were separated, and the aqueous layer was extracted twice with 4-ml portions of ether. The combined extracts were dried over magnesium sulfate, and the ether was distilled to give 0.38 g (85%) of 3-t-butylcyclobutanol as a residue that was not further purified. This residue was analyzed by gas chromatography on the 20-ft SE-30 column which indicated a composition of 91% cis and 9% trans. No other components were observed. Equilibration of 3-t-Butylcyclobutanol.—A 0.6 M solution of

aluminum isopropoxide in isopropyl alcohol was prepared by refluxing 3.28 g of aluminum and 0.16 g of mercuric chloride in 200 ml of isopropyl alcohol (reagent grade, heated at reflux over calcium oxide for 7 hr) for 8 hr.⁸¹ There was a small amount of black precipitate formed that was removed by centrifuging and decanting the clear solution. Enough solution for 5 ampoules was obtained by dissolving 0.125 g of 3-t-butylcyclobutanone (6) in 1.65 ml of the above solution, yielding a solution approxi-mately 0.6 M in each reactant. The solutions were distributed into test tubes, flushed with dry nitrogen, sealed, and immersed in baths at the temperatures indicated in Table I. The baths consisted of various liquids in flasks which were brought to reflux and maintained at their boiling points. The temperatures were found to remain constant within the limits given in Table I and were corrected with a National Bureau of Standards thermometer. The ampoules were removed at the times indicated in Table I, cooled in ice water, and opened immediately. To the contents was added 1 ml of 6 N HCl, and this solution was then extracted with two 1-ml portions of ether. After removal of the ether, the residue was analyzed by gas chromatography on the 20-ft 30% SE-30 column used above for separation of the alcohols. The equilibrium constants were calculated from the ratio of the peak areas obtained by the height times half band width method. Each value in Table I is the average of seven to ten chromatograms from at least two different tubes. Analysis of a mixture of known composition indicated that repsonse corrections were unnecessary.

As a check on the use of the ketone 6 for obtaining the equilibrium constants, mixtures rich in the cis and trans alcohols 5 were each equilibrated separately. A solution of 0.125 g of 3-t-

(31) W. G. Young, W. H. Hartung, and F. S. Crossley, J. Amer. Chem. Soc., 58, 100 (1936).

butylcyclobutanol, rich in either the cis or trans isomer, 0.31 g of ketone 6, and 1.65 ml of 0.6 M aluminum isopropoxideisopropyl alcohol was prepared and equilibrated as above. At 100°, the initial cis and trans rich mixtures gave equilibrium constants of 4.83 ± 0.14 and 4.75 ± 0.13 , respectively. At 154° the initial trans rich mixture gave an equilibrium constant of 3.62 ± 0.07 .

Equilibration of Ethyl 3-t-Butylcyclobutanecarboxylate.-The procedure used to equilibrate the esters was described previously.¹ Sealed ampoules were immersed in the baths described above at the temperatures indicated in Table I and removed at the times given. The ampoules were cooled in ice water, opened, and worked up as before.¹ The concentrate was analyzed by gas chromatography on the 20-ft 30% column used above. The retention times on this column at 130° and 200-ml/min pressure were 51 and 56 min for the cis and trans esters, respectively. The equilibrium constants were obtained by the method above, and the averages of from 9 to 18 chromatograms are given in Table I. A 50:50 mixture was used to obtain the constants at 100, 110, and 135°. As a check on the use of this mixture, pure cis and trans isomers were each independently equilibrated at 80 and 151°. The equilibrium values thus obtained from both sides were identical and have been included in the averages in Table I. Tubes were removed at several times and the compositions were found to be identical. No correction factor was necessary for calculation of the equilibrium constants, as shown by gas chromatogaphic analysis of a known mixture prepared from weighed samples of the pure esters.

Registry No.-cis-1 ethyl ester, 14924-51-7; trans-1 ethyl ester, 14924-52-8; cis-2, 24165-52-4; trans-2, 24165-53-5; cis-3, 24122-09-6; trans-3, 24122-10-9; cis-4, 24122-12-1; trans-4, 24122-13-2; cis-5, 20588-76-5; trans-5, 20476-25-9; 6, 20614-90-8.

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Studies of Benzonorbornene and Derivatives. IV.¹ Bridgehead and 1-Carbinyl Derivatives^{2,3}

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Benzonorbornenyl-1-carbinyl tosylate (1) is investigated as a possible model for a non- π -participatory neophyl system. Its solvolysis compared with that of the nonbenzo analog 9 is retarded 47-fold in acetic acid at 133° and 14-fold in 80% acetone at 25°. No evidence for anchimeric assistance by the aromatic ring was found. Under the vigorous conditions of refluxing hydrobromic acid containing zinc bromide, benzonorbornenyl-1carbinol (8) still failed to allow aromatic migration, although both methano and ethano bridge-migrated products were detected. Benzonorbornenyl-1-carbinyl radical, produced by radical-promoted decarbonylation of the aldehyde 22, did not rearrange. The absence of rearrangement illustrates the necessity of twist in the aro-matic ring during rearrangement. From benzonorbornene-1-carboxylic acid (2) synthetic prodedures to a number of the title compounds are described.

