 (1965).

[18] D. Valentine, N. J. Turro, Jr., and G. S. Hammond, *ibid.*, **86**, 5202 (1964).



β-acetoxy derivative **6**, followed by hydrolysis and methylation, yielded the methoxy compound **7**, identical with the hydrogenation product of CH_3O-**E**. Hydroboration of CH_3O-**E** gave a mixture of the four isomeric alcohols, 6-CH_3O-**A**-OH, 6-CH_3O-**B**-OH, 7-CH_3O-**A**-OH, and 7-CH_3O-**B**-OH, in which the ratio of the pair of **A** to the pair of **B** was 3:7 by vpc.[19] Isolation of the desired 6-CH_3O-**A** derivative is, in principle, based on the following findings. (a) The **A** and **B** alcohols are easily separated by elution chromatography on alumina. (b) The reaction of 6-CH_3O-**A**-OH with thionyl chloride in ether gives very predominantly 6-CH_3O-**A**-Cl with retention, whereas those of 7-CH_3O-**A**-OH as well as **A**-OH produce the **C** chlorides with rearrangement and the **A** chlorides with retention (for **A**-OH, the **C**:**A** ratio was 6:4). No formation of inverted chlorides was observed in any these chlorinations. (c) The homo-para 6-CH_3O-**A**-Cl is much more reactive in solvolysis than the chlorides derived from 7-CH_3O-**A**-OH. Thus, the exo alcohol fraction, 6-CH_3O-**A**-OH plus 7-CH_3O-**A**-OH, was separated, converted into a mixture of chlorides, and then subjected to partial hydrolysis to transform only the reactive homo-para chloride into a mixture of the alcohols, 6-CH_3O-**A**-OH and a rearranged alcohol (7-CH_3O-**C**-OH), in the ratio 79:21. This mixture was isolated from the less reactive chlorides and recrystallized to obtain the main 6-CH_3O-**A**-OH as pure crystals. Action of thionyl chloride upon these crystals yielded predominantly one chloride, 6-CH_3O-**A**-Cl. In contrast, the same reaction with **A**-OH gave two chlorides in the ratio 59:41, which were separated by preparative vpc. Conceivable ring structures for these chlorides are **A** of retention and **C** of rearrangement. Nmr spectra of the chloride from 6-CH_3O-**A**-OH and the minor chloride from **A**-OH are consistent with the **A** structure, but not the **C** structure.[20] As shown in Figure 1, the **A** acetates and chlorides exhibit bridge-

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[19] The methoxy substituent showed no important directing effect on this hydroboration, because this alcohol mixture was converted by treatment with chromic anhydride–pyridine into a mixture of 6-CH_3OF and 7-CH_3OF in the ratio 55:45.

[20] From the present results, an activated aryl group rearranges less than a deactivate done. Participation and rearrangement of the β-aryl group in the thionyl chloride reaction would be an interesting problem which requires further studies.

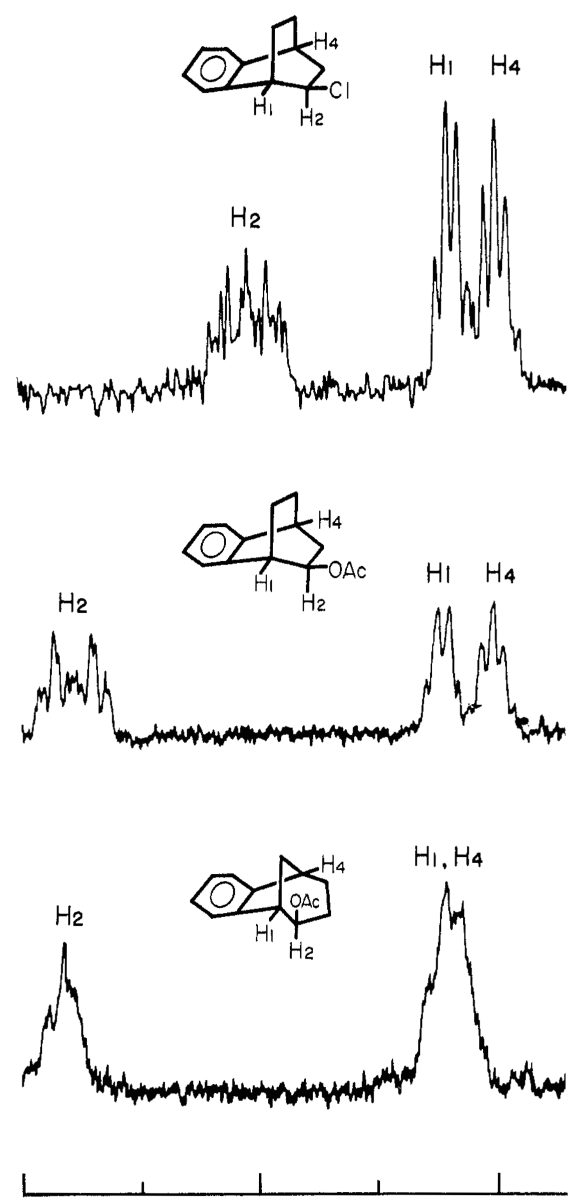


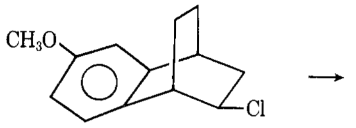
Figure 1.—Protons at bridgeheads and C_2 in the 60-MHz nmr spectra of the [2.2.2] and [3.2.1] derivatives.

head protons as a quartet (C_1 H) and a quintet (C_4 H), while bridgehead protons in the corresponding **C** derivatives appear as a broad signal which is a result of two overlapping multiplets; the structure for **C**-OAc used for comparison has been established.[3] In addition, half-height width, $W_{1/2}$, of the proton signals at C_2 bearing substituents is much larger for the **A** derivatives than for the **C** derivatives. The absence of formation of the **D** derivatives in solvolyses confirmed these **A** chlorides to be free from the **B** chlorides.

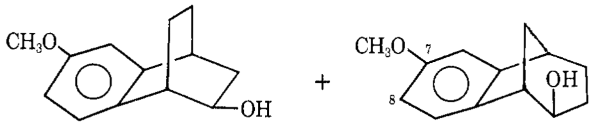
Purification of the chloride fraction, separated from the above-mentioned partial hydrolysis mixture, yielded 7-CH$_3$O-**A**-Cl.

Solvolysis Rates.—Rates for the brosylates were determined in glacial acetic acid containing equivalent sodium acetate by the standard procedure.[3,21] Good first-order kinetics were observed and the infinity titers corresponded to theory. Because of great reactivities of the homo-para exo system, the rate of solvolysis of 6-CH$_3$O-**A**-Cl in 70% aqueous acetone was determined by titration of the liberated hydrochloric acid and compared with those of 7-CH$_3$O-**A**-Cl and **A**-Cl. The rates are summarized in Table I. For comparison, the rate constants at 25 and 77.6° were calculated together with activation parameters. Relative reactivities are recorded at 77.6° because of convenience for comparison with reported data in the benzonorbornenyl system.

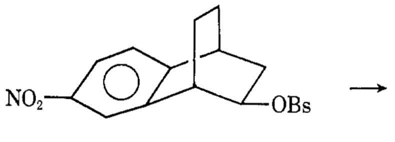
Solvolysis Products.—For product determination, the acetolyses and hydrolyses were carried out under the same conditions as used for the rate studies. Table II summarizes the substituent effects on the product composition in the exo and endo systems. The acetolysis of **A**-OBs has been reported to produce 83% the retained **A**-OAc and 17% the rearranged **C**-OAc. The hydrolysis of **A**-Cl was found to produce the same compounds in the ratio 75:23, not greatly different from the above. The vpc pattern of the hydrolysis products from 6-CH$_3$O-**A**-Cl was very similar and showed two important peaks in the ratio 77:20, together with a very minor peak of 3% ratio. The first product of 77 was proven to be the retained 6-CH$_3$O-**A**-OH. In these connections, the structure of the second important product was assigned as the rearranged 7-CH$_3$O-**C**-OH, although we had not sufficient amounts of the material to allow identification upon an isolated sample.



