Synthesis and Reactions of 1,3-Methanoindan (Benzobicyclo[2.1.1]hexene) Derivatives[1,2]

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Contribution from the Shionogi Research Laboratory, Shionogi & Co., Ltd., Fukushima-ku, Osaka, Japan. Received September 9, 1968

Abstract: To investigate the behavior of carbonium ions formed in the bridged benzocyclene systems, some derivatives of 1,3-methanoindan (the smallest bridged benzocyclene known) have been synthesized. *anti*-9-Chlorobenzonorbornene-2,3-dione (**4**), prepared by oxidation of *anti*-9-chlorobenzonorbornen-2-one with selenium dioxide, was converted to the α-diazo ketone **5** *via* monotosylhydrazone. Photolysis of **5** yielded 1,3-methanoindan-*exo*-8-chloro-*endo*- and -*exo*-2-carboxylic acids with ring contraction. This *endo* acid was treated with lead tetraacetate to give 1,3-methano-*exo*-2-chlorindan (**12**). 1,3-Methano-*exo*-2-indanol was obtained by hydrolysis of **12** and esterified by *p*-toluenesulfonyl chloride. The tosylate **15** thus obtained solvolyzes with retention of configuration at a rate 800 times that of *exo*-5-bicyclo[2.1.1]hexyl tosylate and 33 times that of *anti*-9-benzonorbornenyl tosylate (**20**). Diminishing reactivities, observed in the order **15**, **20**, and 6,7,8,9-tetrahydro-5,9-methano-5H-benzocyclohepten-*exo*-10-yl tosylate, are well explained by a MO treatment of the aryl participation effect.

Derivatives of 1,3-methanoindan, the smallest bridged benzocyclene known, were first synthesized by us[1] and Pomerantz,[3] independently. As part of our interest in the chemistry of bridged benzocyclene, this paper deals with the synthesis and solvolytic behavior of some 1,3-methanoindanyl derivatives. Carbonium ion reactions of the homologous benzonorbornene system have produced a number of significant results concerning the participation effect.[4] The chemistry of the saturated analog, bicyclo[2.1.1]hexane, is under intensive research.[5] Synthesis of unsaturated bicyclo-[2.1.1]hexene was undertaken and recently achieved;[6,7] the major aim of the synthesis is thought to be similar to that of this study.

Results

Preparations. The acid-catalyzed addition reactions of norbornene[8] and benzonorbornadiene (**1**)[9] are preferred by the *exo* attack of the cationic species, followed by the Wagner–Meerwein rearrangement and then capture of the anionic fragment from the *exo* side (eq 1). Addition of hypochlorous acid to **1**, followed by immediate oxidation with nitric acid or chromium trioxide, produced *anti*-9-chlorobenzonorbornen-2-one (**3**). Treatment of **3** with selenium dioxide in nitrobenzene at 180° gave the crystalline chloro diketone **4**. Monotosylhydrazone was generated *in situ* by dissolving **4** and tosylhydrazine in methylene chloride. The resulting solution was poured through a column of basic alumina, giving in the methylene chloride eluate good yields of the α-diazo ketone **5** of a purity suitable for use in the next step. Irradiation of **5** in aqueous dioxane with a 300-W high-pressure mercury lamp yielded a mixture of the epimeric carboxylic acids **6** and **7**, in which the *endo* isomer **7** predominated to the extent of 60%. The presence of a small amount of sodium bicarbonate in the reaction mixture improved the yield somewhat. As reported in a previous communication,[1] the same reaction sequence, starting with 2-benzonorbornenone, led to a mixture of methyl 1,3-methano-*endo*- and -*exo*-2-indancarboxylates. The structure of the *endo* isomer was determined by its nmr spectrum, which was compatible with data reported by Pomerantz for 1,3-methanoindan.[3]

Evidence for the orientation of the carboxyl groups in **6** and **7** was obtained from reactions of their methyl esters **8** and **9** with alkyllithium. Treatment of **9** with *n*-butyllithium afforded the tertiary alcohol **10**, while reaction of **8** with methyllithium yielded, instead of an expected halo alcohol, the cyclic ether **11**. This ether contains no halogen and shows strong infrared absorption bands at 1068 and 985 cm^{-1}, characteristic of a four- or five-membered cyclic ether.[10] The nmr spectrum indicates four aromatic protons at τ 3.06 as an A_2B_2 multiplet, two bridgehead protons at τ 6.86 as a singlet, and six protons at τ 8.63 as a sharp singlet due to the two methyl groups. These patterns were expected due to the existence of a symmetrical axis across the benzene ring in **11**. The remaining two protons at C_8 and C_2 appear as doublets at τ 6.21 and 4.94, respectively; the doublets are due to the long-range coupling between the protons. This is in accord with the observation of Wilberg that the coupling between the *endo*-5 and the bridgehead protons in the bicyclo-[2.1.1]hexane system is negligibly small.[11] Accordingly, the respective formations of **11** and **10** led to the assignment that the chloro and carboxyl groups in **6** and **8** are both *exo* (*cis* to each other) and the cor-

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[1] For a preliminary report of a part of the results, see H. Tanida and Y. Hata, *J. Amer. Chem. Soc.*, **88**, 4289 (1966).

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

[3] M. Pomerantz, *J. Amer. Chem. Soc.*, **88**, 5349 (1966).