Recently our interest in benzonorbornene chemistry coincided with other interests in homoallylic π -electron systems⁴ and ring-size effects in the neophyl rearrangements.⁵ All three of these interests led to the present investigation of benzonorbornenyl-1-carbinyl deriva-

(1) Paper III: J. W. Wilt and P. Chenier, J. Org. Chem., 35, 1571 (1970). (2) Taken from the dissertations of C. A. S., 1964, and H. F. D., Jr., 1969, and the M.S. Thesis of J. P. B., 1966.

(3) Some of the material has appeared in preliminary form: J. W. Wilt and C. A. Schneider, Chem. Ind. (London), 951 (1963); J. W. Wilt, C. A. Schneider, J. P. Berliner, and H. F. Dabek, Jr., Tetrahedron Lett., 4073 (1966),

(4) J. W. Wilt, C. F. Parsons, C. A. Schneider, D. G. Schultenover, and
W. J. Wagner, J. Org. Chem., 33, 694 (1968).
(5) J. W. Wilt, L. L. Maravetz, and J. F. Zawadzki, *ibid.*, 31, 3018 (1966).

tives. Incidental to this work was the synthesis of a number of heretofore unknown bridgehead-substituted benzonorbornenes.6

(6) Of the known synthetic routes to benzonorbornene and derivatives which follow, we felt only one⁶⁰ could be developed for bridgehead substitu- White 1010W, we fail only only on the Knauss, Chem. Ber, 91, 895 (1958); (b) J.
 Meinwald and G. A. Wiley, J. Amer. Chem. Soc., 80, 3667 (1958); (c) K.
 MacKenzie, J. Chem. Soc., 43 (1960); (d) P. D. Bartlett and W. P. Giddings,
 J. Amer. Chem. Soc., 82, 1240 (1960); (e) H. Rakoff and B. H. Miles, J. Org. Chem., 26, 2581 (1961); (f) A. F. Plate and N. A. Belikova, Zh. Obshch. Khim., 30, 3945 (1960); (g) A. F. Plate, N. A. Belikova, and S. Y. Kirichenko, Neftekhimiya, 1, 494 (1961); Chem. Aber, 57, 58166 (1962); (h) K. Alder and M. Fremery, Tetrahedron, 14, 1960 (1961); (i) P. Bruek, Tetrahedron Lett., 449 (1962); (j) H. Tanida, Accounts Chem. Res., 1, 239 (1968). See also ref 1.

STUDIES OF BENZONORBORNENE AND DERIVATIVES

Synthesis and Solvolysis of Benzonorbornenyl-1carbinyl Tosylate (1).—Tosylate 1 has its aromatic ring so positioned that π participation at the carbinyl site should be precluded geometrically. The rigid nature of the bicyclic system simply prevents the twist required of the aromatic ring to achieve the phenonium ion geometry of the transition state. It therefore



seemed worthwhile to measure the effect of the aromatic ring in the solvolysis of this constrained neophyl-like tosylate. It is well recognized that the aromatic ring retards solvolysis by induction (-I effect), but the real magnitude of the effect is normally masked by the accelerating influence of the aromatic ring via π participation.⁷ The calculated value of ca. eightfold given by Streitwieser⁸ is commonly used for this effect, but little direct experimental evidence is available.⁹

Benzonorbornene-1-carboxylic acid (2) was synthesized from norbornene-1-carboxylic acid⁴ via the sequence shown below in Chart I. The sequence was modeled after that of Mackenzie.⁶



 ⁽⁷⁾ E. Kosower, "An Introduction to Physical Organic Chemistry,"
 John Wiley and Sons, Inc., New York, N. Y., 1968, p 125.
 (8) A Strainburg In Chem. Rev. E 513 (1987)

(8) A. Streitwieser, Jr., Chem. Rev., 56, 718 (1956).

Tosylate 1 was then made by the usual method via the carbinol 8. The solvolysis rate data for 1 and other selected tosylates are gathered in Table I. In acetic acid 1 is somewhat slower than neopentyl tosylate or 9 and much slower than neophyl tosylate. As this last is generally considered a model for π -assisted acetolysis,¹⁰ it appears that π participation in 1 has been precluded. However, σ participation (principally by the *ethano* bridge) is unfortunately still possible; so it is difficult to ascribe a value for the -I effect of the aromatic ring on the *completely unassisted* process. In any event, based on neopentyl tosylate and 9, the aromatic ring reduced reactivity 12- and 47-fold at 133°. Based on neophyl tosylate, reactivity was reduced 800-fold at this temperature.