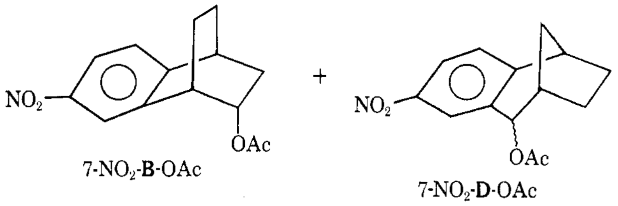
6-CH$_3$O-**A**-Cl



6-CH$_3$O-**A**-OH 7-CH$_3$O-**C**-OH



7-NO$_2$-**A**-OAc + 8-NO$_2$-**C**-OAc + hydrocarbons +



7-NO$_2$-**B**-OAc 7-NO$_2$-**D**-OAc

As the substituents become more electronegative, the products from the exo brosylates become more complex. However, since the products from 7-NO$_2$-**A**-OBs and (NO$_2$)$_2$-**A**-OBs [also, from 7-NO$_2$-**B**-OBs and (NO$_2$)$_2$-**B**-OBs] crystallized well, their separation into pure states was not difficult by preparative layer chromatography. Formation of the acetates of retention was detected from 7-NO$_2$-**A**-OBs, but not from (NO$_2$)$_2$-**A**-OBs. Acetates of inversion were produced

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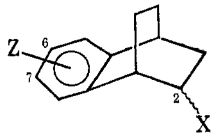
[21] S. Winstein, C. Hanson, and E. Grunwald, *J. Amer. Chem. Soc.*, **70**, 812 (1948); S. Winstein, E. Grunwald, and L. L. Ingraham, *ibid.*, **70**, 821 (1948).

TABLE I

RATE OF SOLVOLYSIS OF 6- AND 7-SUBSTITUTED 1,4-ETHANO-1,2,3,4-TETRAHYDRONAPHTHALEN-2-YL (A AND B) DERIVATIVES



Substituent[a]							
Z	X	Solvent[b]	Temp, °C	k_1, sec^{-1}	$\Delta H^{\ddagger}$, kcal	$\Delta S^{\ddagger}$, cal/deg	Rel rate, 77.6°
H	*exo*-OBs[c]	AcOH	25.0	2.37×10^{-5d}	23.7	−0.2	
			77.6	1.11×10^{-2d}	23.6	−0.5	1
H	*exo*-Cl	70% Me_2CO	89.98	1.76×10^{-5}			
			120.02	2.50×10^{-4}			
			25.0	9.09×10^{-9d}	24.5	−13.3	
			77.6	5.17×10^{-6d}	24.4	−13.6	1
6-CH_3O	*exo*-Cl	70% Me_2CO	25.02	2.25×10^{-6}			
			59.03	1.66×10^{-4}			
			64.89[e]	2.99×10^{-4}			
			25.0	2.25×10^{-6d}	24.1	−3.6	
			77.6	1.16×10^{-3d}	24.0	−3.9	224
7-CH_3O	*exo*-Cl	70% Me_2CO	89.98	1.05×10^{-5}			
			120.02	1.61×10^{-4}			
			25.0	4.36×10^{-9d}	25.2	−12.3	
			77.6	2.98×10^{-6d}	25.1	−12.6	0.58
7-NO_2	*exo*-OBs	AcOH	54.90	2.26×10^{-6}			
			77.88	3.88×10^{-5}			
			25.0	2.89×10^{-8d}	27.7	−0.01	
			77.6	3.76×10^{-5}	27.6	−0.34	3.4×10^{-3}
6-NO_2	*exo*-OBs	AcOH	54.90	1.79×10^{-6}			
			77.80	2.76×10^{-5}			
			25.0	2.67×10^{-8d}	26.7	−3.5	
			77.6	2.70×10^{-5d}	26.6	−3.8	2.4×10^{-3}
6,7-$(NO_2)_2$	*exo*-OBs	AcOH	79.98	3.07×10^{-6}			
			120.55	2.15×10^{-4}			
			121.30	2.18×10^{-4}			
			121.30	2.24×10^{-4}			
			140.12	1.11×10^{-3}			
			25.0	1.74×10^{-9d}	27.9	−5.0	
			77.6	2.37×10^{-6d}	27.8	−5.3	2.1×10^{-4}
H	*endo*-OBs[c]	AcOH	25.0	8.33×10^{-6d}	23.6	−2.7	
			77.6	3.79×10^{-3d}	23.5	−3.0	0.34
7-NO_2	*endo*-OBs	AcOH	54.90	2.39×10^{-5}			
			77.88	3.04×10^{-4}			
			25.0	4.85×10^{-7d}	24.7	−4.4	
			77.6	2.95×10^{-4d}	24.6	−4.8	2.7×10^{-2}
6-NO_2	*endo*-OBs	AcOH	54.90	2.05×10^{-5}			
			77.80	2.71×10^{-4}			
			25.0	3.88×10^{-7d}	25.2	−3.3	
			77.6	2.65×10^{-4d}	25.1	−3.7	2.4×10^{-2}
6,7-$(NO_2)_2$	*endo*-OBs	AcOH	79.98	2.64×10^{-5}			
			100.08	2.35×10^{-4}			
			120.01	1.12×10^{-3}			
			120.05	1.28×10^{-3}			
			120.45	1.35×10^{-3}			
			25.0	2.83×10^{-8d}	25.6	−7.1	
			77.6	2.16×10^{-5d}	25.5	−7.4	2.0×10^{-3} .

[a] The concentrations of brosylates and chlorides were 0.02 *M*. Only in the cases of the dinitro compounds, the concentration was 0.01 *M*. [b] The aqueous acetone is expressed as volume per cent at 24° and the acetic acid contained equivalent amounts of AcONa and 1% acetic anhydride. [c] Calculated by Arrhenius plots of the data in ref 3. [d] Calculated by Arrhenius plots. [e] Determined by conductivity measurements.

from both the brosylates. The acetates of rearrangement, 7-NO_2-**D**-(ax and eq)-OAc and $(NO_2)_2$-**D**-(ax and eq)-OAc, were proven to be identical with the major products from the corresponding epimers, the endo brosylates. Convincing evidence for the structures of these acetates as well as for 7-NO_2-**C**-OAc is obtained from the 60- and 100-MHz nmr spectra, because data for pertinent compounds, for example, the parent **C** and **D** acetates[3] and bicyclo[3.2.1]oct-2-enes,[22] are available (Table IV). Appreciable amounts of hydrocarbons, formed by elimination, were found from 7-NO_2-**A**-OBs and $(NO_2)_2$-**A**-OBs. Those from $(NO_2)_2$-**A**-OBs were composed of an unsaturated compound and a saturated compound. The structure of

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(22) C. W. Jefford, S. Mahajan, J. Waslyn, and B. Waegell, *J. Amer. Chem. Soc.*, **87**, 2183 (1965); C. W. Jefford and K. C. Ramsey, *Tetrahedron*, **24**, 2927 (1968); R. C. DeSelms and C. M. Combs, *J. Org. Chem.*, **28**, 2206 (1963); also, A. R. Katrisky and B. Wallis, *Chem. Ind.* (*London*), 2025 (1964).