[4] (a) H. Tanida, *Accounts Chem. Res.*, **1**, 239 (1968); (b) R. Muneyuki and H. Tanida, *J. Amer. Chem. Soc.*, **90**, 656 (1968), and references cited therein.

[5] As a recent review, see J. Meinwald and Y. C. Meinwald, *Advan. Alicyclic Chem.*, **1**, 1 (1966).

[6] J. Meinwald and F. Uno, *J. Amer. Chem. Soc.*, **90**, 800 (1968).

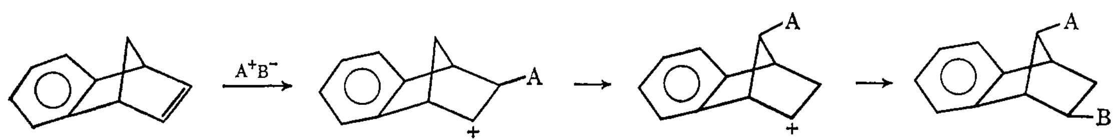
[7] F. T. Bond and L. Scerbo, *Tetrahedron Lett.*, 2789 (1968).

[8] (a) J. D. Roberts, F. O. Johnson, and R. A. Carboni, *J. Amer. Chem. Soc.*, **76**, 5692 (1954); (b) H. C. Brown and K. T. Liu, *ibid.*, **89**, 3900 (1967).

[9] S. J. Cristol and G. W. Nachtigall, *J. Org. Chem.*, **32**, 3727 (1967), and references cited therein.

[10] G. M. Barrow and S. Searles, *J. Amer. Chem. Soc.*, **75**, 1175 (1953).

[11] K. B. Wiberg, B. R. Lowry, and B. J. Nist, *ibid.*, **84**, 1594 (1962).



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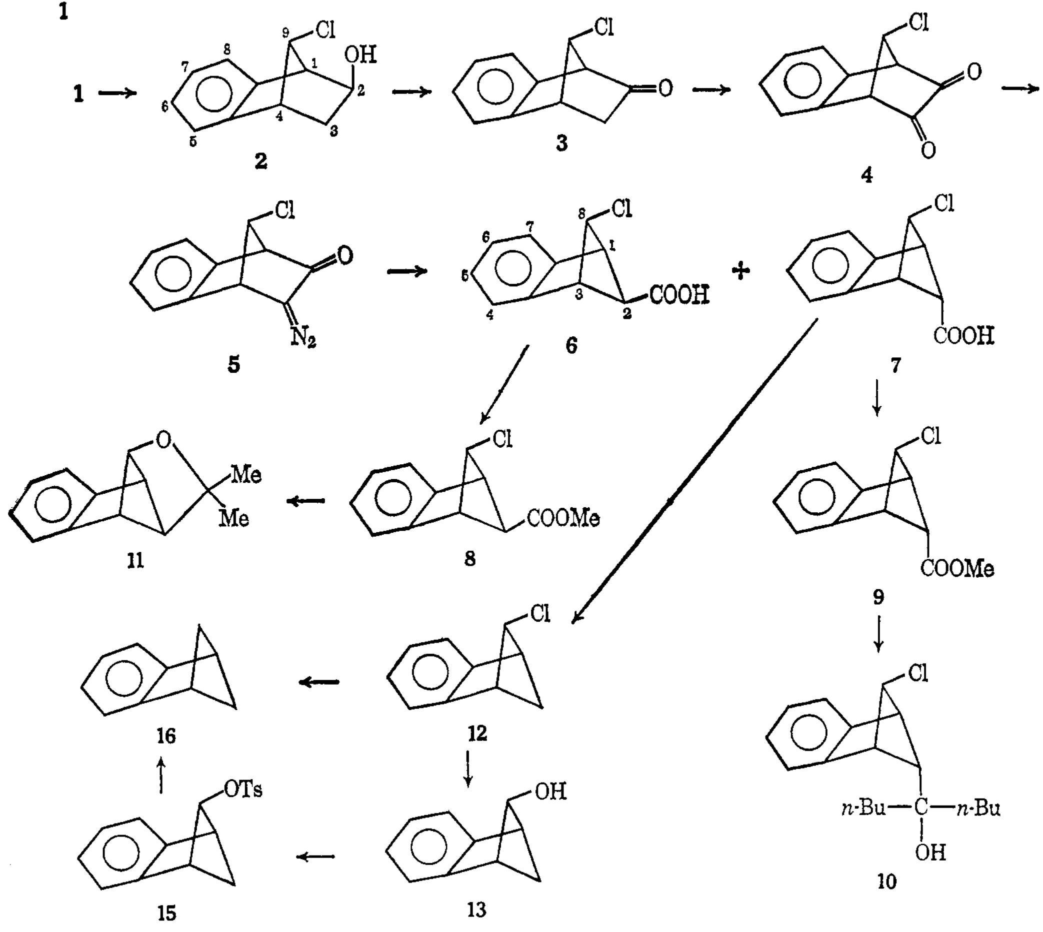
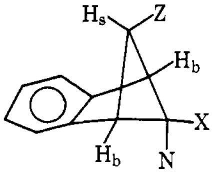


the acetate, 14

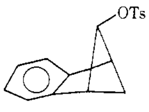
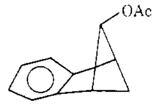
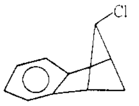
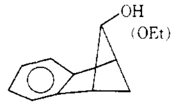
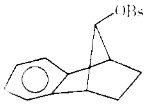
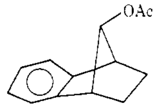
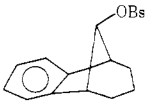
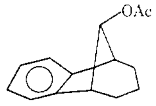
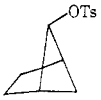
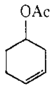
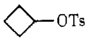
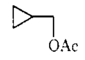
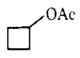
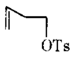
Table I. Nmr Spectra of 1,3-Methanoindans[a,b]