	TABLE I					
Solvolytic Rate Data						
$Tosylate^{a,b}$	Temp, °C ^c	$10^{5}k_{1}$, sec $^{-1}$				
Λ	132.0	1.18 ± 0.04				
	139.0	2.07 ± 0.13				
	156.0	6.66 ± 0.14				
	^{1s} 25	$(8.0 \times 10^{-11})^{e}$				
Ci A						
	139.0	~ 0.3				
	CH_2OTs					
Ci Ci	109.0	2.24 ± 0.10				
Λ	120.0	6.30 ± 0.19				
91	130.0	14.0 ± 0.04				
CH.OTs	25	$(1.1 \times 10^{-9})^{o}$				
Tosylate ^{a,g}						
	110.0	0.102 ± 0.01				
·1 ^ħ	131.0	0.553 ± 0.04				
	154.0	5.57 ± 0.48				
9	99.5	1.13 ± 0.12^i				
	133.0	27.0 ± 1.0				
Neopentyl	133.0	6.8 ^{e,j}				
Neophyl	133.0	470 ^{e,k}				

^a Ca. 0.03 M tosylate solutions were used, except for 11 which was 6×10^{-2} M. ^b In 80% acetone-20% water (v/v) containing ca. 0.033 M sym-collidine. ^c ±0.05°. ^d $\Delta H^* = 25.8 \pm 0.2$ kcal mol⁻¹, $\Delta S^* = -17.9 \pm 0.2$ eu. ^e Extrapolated from data at other temperatures. ^f $\Delta H^* = 26.0 \pm 0.3$ kcal mol⁻¹, $\Delta S^* = -12.4 \pm 0.3$ eu. k_{rel}^{236} for 1, 1; 9, 14. ^e In glacial acetic acid containing acetic anhydride (0.3%) and excess sodium acetate (1.5 mmol/mmol of tosylate). ^h $\Delta H^* = 27.9 \pm 0.2$ kcal mol⁻¹, $\Delta S^* = -13.7 \pm 0.5$ eu. k_{rel}^{136} for 1, 1; neopentyl-OTs, 12; 9, 47; neophyl-OTs, 800. ^e Lit. value, 1.17 $\times 10^{-5}$ sec⁻¹ at 99.7°: R. L. Bixler and C. Niemann, J. Org. Chem., 23, 742 (1958). ⁱ S. Winstein and H. Marshall, J. Amer. Chem. Soc., 74, 1120 (1952). ^kS. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *ibid.*, 74, 1113 (1952).

In 80% acetone at 25° the retardation observed with 1 is 14-fold relative to 9.¹¹ This 14-fold value compares well with the value of 16 obtained in an earlier study⁴ in 60% acetone for the retardation caused by a homoallylic double bond. The comparison emphasizes the inductive similarity of the two π systems, the aromatic

(10) I. L. Reich, A. Diaz, and S. Winstein, ibid., 91, 5635, 5637 (1969).

⁽⁹⁾ Very recently the value 3.7 has been given for the 2-phenylethyl system by J. L. Coke, F. E. McFarlane, M. C. Mourning, and M. G. Jones, J. Amer. Chem. Soc., 91, 1154 (1969).

⁽¹¹⁾ It seems clear that there is no one value for the -I effect of the aromatic ring. This effect will vary with the demand in the transition state for a process, and this demand varies with conditions. So to know the applicable value one must study the reactant in question and an appropriate model under the same conditions. We favor 1 as a model for neophyl systems, even though 1 is not itself probably free from *all* participation.

ring, and the double bond. Indeed, norbornenyl-1carbinyl tosylate (10) and tosylate 1 solvolyzed at comparable rates in 80% acetone at $131^{\circ,12}$ This similarity was demonstrated also by pK_{a} studies (see below).

In Chart II are shown the solvolysis pathways and products observed with 1. Acetolysis of 1 showed poor first-order kinetics (negative drift). An inert, re-



arranged tosylate (12-OTs) could be separated from the reaction material. Although its structure was not proved by independent synthesis, and must therefore be open to question, 12-OTs is probably benzobicyclo[2.2.2]octen-1-yl tosylate. It was not 1 and it is unlikely that it could be benzobicyclo[3.2.1]oct-6en-1-yl tosylate (13-OTs). Attempts to make the latter from the 13 obtained in the hydrolysis study were unsuccessful. The structure 13-OTs is considered unlikely because Bly and coworkers¹³ have demonstrated that the *olefinic* analogs of 12-OTs and 13-OTs differ greatly in acetolytic reactivity. The former is very slow whereas the latter is much faster, faster even than the norbornenyl compound 10. So on this basis one expects 12-OTs to be the bicyclo-[2.2.2]octenyl derivative. Such an assignment of structure is also supported by spectra (see Experimental Section).

The formation of the other products can be formulated in terms of discrete σ -assisted processes (k_{Δ}^{σ}) and unassisted processes (k_s) , as indicated in Chart II. In light of the recent elucidation of σ assistance in acetolysis of neopentyl tosylate,¹⁰ this formulation is probably preferrable to another view involving completely unassisted ionization *followed* by skeletal rearrangement.¹⁴ It should be noted, however, that no product of aromatic migration was observed, so π assistance (k_{Δ}^{π}) , if present at all, is not detectable in this manner.

The change to aqueous acetone effectively removed ion-pair return. Besides starting material 1, there were found only unrearranged alcohol 8 and ethano bridge-migrated product 13. No evidence for 12-OTs or its alcohol was found though trace amounts of the latter cannot be discounted. Once more, no aromatic migration was observed. The structure of 13 was assigned by analogy to the formation of bicyclo [3.2.1]oct-6-en-1-ol in the earlier study of 10 under similar conditions,⁴ and by the proton resonance at δ 2.27, ascribed to the endo C-3 proton. This resonance, also observed in 13-OAc at δ 2.20, was prominent in the bona fide parent hydrocarbon 18 (δ 2.25) but was absent in the benzonorbornenyl-1-carbinyl and benzobicyclo [2.2.2] octenyl series of compounds prepared in this work. We attribute this downfield resonance to a deshielding effect of the aromatic ring, as shown in one conformer of this ring system.