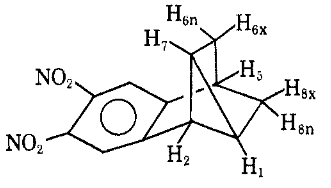
TABLE II

PRODUCTS[a] AND YIELDS[b] IN SOLVOLYSES[c] OF THE A AND B SYSTEMS

Substituent in material		Temp, °C	**A**-OAc	**B**-OAc	**C**-OAc[d]	**D**-OAc	E	Unknown
6-CH_3O	*exo*-Cl	25	77 ± 1		20 ± 1		0	3 ± 1[e]
H	*exo*-OBs[f]	50	83 ± 2	0	17 ± 2	0	0	
H	*exo*-Cl	120	75 ± 1	0	23 ± 1	0	0	2 ± 1[e]
7-CH_3O	*exo*-Cl	120	82 ± 1		15 ± 1		0	3 ± 1[e]
7-NO_2	*exo*-OBs	75	27 ± 2	15 ± 4	20 ± 2	ax 22 ± 4 eq 7 ± 4		9 ± 4[g]
6,7-$(NO_2)_2$	*exo*-OBs	100	0	49 ± 2	0	ax 27 ± 1 eq 0	6 ± 1	15 ± 3[g,h]
H	*endo*-OBs[f]	50	0	0	0	ax 98 ± 2 eq 2 ± 2	0	
7-NO_2	*endo*-OBs	75	0	0	0	ax 93 ± 2 eq 4 ± 3		
6,7-$(NO_2)_2$	*endo*-OBs	100	0	9 ± 3	0	ax 73 ± 2 eq 6 ± 1	4 ± 1	5 ± 3[g,h]

[a] The symbols **A**–**D** indicate the ring systems, as described in the introduction. [b] Per cents of theory. 0% means <1%. Vacancies mean the absence of any peak on vpc assignable to the compounds, though authentic samples are not available at hand. [c] Acetolysis of brosylates. Hydrolysis of chlorides in 70% aqueous acetone. [d] The ax configuration of OAc was proven in the H compound,[f] but presumed in the CH_3O and NO_2 compounds. [e] Vpc appears in the alcohol region. [f] Reference 3. [g] Vpc appears in the hydrocarbon region. [h] The major component is **12**.

the unsaturated one was assigned by nmr as $(NO_2)_2$-**E** (6% yield in Table II). Comparison of the 100-MHz nmr spectrum of the saturated one (Experimental Section) with that of benzo[3,4]tricyclo[3.2.1.$0^{2,7}$]octene[23] suggests the structure of the dinitro derivative of this octene (**12**). The composition of products from the nitro brosylates was determined by integrating repeatedly the area of the –CH–OAc proton and that of the vinyl protons on the 60-MHz nmr spectra of the reaction mixture, using the aromatic protons as internal reference. Yields compatible with the product composition thus obtained were recorded by the amounts of products isolated by thin layer chromatography.



12

Substituents do not significantly affect the product distribution in the acetolysis of endo brosylates. As in the reported case of the parent **B**-OBs,[3] predominant formations of 7-NO_2-**D**-(ax and eq)-OAc and $(NO_2)_2$-**D**-(ax and eq)-OAc were respectively observed in the acetolyses of 7-NO_2-**B**-OBs and $(NO_2)_2$-**B**-OBs (97 and 79% yields). Only in the reaction of $(NO_2)_2$-**B**-OBs were the acetate of retention in 9% yield and the hydrocarbons [4% of $(NO_2)_2$-**E** and 5% of **12**] observed. The previous experiments[24] indicate that all the products, mentioned here and their ratio are those of kinetically controlled solvolyses.

Discussion

The 6-methoxy rate-accelerating effect in the benzonorbornen-2(*exo*)-yl system was the largest yet observed for a neighboring *p*-anisyl group (a factor of 178).[5b,6a,7a] Participation effects in the present system are again strikingly large. The 6-methoxy substituent here accelerates the rate by the same order of magnitude (a factor of 224 in Table I). On the other hand, the homo-meta 7-methoxy substituent depresses the rate slightly (a factor of 0.58), just as in electrophilic aromatic substitution reactions. In these solvolyses, the aryl group controls the stereospecificity and composition of products, so that the **A** and **C** derivatives, in the roughly constant ratio of 8:2, were the exclusive products. The 7-nitro substituent decelerates the rate by a factor of 3.4 × 10^{-3} and some amounts of the inverted product and the **D** acetate were now found. Ordinarily, rate effects due to a neighboring aryl group in acyclic or cyclic β-arylethyl systems are extremely modest, in spite of its significant product control which leads predominantly to retained configuration and rearrangement.[25-28] The aryl group has thus been considered by Winstein as a "marginal" neighboring group. However, both in the present system and in the previous benzonorbornenyl system the ability of aryl groups to participate both in rate determination and product distribution was demonstrated to be very great. Why should this be so? The solvolysis process of β-arylalkyl systems has been widely discussed in terms of a pair of discrete, independent, competing mechanistic pathways: the aryl-assisted route (k_Δ) and the aryl-unassisted but solvent-assisted route (k_s). With the right substrate structure and solvent, k_s becomes equal to an idealized process (k_c) in which neither aryl nor solvent assist.[29] Since Winstein's proposal, the solvolysis of simple primary systems has been considered to proceed with strong assistance in both k_Δ and k_s routes and with the absence of crossover (no leakage)

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(23) R. C. Hahn and L. J. Rothman, *J. Amer. Chem. Soc.*, **91**, 2409 (1969).

(24) Reference 3, footnote 7.

(25) (a) H. C. Brown, K. J. Morgan, and F. J. Chloupek, *J. Amer. Chem. Soc.*, **87**, 2137 (1965); (b) H. C. Brown and C. J. Kim, *ibid.*, **90**, 2082 (1968); (c) C. J. Kim and H. C. Brown, *ibid.*, **91**, 4286, 4287, 4289 (1969).

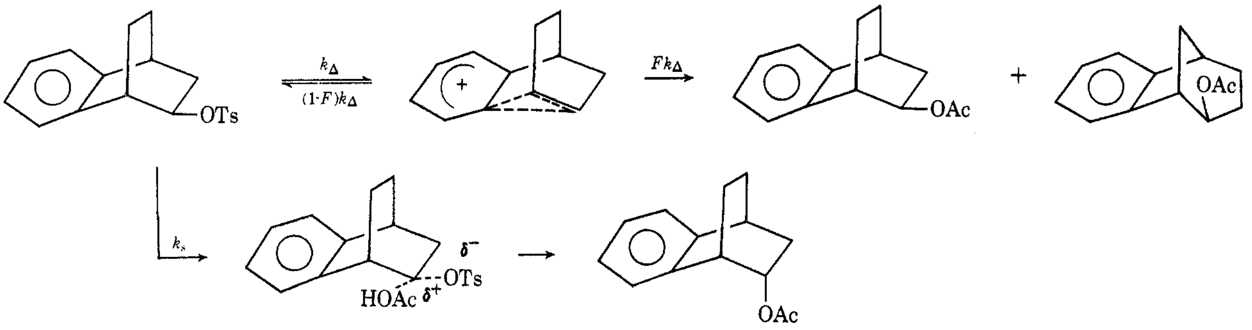
(26) C. J. Lancelot and P. v. R. Schleyer, *ibid.*, **91**, 4291 (1969), and subsequent three communications; J. M. Harris, F. L. Schadt, and P. v. R. Schleyer, *ibid.*, **91**, 7508 (1969).

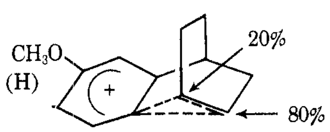
(27) J. E. Nordlander and W. G. Deadman, *ibid.*, **90**, 1590 (1968); J. E. Nordlander and W. J. Kelly, *ibid.*, **91**, 996 (1969).

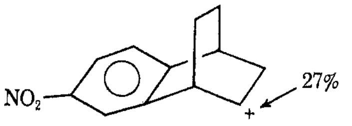
(28) J. I. Coke, F. E. McFarlane, M. C. Mourning, and M. G. Jones, *ibid.*, **91**, 1154 (1969); M. G. Jones and J. I. Coke, *ibid.*, **91**, 4284 (1969).