Compound				Chemical shift in CCl$_4$, τ							
No.	Z	X	N	H_s	H_x	H_n	H_b	Aromatic protons	$J_{H_s-H_n}$	$J_{H_x-H_n}$	Other
12	Cl	H	H	5.88 d	6.28 d-t	7.60 q	6.77 d	2.97 A_2B_2	7.4	6.57	
14	OAc	H	H	5.31 d	6.57 q	7.67 q	6.79 d	2.96 A_2B_2	6.78	6.18	CH$_3$, 7.92 s
13	OH	H	H	5.78 d	6.38 d-t	7.64 q	6.98 d	3.02 A_2B_2	6.45	6.23	
8	Cl	COOCH$_3$	H	5.94 d	. . .	6.73 d	6.31 s	2.89 A_2B_2	5.98	. . .	CH$_3$, 6.28 s
9	Cl	H	COOCH$_3$	6.00 s	5.37 t	. . .	6.47 d	2.91 A_2B_2	. . .	. . .	CH$_3$, 6.67 s
11	-O	C(CH$_3$)$_2$-	H	4.94 d	. . .	6.21 d	6.86 s	3.06 A_2B_2	6.3	. . .	CH$_3$, 8.63 s
16[c]	H	H	H	7.66 q	7.25 m	7.66	6.86 t	3.0 A_2B_2	5.0	4.9	

[a] Tetramethylsilane was used as an internal standard. [b] Abbreviations used: q = quartet, m = multiplet, d-t = doublet of triplets. [c] Reference 3.

Table II. Rates and Products of Solvolysis of 1,3-Methanoindanyl Derivatives and Relevant Compounds

Compound	Solvent	Temp, °C	k, sec^{-1}	Rel reactivity[a]	Product	Ref
	AcOH	55.1 77.0 164.2	1.16×10^{-5} 1.29×10^{-4} 4.67×10^{-1} [c]	1	 Quantitative	*b*
	50% aq EtOH	70.0	4.23×10^{-6}		 Main	*b*
	AcOH	55.0	1.03×10^{-6} [c]	3.1×10^{-2}	 Quantitative	*d*
	AcOH	141.4 162.6 55.0	9.81×10^{-5} 6.78×10^{-4} 2.70×10^{-9} [c]	8.0×10^{-5}	 >99.4%	*e*
	AcOH	164.2	5.82×10^{-4}	1.3×10^{-3}	 Main	*f*
	AcOH	55.1	7.61×10^{-5}	6.6	 65%  22%  13%	*g*

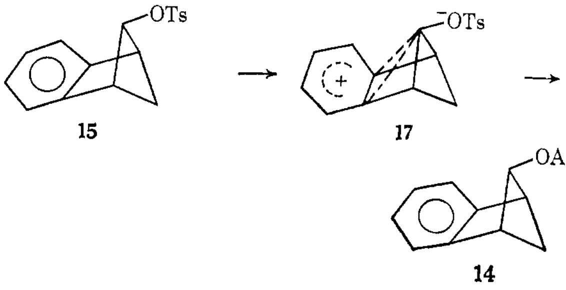
[a] At 55°. As an exception, bicyclo[2.1.1]hexyl tosylate is compared at 164.2°. The rates for the brosylates are converted into those for the tosylates by the use of the factor, ROBs:ROTs = 2.90, and compared with other tosylates. [b] The present study. The concentrations of 1,3-methano-*exo*-2-indanyl tosylate and chloride are 0.0052 and 0.0122 *M*, respectively. Temperatures were controlled to ±0.07°. The acetic acid contained 1.2 equiv of sodium acetate and 1% acetic anhydride. Aqueous ethanol in vol %. [c] Values calculated by Arrhenius plots. [d] H. Tanida, T. Tsuji, and H. Ishitobi, *J. Amer. Chem. Soc.*, **86**, 4904 (1964). [e] Reference 20. [f] Reference 13. [g] J. D. Roberts and V. C. Chambers, *J. Amer. Chem. Soc.*, **73**, 5034 (1951).

responding groups in **7** and **9** are *exo* and *endo* (*trans* to each other), respectively.

The *endo* acid **7** was decarboxylated by treatment with lead tetraacetate and the nmr spectrum of the product **12** was analyzed in detail in connection with other interests, reported separately.[12] Hydrolysis of **12** in aqueous acetic acid led, without ring cleavage, to a mixture of 1,3-methano-*exo*-2-indanol (**13**) and its acetate **14**, which were interconvertible through acetylation or hydrolysis. The *exo* orientation of the hydroxyl group in **13** was established by the nmr spectrum. The proton at C_2 appears as a doublet for the same reason as in **11**. The aromatic protons also indicate the existence of a symmetrical axis. The bridgehead protons at τ 6.98 are coupled with only one *exo* proton (2.7 Hz). The tosylate **15** was prepared by a standard procedure. The formation of 1,3-methanoindan (**16**) in the reductions of **12** and **15** with sodium metal and lithium aluminum hydride, respectively, indicated that no skeletal rearrangement occurred during the above syntheses. The nmr spectral data are summarized in Table I.