The increased preference for ethano (rather than methano) bridge migration in these systems during hydrolysis compared to acetolysis was previously observed and discussed.⁴ The significant increase in unrearranged product during hydrolysis may be the result of increased unassisted solvolysis (k_s). Even though a more ionizing solvent than acetic acid (Y = $-0.7 \ vs. \ -1.6^{15}$), 80% acetone is also more nucleophilic because of its aqueous content. Both features tend to increase overall solvolysis rates, but the latter feature would certainly change the partitioning of the total rate between k_s and k_{Δ} processes relative to acetolysis. Unassisted (k_s) processes proceed without rearrangement;¹⁰ hence **8** predominates in the aqueous acetone.

Cationic Rearrangement of Benzonorbornenyl-1carbinol (8).—Carbinol 8 was subjected to vigorous treatment in hydrobromic acid containing zinc bromide

⁽¹²⁾ J. W. Wilt and H. F. Dabek, Jr., unpublished work.

⁽¹³⁾ R. S. Bly and E. K. Quinn, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, Abstracts, Paper 910. We appreciate the details of this work from Professor Bly.

⁽¹⁴⁾ J. E. Nordlander, S. P. Jindal, P. von R. Schleyer, R. Fort, Jr., J.

J. Harper, and R. D. Nicholas, J. Amer. Chem. Soc., 88, 4475 (1966). (15) Reference 7, p 311.



as shown in Chart III. The bromide isomers were best identified as their parent hydrocarbons formed by reduction. Again the principal rearrangement was *via* ethano bridge migration (as in solvolysis) although the exact product composition was time dependent. But now an increased percentage of methano bridge migration was observed as well. Aromatic migration was still absent (no 20 was observed). The various intermediate ions probably involved and their interconversions as suggested by the solvolysis data previously discussed are also given in Chart III. The severity of the conditions was apparently such that the barrier to either alkyl migration was now more readily surmountable but not the barrier to aromatic migration.

Carbinol 8 was much less easily rearranged (95% reaction at 150° for 6.5 hr) than norbornyl-1-carbinol (21, ca. 100% reaction at 80° for 4 hr¹⁶). Also, ethano bridge migration predominated in 8 whereas methano bridge migration did so in 21. In the rapid reaction of 21, the more acute methano bridge angle in the starting material presumably is of more importance. In the slow reaction of 8 the relative stabilities of the product ions determine the course of the process.¹⁷ Similar but more detailed reasoning has been advanced

- (16) W. P. Whelan, Jr., Dissertation, Columbia University, 1952, pp 61-62.
 - (17) G. S. Hammond, J. Amer. Chem. Soc., 77, 334 (1955).

for the analogous transformations of the related tosylates 9 and 10.4

Decarbonylation of Benzonorbornenyl-1-acetaldehyde (22).—The decarbonylation of aldehyde 22 was investigated because past work¹⁸ has shown that geometric restraint on the aromatic ring can decrease the extent of the neophyl radical rearrangement.

Conversion of acid 2 to its homologous acetic acid 23 via the Arndt-Eistert reaction followed by reduction to alcohol 24 and oxidation of its tosylate produced 22.



Treatment of a 1 M solution of 22 in chlorobenzene with di-*t*-butyl peroxide gave 92% of the theoretical carbon monoxide and *only* 1-methylbenzonorbornene (17).



rearrangement

A control study showed that the other possible hydrocarbons (18-20) were totally absent. So the carbinyl radical no more allowed aromatic migration than did the cation. Moreover, as alkyl shifts in radicals are energetically improbable, the radical underwent chain transfer solely to 17. Under similar conditions less constrained neophyl-type radicals rearrange significantly.⁵

Acidity Constants.—As a final demonstration of the inductive effect of the aromatic ring in acid 2, its pK_a along with those of other relevant acids were determined. The results are collected in Table II, and they further illustrate the similar effects of the homo-allylically positioned vinyl and aromatic functions, *ca.* 0.4–0.5 pK unit compared to the corresponding saturated model in the systems shown. Acid 7 (with its tetrachloroaryl function) is actually somewhat stronger than benzoic acid in 75% acetone.

Synthesis of Various Bridgehead-Substituted Benzonorbornenes.—To illustrate its utility as a precursor to the heretofore unknown 1-substituted benzonorbornenes, acid 2 or its acid chloride was converted into a number of these as given in Chart IV. Experimental details are available upon request, but the methods used were based on those given under the literature references.

⁽¹⁸⁾ J. W. Wilt and C. A. Schneider, J. Org. Chem., 26, 4196 (1961).