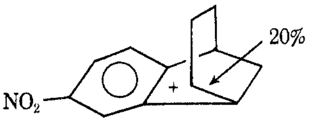
(29) S. Winstein, *Bull. Soc. Chim. Fr.*, 55C (1951); S. Winstein and L. L. Ingraham, *J. Amer. Chem. Soc.*, **77**, 1738 (1955); S. Winstein, E. Allred, R. Heck, and R. Glick, *Tetrahedron*, **3**, 1 (1958).

between k_Δ and k_s, so that product composition (or product stereochemistry) is well correlated with the proportions of k_Δ and k_s. The interpretation in terms of these discrete k_Δ and k_s processes has not been convincing for secondary systems, like the present one, until recently.[30] However, discrete k_Δ and k_s for a secondary system was postulated and experimentally rationalized recently by Schleyer[26] and Winstein.[31] We have employed the interpretation in terms of k_Δ and k_s for the results from benzonorbornen-2-yl brosylates.[7] It has been well recognized that nucleophilic displacement reactions of the S$_N$2 type are extremely difficult at a ring carbon of strained, bridged cyclic compounds. For the same reason, a transition state involving a strong solvent assistance is disfavored, and, as the k_Δ and k_s routes are competing with each other, such an unfavorable situation for k_s enhances k_Δ greatly. The large substituent effects on rate and the stereospecific formation of products are entirely the results of enhanced k_Δ.









Of significance is the **A**-OAc/**C**-OAc product ratio from 7-NO$_2$-**A**-OBs, ~1.3, which is different from the constant ratio, ~4, obtained from the 6-CH$_3$O, H, and 7-CH$_3$O compounds. On the other hand, in the acetolysis of the benzonorbornen-2(*exo*)-yl brosylates, the exo 2-acetates were produced through retention as well as through rearrangement and the ratio of retention to rearrangement was ~1 over the range of substituents from 6-CH$_3$O to 6,7-dinitro.[7a] The constant ratios suggest no leakage from k_Δ. The ratio of the 7-NO$_2$ compound, decreased from 4 to 1.3, may suggest leakage from k_Δ of the deactivated nitrobenzene ring. The observed formation of 7-NO$_2$-**D**-OAc could arise from this leakage. It would be of considerable interest to investigate whether or not the k_Δ process of the 7-NO$_2$ compound forms an intermediate of the same structure to those resulting from the k_Δ process of the 6-CH$_3$O, H, and 7-CH$_3$O compounds. A detailed study of optically active derivatives may be instructive for this interesting problem.[32] The inverted 7-NO$_2$-**B**-OAc in 15% yield can be considered as a direct result of k_s. However, generally weak solvent assistance in the molecule of this kind would not prevent leakage.[7b] Some products besides 7-NO$_2$-**B**-OAc could arise from a leakage of k_s.

A and **C** derivatives were not produced from the reaction of (NO$_2$)$_2$-**A**-OBs suggesting the absence of aryl participation. The formation of (NO$_2$)$_2$-**B**-OAc in 49% yield would be a direct result of k_s. Plotting logarithms of the observed relative rates of the 6-CH$_3$O, H, 7-CH$_3$O, 7-NO$_2$, and 6-NO$_2$ compounds against σ^+ yields a straight line with a ρ of -3.25 at 77.6° (correlation coefficient 0.999, Figure 2). However, the point of the (NO$_2$)$_2$ compound is far above the line defined by the first-named compounds. In the plotting, replacement of the rate for the 7-NO$_2$ compound into the Fk_Δ rate constant, 47% of k_t (a fraction of k_Δ leading to product in an event of internal return[26,28,31]), produces correlation of anchimerically assisted rates and σ^+ constants, with a ρ of -3.52 and a correlation coefficient of 0.995 (Figure 3). Because of the absence of product data, the 6-NO$_2$ point is omitted in this correlation. Extrapolation of the first line gives a σ^+ value of 1.01 for (NO$_2$)$_2$-**A**-OBs, which is considerably less than the value of 1.46 obtained by simple addition of each substituent constant, and that of the Fk_Δ line gives an estimated Fk_Δ of 3.91×10^{-8} sec^{-1} at 77.6° for (NO$_2$)$_2$-**A**-OBs, which amounts to only 1.7% of the observed rate. The smaller σ^+ than that obtained by simple addition is not abnormal, because two ortho nitro groups are not usually independent and sterically or electronically interact each other. No detection of (NO$_2$)$_2$-**A**-OAc and (NO$_2$)$_2$-**C**-OAc in products is compatible with the estimated Fk_Δ value.

Compared to those in the exo series, the substituent effects on rate in the endo series are small; $k_H/k_{7\text{-}NO_2}$ = 290 *vs.* 13. The composition of products from the endo brosylates is independent of substituents, except the minor formation of (NO$_2$)$_2$-**B**-OAc and (NO$_2$)$_2$-**E** from (NO$_2$)$_2$-**B**-OBs. The rates of all the endo brosylates are well correlated with σ, yielding a ρ of -1.50 (correlation coefficient 1000) (Figure 4), so that participation by the aryl group is unimportant here. No deviation

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[30] Indeed, a referee informed us of Winstein's statement, "with simple primary systems there is no crossing over; with secondary and tertiary systems it (the solvolysis) is more likely to have crossover between the different routes." S. Winstein, "Chemica Theorica," Conferenze VIII, Corso Estivo di Chemica, Academia Nationale dei Lincei, Rome, 1965, p 251.

[31] A. F. Diaz and S. Winstein, *J. Amer. Chem. Soc.*, **91**, 4300 (1969).

[32] The present results from the 6-CH$_3$O, H, and 7-CH$_3$O exo brosylates prefer an intermediate of the phenonium ion type[11,33] rather than a nonclassical cation which may involve participation of the C$_{1,6}$-methylene bond, but not that of the benzene π electrons, or rapidly equilibrating set of classical ions, which we considered at an early stage of this research where data from the H brosylate only had been obtained.[8]

[33] D. J. Cram, *J. Amer. Chem. Soc.*, **71**, 3863 (1949); **86**, 3767 (1964). D. J. Cram and T. A. Thomson, *ibid.*, **89**, 6766 (1967); **91**, 1778 (1969).

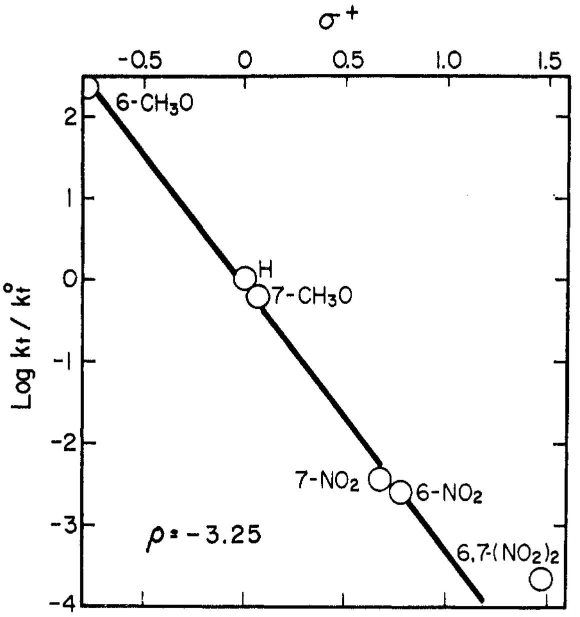

Figure 2.—The ρ–σ^+ treatment of the observed rates in solvolyses of 1,4-ethano-1,2,3,4-tetrahydronaphthalen-2(*exo*)-yl derivatives.