Kinetics and Products. The solvolyses of the tosylate **15** in glacial acetic acid containing 1.2 equiv of sodium acetate and of the chloride **12** in 50% aqueous ethanol were followed by the titration, at intervals, of the toluenesulfonic acid or the hydrochloric acid liberated during the reaction. The observed kinetics were first order in all cases, and the precision of measurement was usually 2% or better. The experimental infinity titers at about ten half-lives are consistently within 2% of the calculated value for each run. Comparison of the reactivities with those of relevant compounds was carried out at 55°.

The acetolysis of **15** at 75°, buffered with the above amount of sodium acetate, produced the acetate **14** with complete retention of configuration in a quantitative yield (eq 2). For discussion, it was considered important to check for the formation of naphthalene. Vpc analysis demonstrated its absence in amounts greater than 1%. Table II lists the rates and products with other pertinent data.



(2)

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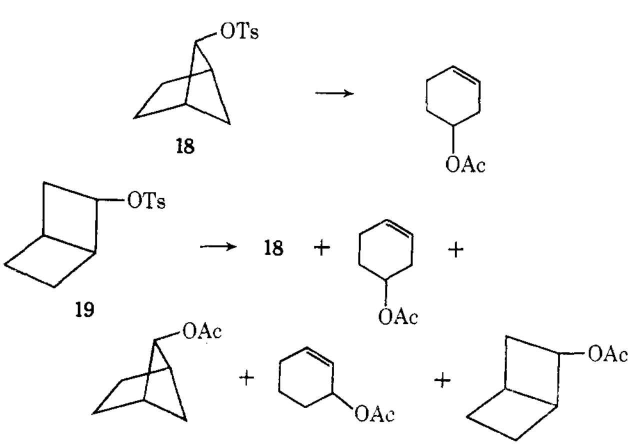
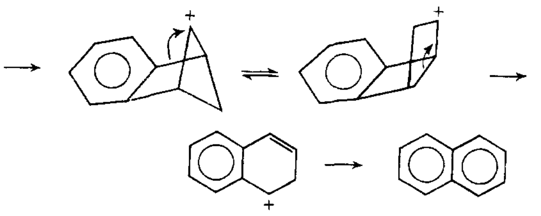
(12) We determined the signs of long-range coupling constants across four single bonds observed in molecules of this kind: K. Tori, M. Ohtsuru, Y. Hata, and H. Tanida, *Chem. Commun.*, 1096 (1968).

Discussion

It was reported that the acetolysis of *exo*-5-bicyclo[2.1.1]hexyl tosylate (**18**) proceeds with rearrangement, forming mainly 4-cyclohexenyl acetate,[13] and that the acetolysis of *exo*-2-bicyclo[2.2.0]hexyl tosylate (**19**) yields, with an internally returned less reactive **18**, 51% 4-cyclohexenyl acetate, 41% *exo*-5-bicyclo[2.1.1]hexyl acetate, 5% 3-cyclohexenyl acetate, and 3% *exo*-2-bicyclo[2.2.0]hexyl acetate.[14] If such a rearrangement takes place in the solvolysis of **15**, the formation of naphthalene is expected (eq 3). However, naphthalene was absent.



15  (3)

The X-ray analysis of methyl 1,3-methano-*exo*-8-bromo-*endo*-2-indancarboxylate performed in our laboratory[15] revealed a C_1–C_2–C_3 angle of 83° and a C_1–C_8–C_3 angle of 82°.[16] Therefore, the most pertinent structural feature of **15** is that it is an extraordinarily strained cyclobutyl derivative. To the best of our knowledge, the solvolysis of all the bicyclic cyclobutyl compounds so far reported, as well as that of monocyclobutyl systems, proceeds accompanied by ring cleavage (if their reaction centers are converted into tertiary derivatives, no cleavage occurs in general). The lessened bond angle in **15** should promote such a cleavage and also decelerate the rate of solvolysis. Accordingly, the present observation constitutes the first example of the retention of a cyclobutane ring in solvolysis.

The parent **18** solvolyzes with ring cleavage, while **15** reacts with retention. Because of this, comparison of the reactivity of **15** with that of **18** may have no meaning from a theoretical point of view. Nonetheless, it should be noted that the rate of solvolysis of **15** is 800 times that of **18** (Table II) and further, from data available,[4a,17] roughly 10^7 times that of 7-norbornyl tosylate. The homologous *anti*-9-benzonorbornenyl arenesulfonate (**20**) solvolyzes, yielding a product with retention, and in spite of the larger C_1–C_9–C_4 angle[18,19] than the C_1–C_2–C_3 angle in **15**, its rate drops to 0.031 that of **15**. In addition, the rate of solvolysis of 6,7,-8,9-tetrahydro-5,9-methano-5H-benzocyclohepten-*exo*-10-yl arenesulfonate (**21**), whose C_1–C_{10}–C_5 angle is estimated from a Cenco–Peterson model as 101°, is slower than that of **15** by a factor of 8.0×10^{-5}.[20] This sulfonate also produces retained 6,7,8,9-tetrahydro-5,9-methano-5H-benzocyclohepten-*exo*-10-yl acetate in a greater than 99.4% yield. These results clearly indicate the presence of some type of participation in the transition state in the solvolysis of both **15** and **20**. In compounds of this series, if the bond-angle effect at the reaction site does exist, it must be relatively unimportant and be overwhelmed by the aryl participation effect. A symmetrical transition state in the solvolysis of **20** was originally suggested by Bartlett and Giddings[21] and clearly evidenced by us.[22] We predict the transition state of a similar symmetrical type in the solvolysis of **15** (**17** in eq 2).[23]