	50% EtOH-H ₂ O (v/v)	75% acetone- H ₂ O (v/v)			
Соон	5.88	7.09			
		6.56			
Соон	5.98	7.61			
Соон	6.37				
Соон	6.20				
Соон	6.62				
Соон	6.35				
Схоон	6.28				
(CH ₃) ₃ CCOOH	6.48	7.64			
COOH	5.50	6.71			

TABLE II ACIDITY CONSTANTS, 25°

Experimental Section

Melting points (Fisher-Johns block) and boiling points are uncorrected. The following instruments were used for spectral work: nmr, Varian A-60A; ir, Perkin-Elmer Model 21 and Infracord, Beckman IR-5A; uv, Beckman DK-2 and Bausch and Lomb Spectronic 505. Nmr data are given in parts per million (δ units) relative to internal TMS, with the usual splitting abbreviations being used. The centers of multiplets are given. Area integrations were within 10% of the proper value. Only significant ir (λ) absorptions are listed, in microns (μ) . Ultraviolet maxima (λ^{max}) are given in millimicrons $(m\mu)$. Gasliquid partition chromatography (glpc) was performed on a Varian Aerograph A-90P with helium gas as carrier. Microanalyses were done by Galbraith Laboratories, Knoxville, Tenn., and by Micro-Tech Laboratories, Skokie, Ill. A number of the preparations were exploratory and the yields may not be optimum. The petroleum ether used throughout the work was a 30-60° boiling point fraction.

5,6,7,8-Tetrachloro-9,9-dimethoxy-1,4:5,8-dimethano-1,2,3,-4,5,5a,8,8a-octahydronaphthalene-1-carboxylic Acid (4).—Norbornene-1-carboxylic acid⁴ (3, 50 g, 0.362 mol) was heated at 165° under nitrogen for 6 hr with 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene¹⁹ (250 g, 0.9 mol). The reaction material occasionally solidified during the process, otherwise upon cooling. The solid mass was triturated with hexane to remove excess reactant, leaving a cream-colored powder (125 g, 85%, mp 218-219°). The material could be recrystallized from methanol as a white crystalline solid: mp 225-227°; $\delta^{\text{CDC1}s}$ 10.23 br (COOH), 3.60 s, 3.55 s (2 OCH₃), 2.77 q (5a,8a-H's, AB, J = 8cps), 2.33 m (4-H), 1.15-1.9 m (all other H's); λ^{Nulol} 3.5-4.0, 5.83, (COOH), 6.19 (C==C).

(19) J. S. Newcomer and E. T. McBee, J. Amer. Chem. Soc., 71, 946 (1949).

Anal. Calcd for C₁₅H₁₆O₄Cl₄: C, 44.80; H, 4.01. Found: C, 44.62; H, 3.96.

Use of toluene or xylene as solvents in the above reaction heated for several days led to 4 in ca. 75% yield.

The methyl ester of 4 was prepared in acetone from the acid and dimethyl sulfate in the presence of sodium carbonate: pale yellow oil, 72%, bp 163–164° (0.1 mm), n^{24} D 1.5379; δ^{CC1_4} essentially same as that of 4 minus the acid proton and with 3.63 s, 3.57 s, 3.47 s (3 OCH₃); λ^{neat} 5.72 (C=O), 6.21 (C=C).

Anal. Caled for C₁₆H₁₈O₄Cl₄: C, 46.18; H, 4.37. Found: C, 46.24, H, 4.19.

The configurations of 4 and its methyl ester were not proved. That shown for 4 in Chart I (text) is probably correct based upon similar compounds.²⁰

5,6,7,8-Tetrachloro-9-keto-1,4:5,8-dimethano-1,2,3,4,5,5a,8,-8a-octahydronaphthalene-1-carboxylic Acid (5).—The procedure given involves critical ratios of reactants. Other proportions gave poor results. Acid 4 (20 g, 0.05 mol) in concentrated sulfuric acid (80 ml) was stirred at 25° for 55 min and then poured slowly onto crushed ice (165 g). The precipitated solid was collected, triturated with water, and dried: 16.8 g, 95%, mp 140-142° dec with loss of carbon monoxide followed by resolidification and eventual melting at ca. 230°; δ^{CDCIs} 10.23 br s (COOH), 2.92 q (upfield pair obscured, 5a,8a-H's, AB, $J \sim 8$ cps), 2.65 m (4-H), 1.3-2.0 m (all other H's); λ^{Nuiol} 2.9-4.0, 5.82 (COOH), 5.45 (9-CO), 6.24 (C=C). As 5 decomposed upon recrystallization from ether-petroleum ether, the crude material was analyzed. The analysis is considered satisfactory allowing for the nature of the compound.

Anal. Calcd for C₁₈H₁₀O₃Cl₄: C, 43.85; H, 2.83. Found: C, 42.97; H, 3.10.