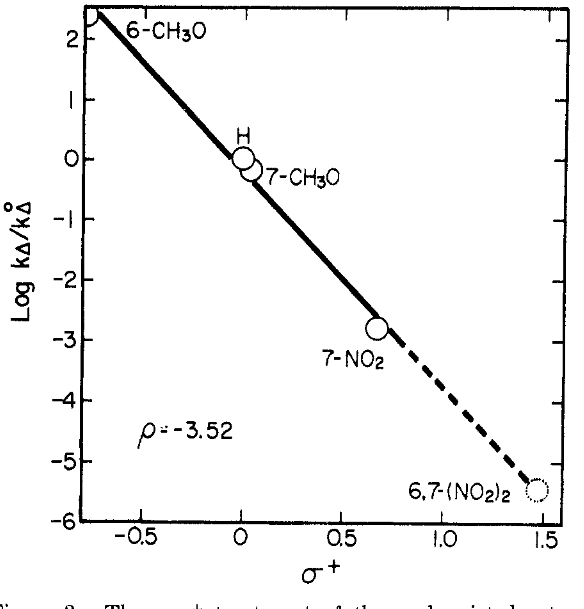

Figure 3.—The ρ–σ^+ treatment of the aryl-assisted rates in solvolyses of 1,4-ethano-1,2,3,4-tetrahydronaphthalen-2(*exo*)-yl derivatives.

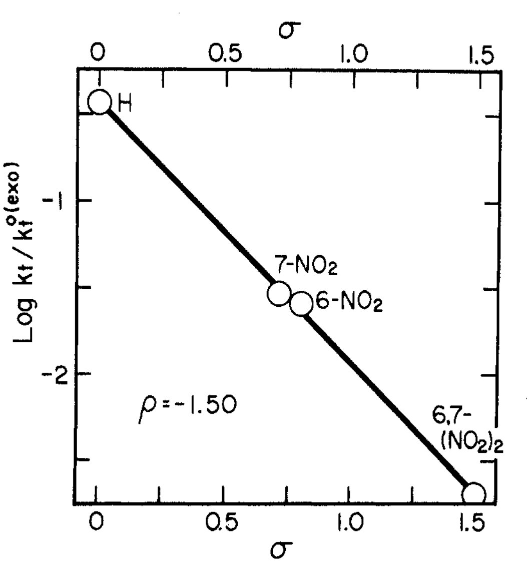

Figure 4.—The ρ–σ treatment of acetolysis rates of 1,4-ethano-1,2,3,4-tetrahydronaphthalen-2(*endo*)-yl brosylates relative to the aromatic-unsubstituted exo brosylate.

of the $(NO_2)_2$ point, in contrast to the exo series, can be understood in terms of the major effect of substituents here being uniformly inductive, not conjugative as in the exo series, so that any interaction between two ortho groups would be much less serious.

The point of interest we should mention finally is the exo:endo rate ratios. The ratio decreases from 2.9 for the H compounds to 0.13 for the 7-NO_2 compounds and then, reaches a plateau value, 0.10 for the 6-NO_2 and 0.11 for the $(NO_2)_2$ compound. Such a constant value was not observed for the benzonorbornenyl system and the ratios decreased steadily over the range of substituents, to a value of ~4 for the dinitro compound.[7b] As the benzene ring in both the exo [2.2.1] and [2.2.2] systems is more and more deactivated, k_s tends to become major in solvolysis. However, the appearance of k_s with deactivating substituents varies from the [2.2.1] to the [2.2.2] system. In the [2.2.1] system a notable degree of k_s needs substitution by the two nitro groups, while in the [2.2.2] system the mononitro substituent is enough to cause a substantial degree of k_s, and substitution by the two nitro groups lowers k_Δ to 1.7% of the total rate and leads to solvolysis by k_s entirely. Any reaction of the SN2 type is not a factor for the exo:endo rate ratio, so that the [2.2.2] system produces a plateau value. The reason why the [2.2.2] system undergoes k_s easier than the [2.2.1] system must be the same to that for the well-known fact that the endo side of [2.2.1] compounds strongly hinders any approaching nucleophile. If correction for k_s is made on the assumption that k_s produces only the **B** acetates from the exo brosylates, the ratios would be 0.11 for the 7-NO_2 compounds and 0.056 for the $(NO_2)_2$ compounds. If the correction is made assuming that k_s produces all the products other than the **A** and **C** acetates, the ratios would be 0.061 for the 7-NO_2 compounds and 0 (infinitely small) for the $(NO_2)_2$ compounds. Constant decrease is seen.

Experimental Section

Melting points were taken by capillary and are corrected. Boiling points are uncorrected. Infrared spectra were determined with a Nippon Bunko DS-402-G spectrometer, ultraviolet spectra with a Beckman DK-2A spectrometer, and nmr spectra with a Varian A-60A and/or HA-100. Vpc analyses were performed on a Hitachi Model K-53.

Properties and analyses of the new compounds prepared in the present study are summarized in Table III. Nmr data of the protons at C_2 and bridgeheads, which are useful for discrimination of the present ring systems, are summarized in Table IV.

Kinetic Measurements.—The acetolysis conditions and procedure were the same as previously reported.[8,21]

For hydrolysis, the chlorides were dissolved at a concentration of 0.02 *M* in 70% (v/v) aqueous acetone, which was prepared by mixing seven parts of acetone and 1 part of water at 24°. Aliquots (2-ml portions) were sealed into ampoules, which were then placed in a constant temperature bath. Ampoules were removed at recorded intervals and rapidly cooled, and the contents were run into 20 ml of cold (0°) dry acetone to stop the reaction. Hydrogen chloride generated was titrated with 0.0046 *N* sodium hydroxide using a Metrohm Herisau Potentiograph E 336A.

TABLE III

PROPERTIES AND ANALYSES

Ring system[a]	Substituent		Mp or bp[b] (mm), °C	Formula
	In aromatic	In aliphatic		
A	6-CH_3O	2-OH	128–129	$C_{13}H_{16}O_2$[g]
	6-CH_3O	2-Cl	[116–117 (3)][c]	$C_{13}H_{15}ClO$[g]
	7-CH_3O	2-Cl	[120–121 (2)][d]	$C_{13}H_{15}ClO$
	H	2-Cl	[97–98 (3)][e]	$C_{12}H_{13}Cl$
	6-NO_2	2-OH	114.5–116.0	$C_{12}H_{13}NO_3$[g]
	6-NO_2	2-OBs	153–154[f]	$C_{18}H_{16}BrNO_5S$[g]
	7-NO_2	2-OH	130–131.5	$C_{12}H_{13}NO_3$[g]
	7-NO_2	2-OBs	145–146[f]	$C_{18}H_{16}BrNO_5S$[g]
	7-NO_2	2-OAc	116–117	$C_{14}H_{15}NO_4$[g]
	6,7-$(NO_2)_2$	2-OH	139.5–140.5	$C_{12}H_{12}N_2O_5$[g]
	6,7-$(NO_2)_2$	2-OBs	174–175	$C_{18}H_{15}BrN_2O_7S$[g]
	6,7-$(NO_2)_2$	2-OAc	144.5–145.5	$C_{14}H_{14}N_2O_6$[g]
B	6-NO_2	2-OH	141.5–142.5	$C_{12}H_{13}NO_3$[g]
	6-NO_2	2-OBs	133–134[f]	$C_{18}H_{16}BrNO_5S$[g]
	7-NO_2	2-OH	111–112	$C_{12}H_{13}NO_3$[g]
	7-NO_2	2-OBs	140–141[f]	$C_{18}H_{16}BrNO_5S$[g]
	7-NO_2	2-OAc	99.5–101	$C_{14}H_{15}NO_4$[g]
	6,7-$(NO_2)_2$	2-OH	105–106	$C_{12}H_{12}N_2O_5$[g]
	6,7-$(NO_2)_2$	2-OBs	160–161	$C_{18}H_{15}BrN_2O_7S$[g]
	6,7-$(NO_2)_2$	2-OAc	123.5–124.5	$C_{14}H_{14}N_2O_6$[g]
C	8-NO_2	2-OAc	112–113.5	$C_{14}H_{15}NO_4$[g]
D	7-NO_2	5(ax)-OAc	102–103	$C_{14}H_{15}NO_4$[g]
	7,8-$(NO_2)_2$	5(ax)-OAc	154.5–155	$C_{14}H_{14}N_2O_6$[g]
F	6-NO_2	2-One	138.5–139.5	$C_{12}H_{11}NO_3$[g]
	7-NO_2	2-One	147–148	$C_{12}H_{11}NO_3$[g]
	6,7-$(NO_2)_2$	2-One	146.5–147	$C_{12}H_{10}N_2O_5$[g]

[a] The symbols **A–D** for ring systems are referred to in the introduction. [b] The boiling points are presented in brackets. [c] n^{25}D 1.5687. [d] n^{25}D 1.5668. [e] n^{25}D 1.5696. [f] Decomposition. [g] Satisfactory combustion analytical data (±0.4%) were provided for those compounds. Ed.