Why does benzene participate in a most effective way in the solvolysis of **15**? A satisfactory answer is provided by a general MO treatment of the interaction between the benzene π electrons and the developing p orbital at the reaction site, as carried out by Winstein and Simonetta on homoallylic cations.[24] Figure 1 shows bond lengths, bond angles, and the like, which are needed for calculation. The distance between the cationic center (a) and the juncture carbon of the aromatic and aliphatic parts (c) is given by l. The rectangle cc″d″d stands perpendicular to the aromatic plane at the junction. The axis of the leaving group, aZ, intersects at d″ with this rectangle. The angle θ_1 is formed by the intersection of the two planes, ac″d″ and acd. The two sets of two lines, ad and ac, and ac and cd, make angles θ_2 and θ_3, respectively. Principally on the basis of available X-ray data,[15,18,19] for **15**, l = 2.33 Å, θ_1 = 15° 46′, θ_2 = 13° 41′, and θ_3 = 61° 37′: for **20**, l = 2.31 Å, θ_1 = 16° 52′, θ_2 = 24° 10′, and θ_3 = 69° 11′. The values for **21** estimated from a Cenco–Peterson model are l = 2.33 Å, θ_1 = 15° 50′, θ_2 = 30° 30′, and θ_3 = 75°. The overlap integral is calculated from the equation

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(13) K. B. Wiberg and R. Fenoglio, *Tetrahedron Lett.*, 1273 (1963).

(14) R. N. McDonald and C. E. Reineke, *J. Org. Chem.* **32**, 1878 (1967).

(15) T. Tsukuda, T. Sato, M. Shiro, Y. Hata, H. Tanida, and H. Koyama, Abstracts of the 21st Annual Meeting of the Chemical Society of Japan, Osaka, 1968, series 1, p 182.

(16) G. Dallinga and L. H. Toneman, *Rec. Trav. Chim.*, **86**, 171 (1967), reported a C_1–C_5–C_4 angle of 85.4° for bicyclo[2.1.1]hexane, obtained through electron diffraction.

(17) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Amer. Chem. Soc.*, 77, 4183 (1955).

(18) The C_1–C_9–C_4 angle in *syn*-9-benzonorbornenyl brosylate is 97° (X-ray analysis): T. Sato, M. Shiro, and H. Koyama *J. Chem. Soc.*, *B*, 935 (1968).

(19) The C_1–C_7–C_4 angle in *anti*-7-norbornenyl *p*-bromobenzoate was reported as 96° (X-ray analysis): A. C. Macdonald and J. Trotter, *Acta Cryst.*, **19**, 456 (1965)

(20) Private communication from Y. Takano, Shionogi Research Laboratory, Osaka. We thank him for results prior to publication.

(21) P. D. Bartlett and W. P. Giddings, *J. Amer. Chem. Soc.*, **82**, 1240 (1960).

(22) H. Tanida and H. Ishitobi, *ibid.*, **88**, 3663 (1966).

(23) *endo*-8-Bicyclo[3.2.1]octyl arenesulfonate solvolyzes at almost the same rate as that of **21**; however, 98% of the products are inverted and rearranged, and 2% of those are retained. The rate constant of this sulfonate at 55° is obtained as 7.5×10^{-10} sec^{-1} by extrapolating the data of C. S. Foote and R. B. Woodward, *Tetrahedron*, **20**, 687 (1964). Therefore, the retention in **21** may suggest a small amount of participation of the benzene ring.

(24) M. Simonetta and S. Winstein, *J. Amer. Chem. Soc.*, **76**, 18 (1954).

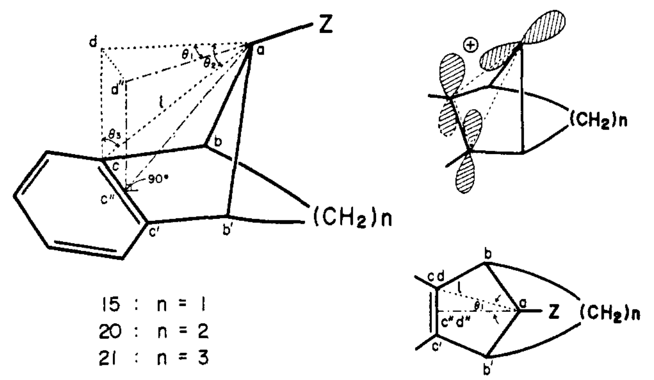
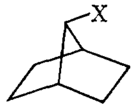


Figure 1. The geometry of benzobicyclo[2.1.*n*]alkenes.

$$S_{ac} = S_{\sigma\sigma} \cos \theta_1 \cos \theta_2 \cos \theta_3 + S_{\pi\pi} \cos \theta_1 \sin \theta_2 \sin \theta$$

where the values $S_{\sigma\sigma}$ and $S_{\pi\pi}$ are obtained for the respective l from the table of Mulliken, *et al.*[25] The total overlap integrals ($S_{ac} + S_{ac'}$) thus obtained were 0.14 for **15**, 0.11 for **20**, and 0.09 for **21**, which are in the order of the observed reactivities.[26] Thus, the present results typically demonstrate the usefulness of a calculation of this type.

anti-7-Norbornenyl tosylate solvolyzes 10^{11} times faster than 7-norbornyl tosylate. From the present results, we predict that bicyclo[2.1.1]hex-2-en-*exo*-5-yl tosylate is more reactive than *anti*-7-norbornenyl tosylate.