5,6,7,8-Tetrachloro-1,4-methano-1,2,3,4,5a,8a-hexahydronaphthalene-1-carboxylic Acid (6).—Acid 5 (150 g, 0.421 mol) was slowly heated to reflux in o-dichlorobenzene (1500 ml).^{20a,b} Evolution of carbon monoxide²¹ continued for 2 hr, after which the solvent was removed under reduced pressure with a nitrogen bleed. The residue was triturated with benzene to give 6 as a tan solid (132.5 g, 89.5%, mp 230-232°). The acid was recrystallized from methanol: microcrystalline white solid, mp 240-241°, δ^{pyriding} 3.33 q (5a,8a-H's, AB, J = 12 cps), 2.72 m (4-H), 1.4-2.5 m (all other H's); λ^{Nuiol} 3.4-4.4, 5.96 (COOH), 6.23 (C==C); $\lambda^{\text{max}}_{\text{OHCIs}}$ 282 (ϵ 3267), 293 (3367), 306 (3367), 319 (3233).²²

Anal. Calcd for C₁₂H₁₀O₂Cl₄: C, 43.94; H, 3.07. Found: C, 44.12; H, 2.69.

ar-Tetrachlorobenzonorbornene-1-carboxylic Acid (7).—A mixture of bromine (82 g, 0.51 mol), acid 6 (128 g, 0.39 mol), and chlorobenzene (650 ml) was heated under reflux with stirring for 7.5 hr. Hydrogen bromide was steadily evolved. The solvent was removed on a rotary evaporator and the solid residue triturated with hexane and dried to give crude 7 (~128 g, 100%, mp 200-202°). Recrystallization from aqueous methanol produced a glistening crystalline solid: mp 204-205.5°, $\delta_{\rm pyridine}$ 3.7 m (bridgehead H), 1.0-2.9 m (other ring H's); $\lambda^{\rm Nujol}$ 3.2-4.0, 5.90 (COOH) 13.15; $\lambda_{\rm CHCls}^{\rm max}$ 247 (ϵ 3217), 284 (1283), 295 (1300).²²

Anal. Calcd for $C_{12}H_8O_2Cl_4$: C, 44.20; H, 2.48. Found: C, 44.11; H, 2.51.

The methyl ester was prepared by reaction of 7 with diazomethane. The white crystalline product was recrystallized several times from methanol: mp 123-124.5°, δ^{CC14} 3.90 s

(20) (a) S. B. Soloway, Dissertation, University of Colorado, 1955;
 J. G. Martin and R. K. Hill, Chem. Rev., 61, 537 (1961); (b) C. F. H. Allen and J. Van Allan, J. Amer. Chem. Soc., 64, 1260 (1942).

(21) The decarbonylation is probably concerted and sigmasymmetric (disrotary); cf. J. E. Baldwin, Can. J. Chem., 44, 2051 (1966).

(22) MacKenzie⁶⁰ employed uv spectra to differentiate hydroaromatic and aromatic compounds in a similar series. For the following tetrachlorodihydro aromatic substance (i) prepared by him the uv λ^{\max} are: 279, 290,



302, and 316 m μ . The aromatized compound (ii) possessed λ^{max} at 222, 284, and 292 m μ . In each case the agreement with compounds 6 and 7 is good.

		Analyses, %ª			
x	Mp, bp (mm), °C	C	H	$\mathbf{X} \operatorname{spectra}^{b}$	Lit. ref
CONH_2	156-157	76.98	7.00	5.7-7.0 m	c
	(from benzene)	77.26	6.99	3.00, 3.15,	
				6.0-6.2	
\mathbf{CN}	^d	85.17	6.55		е
		85.04	6.58	4.5	
CHO1	^d	83.68	7.03	10.15 s	g
		83.67	7.09	3.6, 3.7, 5.81	
COOCH ₃	106-110(0.2)	77.20	6.98	3.67 s	h
		77.00	7.18	5.81	
$\mathrm{COCH}_{\mathfrak{z}^{i,j}}$	90-93 (0.1)	<i>83.83</i>	7.58	2.25 s	k
		83.72	7.68	5.9, 7.4	
OCOCH3 ¹	82-84(0.2)	77.2	6.980	2.10 s	m
		77.31	7.14	5.78, 8.08	
ОН	^d	82.46	7.55	$6.0 s^n$	0
		82.29	7.43	3.05	
Br	68-70(0.1)	59.21	4.97	· · · · ^p	q
		59.42	5.13		-
NH ₃ + Cl ^{-r,s}	240–245 dec	Cl ^t 18.12,		7.0-8.5	m
	(from ether-butanol)	18.21		3.3 - 4.3	
Cl	^d	73.95	6.21	<i>p</i>	u
		74.10	6.30		