The runs were followed to about 80% completion and first-order plots were linear. As one exception, plots beyond 30% completion for *p*-CH_3O-**A**-Cl showed a little upward curvature (the reaction became slower); so here the rate constants were calculated by plotting until 30% reaction.

Addition of Diborane to 1,4-Ethano-1,4-dihydronaphthalene (E).—To a stirred solution of 46.8 g of **E** in 250 ml of tetrahydrofuran, there was introduced at about 5° gaseous diborane which was generated by adding 120 g of boron trifluoride etherate to a solution of 22.8 g of sodium borohydride in 250 ml of diglyme. After standing overnight at room temperature, the excess hydride was decomposed, and the organoborane formed was oxidized with 150 ml of 3 *N* sodium hydroxide and 50 ml of 30% hydrogen peroxide. After 2 hr at room temperature, the reaction mixture was concentrated by distilling the tetrahydrofuran under reduced pressure and extracted with ether. The extract was washed with dilute hydrochloric acid and water, dried, and evaporated. Excess **E** was recovered by distillation under reduced pressure, and the remainder was acetylated with acetic anhydride. Vacuum distillation gave 46 g of a mixture of **A**-OAc and **B**-OAc at the ratio 3:7.

6- and 7-Nitro-1,4-ethano-1,2,3,4-tetrahydronaphthalen-2-one (6-NO_2-F and 7-NO_2-F).—Procedures for mononitration and dinitration of the 3:7 mixture of **A**-OAc and **B**-OAc were essentially the same as performed for benzonorbornen-2-yl acetates.[7a] A mixture of the mononitrated acetates was hydrolyzed by refluxing it in a mixture of 10% hydrochloric acid and ethanol, and then converted into a mixture of ketones by treatment with chromic anhydride–pyridine. Treatment by preparative layer chromatography on Kieselgel GF_{254} nack Stahl (Merck) isolated samples of 6-NO_2-**F** and 7-NO_2-**F**, which were repeatedly recrystallized to constant melting points.

100-MHz nmr spectra in acetone-*d*$_6$: 6-NO_2-**F** reveals C_5H at τ 1.78 (singlet), C_7H at 1.82 (quartet), and C_8H at τ 2.43 (ortho coupling, J = 7.5 Hz); 7-NO_2-**F** reveals C_5H at τ 2.38 (ortho coupling, J = 7.0 Hz), C_6H at 1.79 (quartet), and C_8H at 1.84 (singlet). For 6-NO_2-**F**, ir (CCl_4) 1738.5 cm^{-1}; uv max (95% C_2H_5OH) 221.5 mμ (ϵ 9260) and 276 (8820), a shoulder at 302 (5890). For 7-NO_2-**F**, ir (CCl_4) 1744.5 cm^{-1}; uv max (95% C_2H_5OH) 213.5 mμ (ϵ 17600) and 275 (9450).

6-Nitro-1,4-ethano-1,2,3,4-tetrahydronaphthalen-2(*exo* and *endo*)-ols (6-NO_2-A-OH and 6-NO_2-B-OH).—Reduction of 6-NO_2-**F** with lithium borohydride in tetrahydrofuran led to a mixture of 6-NO_2-**A**-OH and 6-NO_2-**B**-OH, which were separated by elution chromatography over alumina. Preparation of 7-NO_2-**A**-OH and 7-NO_2-**B**-OH was similar.

6,7-Dinitro-1,4-ethano-1,2,3,4-tetrahydronaphthalen-2(*exo* and *endo*)-ols [$(NO_2)_2$-A-OH and $(NO_2)_2$-B-OH].—A mixture of four isomeric mononitroacetates (homo-para and -meta, and exo and endo) was further nitrated. After work-up, elution chromatography over alumina gave $(NO_2)_2$-**A**-OH and $(NO_2)_2$-**B**-OH.

The Enone 2.—Detailed accounts of dimerization of cyclohexadiene have been reported.[16a] The dimer used here showed bp 88–90° (8 mm) and n^{25}D 1.525. To a stirred solution of chromic anhydride–pyridine complex, prepared from 62.5 g of the anhydride and 600 ml of pyridine under nitrogen atmosphere, was added a solution of 20 g of the dimer in 40 ml of pyridine, and the mixture was allowed to stand for 65 hr at room temperature with stirring. The organic components in the reaction mixture were extracted with four 500-ml portions of ethyl acetate. The acetate extracts were passed through neutral alumina and evaporated *in vacuo*. Treatment of the residue (17 g) by elution chromatography over alumina, using a mixture solvent of petroleum ether and ether, gave **2** in 46% yield: bp 108–110° (3 mm); $n^{24.5}$D 1.5584; ir (CCl_4) 1673 cm^{-1} (C=O); uv max (95% C_2H_5OH) 251 mμ (ϵ 14,200); nmr ($CDCl_3$) τ 3.80 (m, 2, -CH=CH-), 4.20 (d, 1, =CH-C=O). The semicarbazone had mp 218–219°.

Anal. Calcd for $C_{13}H_{17}N_3O$: C, 67.50; H, 7.41; N, 18.17. Found: C, 67.52; H, 7.40; N, 18.28.

6-Methoxy-1,4-ethano-1,4-dihydronaphthalene (CH_3O-E).—To a stirred solution of 10 g (57.5 mmol) of **2** in 400 ml of anhydrous dioxane containing 1% hydrogen chloride gas was added 16.9 g (74.7 mmol) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone. After stirring for 2 hr at room temperature, precipitated hydroquinone was filtered off and washed with benzene. The combined dioxane and benzene solution was poured into a mixture of 800 ml of ethyl acetate and 500 ml of 3% aqueous sodium bicarbonate. The ethyl acetate layer was separated, washed with saturated sodium chloride solution, then with water, dried, and evaporated. The residue was dissolved in chloroform and passed through a column packed with Kieselgel, 0.2–0.5 mm (Merck). Evaporation of the chloroform left 2.95 g (17.2 mmol) of crude 6-hydroxy-1,4-ethano-1,4-dihydronaphthalene (OH-**E**). Methylation of OH-**E** was carried out with 4.33 g (34.4 mmol) of dimethyl sulfate in 160 ml of acetone, in which was suspended 4.75 g of anhydrous potassium carbonate. The work-up gave 2.08 g of CH_3O-**E**: bp 92–94° (3 mm); n^{25}D 1.5660; uv max (95% EtOH) 230 mμ (ϵ 3750), 278 (1940), 284 (1710).

Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 84.08; H, 7.64.