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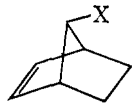
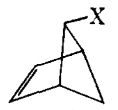


10^{11}



$10^{>11}$

Experimental Section

Melting points are corrected. Nmr spectra were determined on a Varian A-60 spectrometer using tetramethylsilane (τ 10.00) as internal standard in carbon tetrachloride or in deuteriochloroform. Gas chromatographic analyses were carried out on a Hitachi Perkin-Elmer Model F-6 or F-6-D using helium as a carrier gas. Infrared spectra were measured on a JASCO Model IR-S.

anti-**9-Chlorobenzonorbornen-2-one (3).** A mixture of 30.0 g (0.197 mol) of benzonorbornadiene (**1**) and 710 ml (0.212 mol) of freshly prepared aqueous hypochlorous acid was stirred at room temperature for 4 hr and allowed to stand overnight. The mixture was extracted with ether and the ether solution washed with aqueous sodium bicarbonate and dried. Removal of the ether left crude *anti*-9-chloro-*exo*-2-benzonorbornenol (**2**), which was distilled at 95–100° (1 mm) accompanied by slight decomposition. This was used without further purification in the next step.

A mixture of **2** and 280 ml of 32% nitric acid was heated on a steam bath for 15 min with occasional shaking.[27] The mixture was cooled to room temperature, diluted with water, and extracted with ether. The ether solution was washed with aqueous sodium bicarbonate, dried, and distilled under reduced pressure. The fraction (26 g) distilled at 109–110° (0.62 mm) was pure **3**; ir (CCl_4) 1800 (w), 1760 (s), 1460 (w), 1408 (w), 1263 (m), and 1082 (m) cm^{-1}; nmr (CCl_4) τ 2.86 (m, 4, aromatic), 5.63 (m, 1, *syn*-H_9), 6.37 (t, 1, H_4), 6.45 (d, 1, H_1), 7.32 (d of d, 1, *exo*-H_3), and 8.20 (d of d, 1, *endo*-H_3); $J_{exo\text{-}H_3,endo\text{-}H_3}$ = 17 Hz and $J_{endo\text{-}H_3,syn\text{-}H_9}$ = 2.3 Hz. This long-range coupling is evidence of the *exo* orientation of the chlorine atom in **3**.[28]

Anal. Calcd for $C_{11}H_9OCl$: C, 68.50; H, 4.68. Found: C, 68.20; H, 4.75.

anti-**9-Chlorobenzonorbornene-2,3-dione (4).** Selenium dioxide was purified by sublimation with a few drops of concentrated nitric acid and pulverized. A mixture of 20.0 g (0.104 mol) of **3**, 32 g (0.29 mol) of selenium dioxide, and 80 ml of nitrobenzene was stirred and heated at 180° for 4 hr. The mixture was cooled to room temperature and diluted with ether to precipitate selenium. The selenium was filtered off and the solvent removed under reduced pressure. The remaining reddish crystals (16 g) were recrystallized from cyclohexane or benzene to yield 10 g (47%) of **4**, mp 143–144.5°; ir (CCl_4) 1765 (s), 1783 (s), 1458 (w), 1245 (m), and 1109 (m) cm^{-1}; nmr ($CDCl_3$) τ 2.68 (A_2B_2 type, m, 4, aromatic), 4.85 (t, 1, H_9), and 5.86 (d, 2, bridgehead).

Anal. Calcd for $C_{11}H_7O_2Cl$: C, 63.94; H, 3.42; Cl, 17.16. Found: C, 63.64; H, 3.44; Cl, 17.26.

Methyl 1,3-Methano-*exo*-8-chloro-*exo*- and -*endo*-2-indancarboxylates (8 and 9). To 28 g (0.126 mol) of **4** in 560 ml of methylene chloride was added 30.5 g (0.164 mol) of *p*-toluenesulfonylhydrazine and 29 g of dry magnesium sulfate. The resulting suspension was stirred at room temperature for 3 hr. The solution thus obtained was poured onto 1 kg of alumina in a column and eluted with methylene chloride. The bright yellow solution eluted was stripped of the solvent to yield an orange-yellow glassy solid having a characteristic absorption band at 2120 cm^{-1} in the infrared region. This α-diazo ketone **5** could be used without further purification in the next irradiation.

A solution of **5** in 800 ml of spectrograde dioxane and 400 ml of distilled water containing 15 g of sodium bicarbonate was stirred at 15–20° and irradiated at room temperature under nitrogen atmosphere using a 300-W high-pressure mercury lamp filtered by a Pyrex glass tube. When the infrared spectrum showed no remaining diazo peak, the solution was made alkaline with potassium carbonate and extracted with ether several times to remove neutral products. The aqueous layer was carefully acidified with cold dilute hydrochloric acid and extracted with ether; then the ether solution was washed with water. After drying, removal of the solvent gave 6.25 g of a semisolid containing the acids **6** and **7**. The solid was purified by recrystallization from chloroform or by conversion into a methyl ester mixture with diazomethane, followed by distillation. Distillation gave 3.5 g (12%) of a 2:3 mixture of **8** and **9**. Separation of **8** and **9** was accomplished by elution chromatography over Florisil, using a mixed solvent of ether and pentane. Pure **8**, mp 75.2–75.7°, and **9**, mp 103–103.5°, were obtained. Infrared spectra in CCl_4 show bands, for **8**, at 1740 (s), 1431 (m), 1338 (m), 1272 (s), 1228 (s), 1200 (m), and 1039 (m) cm^{-1} and, for **9**, at 1743 (s), 1433 (w), 1343 (w), 1261 (w), 1228 (s), 1203 (m), 1055 (m), and 1045 (m) cm^{-1}.