CHART IV **1-SUBSTITUTED BENZONORBORNENES**



^a Microanalyses were performed by Micro-Tech Laboratories, Skokie, Ill. The italicized values are the calculated figures. ^b The italicized spectra are nmr δ values indicative of the group X. Solutions in CCl₄ or CDCl₃ were used. The spectra were determined at 60 MHz relative to TMS. The other (λ) spectral data are infrared maxima indicative of the group X. Spectra were determined at 60 MHz relative to TMS. The other (λ) spectral data are infrared maxima indicative of the group X. Spectra were determined on neat liquids or on KBr disks of solids. ^e R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 5th ed, John Wiley & Sons, Inc., New York, N. Y., 1964, p 235. ^d Not determined. The material was collected by gas-liquid partition chromatography or by molecular distillation. ^e J. Thurman, *Chem. Ind.* (London), 752 (1964). ^f 2,4-Dinitrophenylhydrazone, mp 173.5-175° from ethyl acetate. *Anal.* Calcd for C₁₈H₁₈O₄N₄: N, 15.91. Found: N, 16.19. ^g H. C. Brown and R. F. McFarlin, *J. Amer. Chem. Soc.*, 80, 5372 (1958). ^b From the acid 2 and diazomethane. ⁱ 2,4-Dinitrophenylhydrazone, mp 161-162° from ethyl acetate. *Anal.* Calcd for C₁₈H₁₈O₄N₄: N, 15.14. ^j Oxime, mp 120.5-129° from aqueous methanol. It is a mixture of stereoisomers. *Anal.* Calcd for C₁₃H₁₆ON: N, 6.96. Found: N, 7.13. ^k C. DePuy, G. Dappen, K. Eilers, and R. Klein, *J. Org. Chem.*, 29, 2813 (1964). ⁱ Other methods of synthesis were also employed. The best is referenced. ^m J. W. Wilt, C. F. Parsons, C. A. Schneider, D. G. Schultenover, and W. J. Wagner, *J. Org. Chem.*, 33, 694 (1968). ⁿ Varies with concentration and ^a Microanalyses were performed by Micro-Tech Laboratories, Skokie, Ill. The italicized values are the calculated figures. ^b The C. F. Parsons, C. A. Schneider, D. G. Schultenover, and W. J. Wagner, J. Org. Chem., 33, 694 (1968). "Varies with concentration and temperature. Saponification of the acetate with alkali. » No characteristic spectra. «C. Grob, M. Ohta, R. Renk, and A. Weiss, *Helv. Chim. Acta*, 41, 1191 (1959). ^{*} Acetamide, mp 156.5-157.5° from aqueous methanol. *Anal.* Calcd for $C_{13}H_{15}ON$: C, 77.58; H, 7.51. Found: C, 77.62; H, 7.55. ^{*} Benzamide, mp 150.5-151.5° from aqueous methanol. *Anal.* Calcd for $C_{13}H_{15}ON$: C, 82.10; H, 6.51. Found: C, 81.96; H, 6.45. ^{*} Volhard determination of ionic chloride. ^{*}J. Kochi, J. Org. Chem., **30**, 3265 (1965); J. Amer. Chem. Soc., 87, 2500 (1965).

(COOCH₃), 3.81 m (bridgehead H), 2.5–1.2 series of multiplets (other ring H's); λ^{CCl_4} 5.83, 8.0 (-COOCH₃).

Anal. Calcd for C13H10O2Cl4: C, 45.92; H, 2.96. Found: C, 46.26; H, 2.97.

Benzonorbornene-1-carboxylic Acid (2).-Acid 7 (11.7 g, 0.036 mol) and aqueous potassium hydroxide (81 g of 85% material) in 800 ml of water were stirred on a steam bath until homogeneous. Raney nickel catalyst²³ (powder, 50 g) was then added portionwise with stirring at a rate that kept the foaming under control. When all the catalyst had been added, the solution was stirred on the steam bath for 4 hr. The cooled solution was filtered from the catalyst and combined with aqueous washings of the catalyst. Acidification of this filtrate with concentrated hydrochloric acid (Congo Red endpoint) threw down acid 2. The acid was taken up in ether, washed, dried, and recovered by evaporation as an off-white, crystalline solid negative to Beilstein's test for halogen $(6.4 \text{ g}, 95\%, \text{mp 88-90}^\circ)$. The acid could be recrystallized from heptane or hexane as colorless prisms [mp 93-94°, δ^{CO14} 12.9 s (COOH), 7.47 m (peri Ar-H, adjacent to COOH), 7.1 sharp m (other Ar-H), 3.37 m (bridgehead H), 1.0-2.7 m (other ring H's); λ^{Nujol} 3.3-4.0, 5.95 (ČOOH), 6.32, 13.3 (Ar-H); $\lambda_{\text{CHCls}}^{\text{max}}$ 264 (e 1340), 271 (1320).

(23) Several other methods of reductive dechlorination were attempted with varying degrees of success. The preferred one in our hands is that described, modeled after that of N. P. Buu-Hoi, N. Dat Xuong, and N. van Bac, Bull. Soc. Chim Fr., 2442 (1963).

Anal. Calcd for C₁₂H₁₂O₂: C, 76.56; H, 6.44. Found: C, 76.51; H, 6.54.

The deshielding of the aromatic proton noted above is characteristic of most 1-substituted benzonorbornenes and is helpful in structural assignment. There are exceptions, however (e.g., carbinol 8).

The S-benzylisothiuronium salt of 2 was made in the usual way (mp 146-147°).²⁴ Anal. Calcd for $C_{20}H_{22}O_2N_2S$: C, 67.80; H, 6.21. Found:

C, 67.50; H, 6.43. The spent catalyst from the above preparation of 2 could not

be used effectively again. Only partial dechlorination of 7 was observed. Application of the above procedure at room temperature to acid 6 produced 1,4-methanodecahydronaphthalene-1-carboxylic acid (73%).²⁵ The acid was sublimed, recrystallized from heptane, and resublimed: white crystalline solid, mp 124.5-126°, neut equiv 205, calcd 205; δ^{CC14} 12.4 s (COOH), 1.0–2.2 m (all other H's); λ^{Nujol} 3.3–4.0, 5.92 (COOH), 13.7; blank in uv.