6- and 7-Methoxy-1,4-ethano-1,2,3,4-tetrahydronaphthalen-2(*exo*)-yl Chlorides (6-CH_3O-A-Cl and 7-CH_3O-A-Cl).—A mixture of exo and endo epimers of 6- and 7-methoxy-1,4-ethano-1,4-dihydronaphthalen-2-ols (the exo:endo ratio was 3:7) was prepared from CH_3O-**E**, by a similar hydroboration to that described above. To enrich the exo component, the mixture (5.2 g) was added to a solution of 6.75 g of aluminum isopropoxide in 130 ml of xylene containing 3–4 drops of acetone, and heated for 15 hr at 150°. The mixture was poured into 170 ml of ice–water containing 2 g of sodium hydroxide and extracted with ether. Evaporation of ether left a 4:6 mixture of the exo and endo epimeric alcohols, which were separated by elution chromatography on neutral alumina containing 6% water. The exo mixture (1.09 g) (6-CH_3O-**A**-OH plus 7-CH_3O-**A**-OH) was treated with 3.82 g of thionyl chloride in 40 ml of ether to produce a mixture of chlorides (1.21 g), whose vpc showed three peaks in the ratio of 70:28:2. The peak of 70 was considered to be due to 6-CH_3O-**A**-Cl plus 7-CH_3O-**A**-Cl and that of 28 to be due to 8-CH_3O-**C**-Cl. The peak of 2 was CH_3O-**E**. Hydrolysis of this mixture at 80° for 6 hr in 55 ml of 70% aqueous acetone containing 907 mg of sodium bicarbonate produced a mixture of alcohols and chlorides, the alcohol fraction of which was separated by elution chromatography over Kieselgel, 0.2–0.5 mm (Merck). This fraction was shown by vpc to be composed of 6-CH_3O-**A**-OH and a rearranged alcohol, for which the structure of 7-CH_3O-**C**-OH was assigned, in the ratio 79:21. Recrystallization from ether gave as pure crystals the main 6-CH_3O-**A**-OH, in which the absence of 7-CH_3O-**A**-OH

Table IV

NMR Chemical Shifts, τ, in $CDCl_3$ at 60 MHz[a]

Compd				
	Substituent			
Ring	In aromatic	In aliphatic	>CH-X	Bridgehead
A	H	2-OH	~6.1 (m)	~7.0 (2 H, m′)
	H	2-OAc	~5.2 (m)	6.79 (qua), 7.01 (qui)
	H	Cl	~6.0 (m)	6.82 (qua), 7.00 (qui)
	$6\text{-}NO_2$	2-OH	6.10 (m)	6.81 (2 H, m′)
	$7\text{-}NO_2$	2-OH	6.18 (m)	6.83 (2 H, m′)
	$7\text{-}NO_2$	2-OAc	5.25 (m)	6.64 (qua), 6.83 (qui)
	$6,7\text{-}(NO_2)_2$	2-OH	6.05 (m)	6.75 (2 H, m′)
	$6,7\text{-}(NO_2)_2$	2-OAc	~5.2 (m)	6.54, 6.73
	$6\text{-}CH_3O$	2-OH	~6.1 (m)	~7.1 (2 H, m′)
	$6\text{-}CHO_3$	2-Cl	~6.0 (m)	6.90 (qua), 7.08 (qui)
	$7\text{-}CH_3O$	2-Cl	~6.0 (m)	6.90 (qua), 7.08 (qui)
B	H	2-OH	~6.0 (m)	7.00 (2 H, m′)
	H	2-OAc	~4.9 (m)	6.80, 6.97
	$6\text{-}NO_2$	2-OH	5.82 (d–t), $J_{2,3}$ = 8.8 Hz	6.80 (2 H, m′)
	$7\text{-}NO_2$	2-OH	5.82 (d–t), $J_{2,3}$ = 8.8 Hz	6.83 (2 H, m′)
		2-OAc	4.87 (d–t), $J_{2,3}$ = 9.0 Hz	6.64, 6.83
B	$6,7\text{-}(NO_2)_2$	2-OH	5.75 (d–t), $J_{2,3}$ = 8.6 Hz	6.73 (2 H, m′)
	$6,7\text{-}(NO_2)_2$	2-OAc	4.82 (d–t), $J_{2,3}$ = 8.8 Hz	6.55, 6.75
C	H	2-OH	6.13 (m)	~6.9 (2 H, m′)
	H	2-OAc[b]	5.17 (m)	~6.8 (2 H, m′)
	$8\text{-}NO_2$	2-OAc	5.03 (m)	6.65 (2 H, m′)
	$7\text{-}CH_3O$	2-OAc[b]	5.20 (m)	~6.9 (2 H, m′)
D	$7\text{-}NO_2$	2(ax)-OAc	4.33 (d), $J_{4,5}$ = 2.7 Hz	6.75 (m), 7.30 (m)
	$6,7\text{-}(NO_2)_2$	2(ax)-OAc	4.33 (d), $J_{4,5}$ = 2.8 Hz	6.69 (m), 7.26 (m)
	$6,7\text{-}(NO_2)_2$	2(eq)-OAc	3.85 (d), $J_{4,5}$ = 5.0 Hz	

[a] d = doublet, t = triplet, qua = quartet, qui = quintet, m = multiplet, m′ = overlapping multiplet, and d–t = doublet of triplets.
[b] In CCl_4.

was confirmed by transforming it into the ketone $6\text{-}CH_3O\text{-}$**F**,[34] suitable for vpc analysis.

Treatment of 230 mg of $6\text{-}CH_3O\text{-}$**A**-OH with 816 mg of thionyl chloride in 14 ml of ether gave $6\text{-}CH_3O\text{-}$**A**-Cl, homogeneous on vpc.

The chloride fraction of the hydrolysis mixture (a mixture of $7\text{-}CH_3O\text{-}$**A**-Cl and $8\text{-}CH_3O\text{-}$**C**-Cl as well as the minor $CH_3O\text{-}$**E**) was further subjected to hydrolysis by treating it at 130° for 5 hr in 70% aqueous dimethylformamide containing sodium bicarbonate to change only the more reactive $8\text{-}CH_3O\text{-}$**C**-Cl into alcohols. The work-up isolated a mixture of the unchanged chloride, $7\text{-}CH_3O\text{-}$**A**-Cl, and the minor $CH_3O\text{-}$**E** from the alcohols formed. This mixture was treated by the standard hydroboration reaction to convert $CH_3O\text{-}$**E** into alcohols, without influence on $7\text{-}CH_3O\text{-}$**A**-Cl. Thus, $7\text{-}CH_3O\text{-}$**A**-Cl was easily separated in a pure state from the alcohols by elution chromatography over Kieselgel, 0.2–0.5 mm (Merck), using benzene.

Gas Chromatographic Analyses.—Analyses were carried out on a Hitachi gas chromatograph Model K-53 equipped with a hydrogen flame ionization detector using any of the columns: (A) 2 m × 3 mm stainless steel column packed with 5% XE 60 on Chromosorb W; (B) a 1 m × 3 mm stainless steel column packed with 4% KF 54 on the same support; (C) a 1 m × 3 mm stainless steel column packed with 5% diethylene glycol succinate polyester on the same support. Nitrogen gas was used as a carrier gas. Retention times of **E** and $CH_3O\text{-}$**E** were 9 min 20 sec at 110° of column A with a pressure of 1 kg/cm^2 of nitrogen and 7 min at 130° of column B with a pressure of 1.5 kg/cm^2, respectively. Those of **A**-OH and **B**-OH were 9 min and 13 min 50 sec, respectively, at 130° of column B with a pressure of 1.0 kg/cm^2. Those of 6- and $7\text{-}CH_3O\text{-}$**A**-OH were the same 11 min, and those of 6- and $7\text{-}CH_3O\text{-}$**B**-OH were the same 13 min 6 sec, at 190° of column A with a pressure of 1.5 kg/cm^2. Those of $6\text{-}CH_3O\text{-}$**A**-OH and $7\text{-}CH_3O\text{-}$**C**-OH were 12 min 24 sec and 10 min 18 sec, respectively, at 150° of column B with a pressure of 1.5 kg/cm^2. That of $6\text{-}CH_3O\text{-}$**F** was 16 min 12 sec at 190° of column A with a pressure of 1.5 kg/cm^2. Those of $6\text{-}CH_3O\text{-}$**A**-Cl and $7\text{-}CH_3O\text{-}$**A**-Cl were 6 min and 5 min 48 sec, respectively, at 150° of column C with a pressure of 1.5 kg/cm^2. Those of **E**, **C**-Cl, and **A**-Cl were 2 min 36 sec, 7 min 18 sec, and 8 min 24 sec, respectively, at 130° of column B with a pressure of 1.0 kg/cm^2.