Anal. Calcd for $C_{12}H_{11}O_2Cl$: C, 64.73; H, 4.98; Cl, 15.92. Found for **8**: C, 64.88; H, 5.05; Cl, 15.99. Found for **9**: C, 64.82; H, 5.08.

Hydrolysis of 9. A solution of 340 mg (1.44 mmol) of **9** and 0.5 g of potassium hydroxide in 5 ml of methanol was stirred at room temperature overnight. The mixture was poured into water and extracted with ether. Removal of the solvent followed by sublimation gave 0.26 g (84%) of **7**, mp 206° dec. A sample for analysis was obtained by recrystallization from chloroform, mp 206° dec. Esterification of **7** with diazomethane in ether gave only **9**.

Anal. Calcd for $C_{11}H_9O_2Cl$: C, 63.32; H, 4.35. Found: C, 63.12; H, 4.36.

1,3-Methano-*exo*-8-chloroindan-*endo*-2-yldi-*n*-butylcarbinol (10). A solution of 0.7 mmol of *n*-butyllithium in hexane (approximately a 15% solution) was added to a stirred solution of 55 mg (0.25 mmol) of **9** in 3 ml of tetrahydrofuran and the mixture heated at 50° for 10 min. The resulting solution was poured into 30 ml of distilled water and extracted with ether. After the ether solution was washed with water and dried, the solvent was removed to yield a white crystalline solid. Distillation of this material gave 0.06 g (72%) of **10** as colorless crystals, mp 62–63°; ir (CCl_4) 3620 (m), 2950 (s), 2850 (m), 1468 (w), 1460 (m), 1450 (w), 1372 (w), 1270 (m), and 1180 (m) cm^{-1}.

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[25] R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

[26] This type of calculation may be found in J. D. Roberts, "Molecular Orbital Calculations," W. A. Benjamin, Inc., New York, N. Y., 1961, pp 82–90.

[27] The reaction, if concentrated nitric acid is used, sometimes proceeds violently. The use of dilute nitric acid is recommended.

[28] (a) P. M. Subramanian, M. T. Emerson, and N. A. LeBel, *J. Org. Chem.*, **30**, 2624 (1965); (b) J. W. Wilt, G. Gutman, W. J. Ranus, Jr., and A. R. Zigman, *ibid.*, **32**, 893 (1967).

Anal. Calcd for $C_{19}H_{27}OCl$: C, 74.36; H, 8.87; Cl, 11.55. Found: C, 74.29; H, 8.78; Cl, 11.67.

9,9-Dimethyl-2,1,3-(epoxyethanylylidene)indan (11). A solution of 1.8 mmol (1.5 ml) of methyllithium in ether was added to a stirred solution of 0.11 g (0.5 mmol) of **8** in 6 ml of ether under ice cooling. The colorless solution soon became muddy to white due to the deposit of lithium chloride, and then the color turned gradually to a clear reddish-brown. After stirring for 1 hr, the solution was poured into distilled water, extracted with ether, and dried. Removal of the solvent gave a brown oil, which was dissolved in pentane for elution chromatography over Florisil. The fraction that was eluted by a 9:1 mixture of pentane and ether contained 35 mg (38%) of **11** as white crystals, mp 121°. An analytical sample was obtained by recrystallization from pentane, followed by sublimation under reduced pressure at 60–80°, mp 121.5–122.5°; ir (CCl_4) 1460 (m), 1385 (w), 1371 (m), 1296 (s), 1220 (m), 1155 (m), 1068 (s), and 985 (s) cm^{-1}.

Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.44; H, 7.54.

The reaction of **8** and *n*-butyllithium in tetrahydrofuran did not afford any analytically pure material. The reaction mixture was quenched by pouring it into distilled water. Titration of lithium chloride formed by the reaction showed that dehalogenation proceeded quantitatively.

1,3-Methano-*exo*-2-chloroindan (12). A mixture of 0.65 g (3.1 mmol) of **7**, 2.30 g (5.2 mmol) of lead tetraacetate, and 9 ml of glacial acetic acid was stirred at room temperature; then 3.30 g (39.3 mmol) of anhydrous potassium carbonate was added and the mixture immediately flushed with nitrogen. The reaction flask was placed in an oil bath at 70° for 3 hr and the resulting solution poured into water. The extracted etherate was treated with aqueous sodium bicarbonate, and 0.13 g (20%) of **7** was recovered. Distillation of the neutral fraction gave 0.18 g (35%) of **12** as a colorless oil, bp 102–105° (14 mm), $n^{24}D$ 1.5723; ir (CCl_4) 1460 (s), 1446 (m), 1429 (w), 1263 (s), 1223 (m), 1187 (m), 1030 (s), 1003 (w), and 885 (m) cm^{-1}.