Acetolysis Products from $(NO_2)_2$-B-OBs.—A solution of 145 mg (3 × 10^{-4} mol) of the brosylate in 15 ml of acetic acid containing 0.022 *M* sodium acetate was sealed in a tube and heated for 70 hr at 100°. The acetic acid was evaporated *in vacuo*, and the residue added into water and extracted with chloroform. The chloroform solution was washed with cold aqueous sodium carbonate, dried with anhydrous sodium sulfate, and evaporated. Preparative layer chromatography on Kieselgel GF_{254} (Merck)

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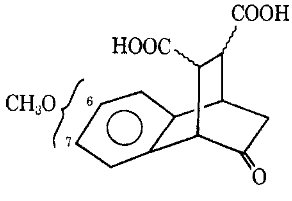
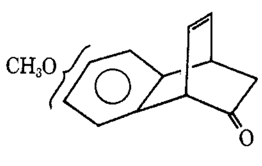
[34] Treatment of the 6- and 7-methoxyketocarboxylic acids (**13** and **14**)[35] with lead tetraacetate in pyridine affords, respectively, the unsaturated ketones, **15** and **16**, though the yields are unsatisfactory. Hydrogenations of **15** and **16** gives compounds indentical with $6\text{-}CH_3O$**F** and $7\text{-}CH_3O$**F**. We thank Drs. K. Takeda and K. Kitahonoki for providing authentic samples of these compounds.



13, CH_3O at C-6
14, CH_3O at C-7



15, CH_3O at C-6
16, CH_3O at C-7

[35] K. Takeda, S. Hagishita, M. Sugiura, K. Kitahonoki, I. Ban, S. Miyazaki, and K. Kuriyama, *Tetrahedron*, **26**, 1435 (1970).

with a 9:1 solvent mixture of benzene and ether showed five bands. The first band, R_f 15.2, was shown by nmr to be composed of $(NO_2)_2$-**E** and the tricyclic **12**. The second band, R_f 10.2, was obtained as $(NO_2)_2$-**D**(ax)-OAc; the third band, R_f 9.6, as $(NO_2)_2$-**D**(eq)-OAc; the fourth band, R_f 8.5, as $(NO_2)_2$-**A**-OAc; the fifth band, R_f 6.2, as $(NO_2)_2$-**B**-OAc. The yields in Table II were determined by nmr spectroscopy and from the relative amounts of the thus isolated products. Because of insufficient amounts, isolation of samples of $(NO_2)_2$-**E** and **12**, satisfactory for analysis, was unsuccessful. The 100-MHz nmr of the crude **12** shows H_{6x} and H_{8x} at τ 8.03 (quartet, $J_{6x,6n}$ and $J_{8x,8n}$ = 11.6 Hz, $H_{6x,5}$ and $J_{8x,5}$ = 5.0 Hz), H_{6n} and H_{8n} at 9.03 (doublet), H_5 at 6.75 (triplet), H_2 at 7.66 (triplet, $J_{H_2H_1}$ and $J_{H_2H_7}$ = 7.4 Hz), and H_1, H_7 at 8.07 (doublet). Studies of products from other nitro brosylates were carried out in a similar way.

Infrared Hydroxyl Stretching Bands.—Spectra were taken in carbon tetrachloride and the concentration of alcohols were less than 0.003 M. **A**-OH, 6-NO_2-**A**-OH, and 7-NO_2-**A**-OH show only a free band at 3622, 3620, and 3620 cm^{-1}, respectively. **B**-OH shows a week free band at 3619 cm^{-1} and an associated band $(OH \cdots \pi)$ at 3584 cm^{-1}. 6-NO_2-**B**-OH and 7-NO_2-**B**-OH show free bands at 3615 and 3613 cm^{-1}, respectively, as well as associated bands at 3594 and 3593 cm^{-1}, respectively. In both the nitro alcohols, the intensities of the associated bands are a little weak relative to those of the free bands.

Registry No.—**A** (Z, X) (6-CH_3O, 2-OH), 27142-14-9; (6-CH_3O, 2-Cl), 27142-15-0; (7-CH_3O, 2-Cl), 27142-16-1; (H, 2-Cl), 27189-22-6; (H, 2-OH), 13153-77-0; (H, 2-OBs), 16938-83-3; (H, 2-OAc), 16938-84-4; (6-NO_2, 2-OH), 27142-17-2; (6-NO_2, 2-OBs), 27142-18-3; (7-NO_2, 2-OH), 27142-19-4; (7-NO_2, 2-OBs), 27142-20-7; (7-NO_2, 2-OAc), 27142-21-8; (6,7-$(NO_2)_2$, 2-OH), 27142-22-9; (6,7-$(NO_2)_2$, 2-OBs), 27189-23-7; (6,7-$(NO_2)_2$, 2-OAc), 27150-76-1; **B** (Z, X) (H, 2-OH), 13153-78-1; (H, 2-OBs), 16938-82-2; (H, 2-OAc), 27149-76-4; (6-NO_2, 2-OH), 27149-77-5; (6-NO_2, 2-OBs), 27149-78-6; (7-NO_2, 2-OH), 27149-79-7; (7-NO_2, 2-OBs), 27149-80-0; (7-NO_2, 2-OAc), 27149-81-1; (6,7-$(NO_2)_2$, 2-OH), 27149-82-2; (6,7-$(NO_2)_2$, 2-OBs), 27149-83-3; (6,7-$(NO_2)_2$, 2-OAc), 27149-84-4; **C** (Z, X) (H, 2-OH), 16938-90-2; (H, 2-OAc), 27149-86-6; (8-NO_2, 2-OAc), 27149-87-7; (7-CH_3O, 2-OAc), 27149-88-8; **D** (Z, X) (7-NO_2, 2(ax)-OAc), 27149-89-9; (7-NO_2, 5(ax)-OAc), 27149-90-2; (6,7-$(NO_2)_2$, 2(ax)-OAc), 27149-91-3; (6,7-$(NO_2)_2$, 2(eq)-OAc), 27149-92-4; (7,8-$(NO_2)_2$, 5(ax)-OAc), 27149-93-5; **E** (Z) (CH_3O), 27150-77-2; **F** (Z, X) (6-NO_2, 2-one), 27150-78-3; (7-NO_2, 2-one), 27150-79-4; (6,7-$(NO_2)_2$, 2-one),,27150-80-7; **2**, 27150-81-8.

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The 1-Aza-2,4,6-cyclooctatriene–7-Azabicyclo[4.2.0]octadiene Valence Tautomeric Equilibrium. A Study of Substituent Effects and an Attempted Synthesis of Azetes (Azacyclobutadienes)[1]

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Five derivatives of the 1-aza-2,4,6-cyclooctatriene system have been prepared. The concentration of each polyene in equilibrium with its valence tautomeric 7-azabicyclo[4.2.0]octatriene form has been evaluated quantitatively by nmr spectroscopy. It was noted that the bicyclic form is favored in all instances, although to varying degrees, and explanations of such behavior are advanced. The attempted utilization of these substances in the preparation of azete (azacyclobutadiene) derivatives is described.

The last two decades have witnessed the methodical compilation of much experimental data concerning reversible transformations that occur without the migration of atoms or groups, now commonly referred to as valence tautomeric equilibria.[3] However, despite the fact that quantitative evidence for a wide variety of structural types is currently available, our basic understanding of the causative factors that control the individual positions of equilibrium is lacking in many instances. Particularly relevant examples in this connection are the cycloheptatriene–norcaradiene,[4] cyclooctatriene–bicyclo[4.2.0]octadiene,[5] oxepin–benzene oxide,[3d,f] 1H-azepine–azanorcaradiene,[3f,6] and azocine–azabicyclo[4.2.0]octatriene[7] tautomeric pairs. To illustrate, Huisgen and coworkers[5d] have recently determined the equilibrium position of the 1,3,5-cyclooctatriene (**1**)–bicyclo[4.2.0]octadiene (**2**) valence tauto-

1 **2**

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