Anal. Calcd for $C_{10}H_9Cl$: C, 72.96; H, 5.51; Cl, 21.53. Found: C, 73.23; H, 5.61; Cl, 21.07.

Dehalogenation Reaction of 12. A mixture of 0.16 g (1 mmol) of **12**, 1 ml of dry dioxane, and a large excess of chipped sodium metal was heated at 100° for 10 min in a nitrogen stream. After cooling to room temperature, the reaction mixture was quenched by the addition of water and extracted with pentane. The solvent was stripped off and the remaining oil distilled to obtain **16** in a quantitative yield. The nmr spectrum of this compound was identical with that reported.[3]

Anal. Calcd for $C_{10}H_{10}$: C, 92.26; H, 7.74. Found: C, 92.25; H, 8.12.

1,3-Methano-*exo*-2-indanol (13) and Its Acetate (14). A solution of 0.08 g (0.5 mmol) of **12** in 3 ml of 50% aqueous acetic acid was put into a sealed tube and heated for 20 hr at 105°. After cooling, the reaction solution was poured into water and extracted with ether several times. The ether solution was washed with saturated sodium bicarbonate and cold water and dried. The solvent was removed to yield 70 mg of a semisolid material which was a mixture of an alcohol and an acetate. The mixture was cooled on an ice bath and a few drops of pentane added. The pentane layer contained mainly **14** and was treated by column chromatography over Florisil. Distillation of the eluate under reduced pressure afforded 10 mg of **14**; $n^{24.6}D$ 1.5340; ir (CCl_4) 1745 (s), 1460 (w), 1375 (w), 1231 (s), 1198 (m), 1046 (m), and 1036 (w) cm^{-1}.

Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.55; H, 6.43.

Crystals insoluble in pentane (21 mg) were sublimed at 80° (1 mm) and then recrystallized from *n*-hexane to yield 19 mg (26%) of **13**, mp 98°, as colorless prisms; ir (CCl_4) 3650 (w), 1458 (w), 1210 (w), 1193 (s), 1180 (m), 1063 (s), and 846 (w) cm^{-1}. Treatment of **13** with acetic anhydride in pyridine afforded **14**.

Anal. Calcd for $C_{10}H_{10}O$: C, 82.16; H, 6.90. Found: C, 81.92; H, 6.92.

1,3-Methano-*exo*-2-indanyl *p*-Toluenesulfonate (15). A solution of 19.5 mg (0.13 mmol) of **13** in 0.5 ml of dry pyridine was cooled on an ice bath and 30 mg (0.16 mmol) of *p*-toluenesulfonyl chloride added. The reaction vessel was kept at 0–5° overnight, and the pyridine solution then poured onto ice and extracted with ether. The ether solution was washed, under cooling, with dilute sulfuric acid, water, and sodium bicarbonate, and then dried. Evaporation of the solvent gave 38 mg of a solid. This solid was eluted over 1 g of alumina in a column with ether and recrystallized from *n*-hexane to yield 19 mg (50%) of **15**, mp 76–77°; ir (CH_2Cl_2) 1603 (s), 1365 (s), 1189 (s), 1176 (s), 1098 (m), 1042 (m), 970 (s), and 865 (s) cm^{-1}.

Anal. Calcd for $C_{17}H_{16}O_3S$: C, 67.97; H, 5.73. Found: C, 67.73; H, 5.44.

Lithium aluminum hydride reduction of **15** in tetrahydrofuran gave **16** in a poor yield.

Kinetic Measurements. The acetolysis reactions were run in an anhydrous acetic acid solution,[29] which was 0.00646 *M* in sodium acetate and 0.00519 *M* in **15**. Samples (1 ml) in individually sealed ampoules were removed at appropriate intervals and cooled in an ice bath. The contents of each ampoule were diluted with 1 ml of acetone and the residual sodium acetate titrated with 0.00769 *M* perchloric acid in acetic acid on a E-336A Metrohm-Herisau potentiograph. The experimental infinity titers at ten half-lives were consistently within 2% of the calculated values. Plots of log $(A_\infty - A_t)$ *vs.* time were uniformly linear, where A_∞ and A_t are titers at infinity and at any time *t*, respectively.

Aqueous ethanol (ethanol–water, 50:50 v/v at 25°), for the hydrolysis of **12**, was prepared by adding the correct weight of water to a known weight of absolute ethanol. The chloride **12** was dissolved in 50% aqueous ethanol in a volumetric flask to prepare the solution adjusted to 0.01215 *M* in ester. The reaction procedure was similar to that in the acetolysis of **15**, but 0.01 *M* sodium hydroxide in water was used as the standard solution for titration.

Acetolysis Products. The acetolysis solution (acetolysis performed at 75° for ten half-lives) was analyzed by vpc. The vpc columns used were a 3 mm × 2 m stainless tube packed with 10% diethylene glycol succinate polyester on 60–80 mesh Chromosorb W, a 0.5 mm × 45 m Golay column coated with SE-30 silicone oil gum rubber, and 0.25 mm × 45 m Golay columns coated with Apiezon L and Ucon oil LB-550X. Analysis of the products obtained with these four kinds of columns showed only one component, and its retention time was identical with that of an authentic sample of **14**. The yield was estimated using an internal reference.

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(29) S. Winstein, E. Grunwald, and L. L. Ingraham, *J. Amer. Chem. Soc.*, **70**, 821 (1948).