Anal. Calcd for C₁₂H₁₈O₂: C, 74.23; H, 9.28. Found: C, 74.23; H, 9.59.

⁽²⁴⁾ D. J. Pasto and C. R. Johnson, "Organic Structure Determination," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1969, p 404.

⁽²⁵⁾ Therefore this method²³ seems too vigorous, even under these milder conditions, for the production of unsaturated acids.

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The amide of the acid above was prepared in standard fashion²⁶ from the acid chloride and ammonia (white solid, mp 205–206° from methanol-water).

Anal. Calcd for C₁₂H₁₉OH: C, 74.61; H, 9.84. Found: C, 74.37; H, 9.89.

Benzonorbornenyl-1-carbinol (8).—Reduction of acid 2 with lithium aluminum hydride in ether in standard fashion produced carbinol 8: 99%, a difficult compound to work with but which could be recrystallized from heptane and then sublimed; mp 58-59°; $\delta^{\rm CCl_4}$ 7.03 sharp m (Ar-H), 4.05 q (-CH₂OH, AB due to adjacent asymmetric carbon, J = 11 cps, outer lines weak), 3.27 m (bridgehead H), 2.50 s (OH, removed by D₂O), 0.83-2.17 m (other ring H's); $\lambda^{\rm Nuiol}$ 3.0, 9.66, 9.75 (>C-CH₂OH), 13.3 (Ar-H). Repeated attempts did not improve the analysis and the alcohol is characterized better as its tosylate.

Anal. Caled for C₁₂H₁₄O: C, 82.76; H, 8.05. Found: C, 83.20; H, 8.24.

Benzonorbornenyl-1-carbinyl Acetate (8-OAc).—Reaction of carbinol 8 with acetic anhydride in pyridine under reflux, followed by a quench in water and treatment with dilute hydrochloric acid, afforded 8-OAc as an oil that was taken up in benzene, dried, and distilled under vacuum in a micro Hickman still for the analytical sample: 91%, δ^{CCl_4} 7.27 s (Ar-H), 4.75 q (-CH₂O-, AB due to adjacent asymmetric carbon, J = 12 cps, outer lines weak), 3.43 m (bridgehead H), 2.08 s (-OCOCH₃), 1.08-2.33 m (other ring H's); λ^{neat} 5.72, 8.04, 9.61 (-CH₂OCOCH₃), 13.2 (Ar-H).

Anal. Caled for C₁₄H₁₆O₂: C, 77.74; H, 7.46. Found: C, 77.72; H, 7.39.

Benzonorbornenyl-1-carbinyl tosylate (1) was prepared in the usual way from 8 with *p*-toluenesulfonyl chloride in pyridine:²⁷ 68%, mp 95.5–96.5° from benzene-pentane, δ^{CCl_4} (partial), 4.60 apparent s (-CH₂OSO-),3.35 m (bridgehead H); λ^{Nujol} 7.36, 8.4, 8.5 (-OSO₂-).

Anal. Calcd for $C_{19}H_{20}O_{3}S$: C, 69.51; H, 6.10. Found: C, 69.40; H, 6.13.

ar-Tetrachlorobenzonorbornenyl-1-carbinol and Tosylate 11.— Acid 7 was reduced to the carbinol with lithium aluminum hydride in ether (reflux, 24 hr). Upon recrystallization from hexane it was microcrystalline: 80%, mp 116.5-117°; $\delta^{\rm CCl_4}$ 4.35 q (-CH₂O-, AB due to adjacent asymmetric carbon, J = 11cps), 3.65 m (bridgehead H), 2.55 m (OH), 1.0-2.5 m (other ring H's); $\lambda^{\rm KBr}$ 3.15, 9.55, 9.75 (>C-CH₂OH).

Anal. Calcd for C₁₂H₁₀OCl₄: C, 46.19; H, 3.23. Found: C, 46.57; H, 3.34.

Tosylate 11 was prepared in pyridine from the carbinol and *p*-toluenesulfonyl chloride: 80%, mp 153–153.5° from hexane; $\delta^{\text{CDC1}_{8}}$ 8.1–7.28 q (AB, Ar–H), 4.83 q (–CH₂O–, AB due to adjacent asymmetric carbon, J = 10 cps), 3.63 m (brigehead H), 2.46 s (Ar–CH₃), 2.2–1.15 m (other ring H's) $\lambda^{\text{KB}_{\text{F}}}$ 7.38, 8.41, 8.55 (–OSO₂–).

Anal. Calcd for C₁₀H₁₆O₃Cl₄S: C, 48.95; H, 3.46. Found: C, 49.09; H, 3.54.

Solvolysis Rate Studies.—Attempts to study tosylates 1 and 11 in 60% acetone–40% water (as was done earlier with tosylates 9 and 10) were thwarted by lack of solubility. The tosylates were therefore studied in 80% acetone (distilled from potassium permanganate)–20% deionized water (v/v), containing symcollidine (redistilled) using sealed ampoules thermostated at various temperatures (see Table I).²⁸ Tosylate 11 was studied only at one temperature. Ampoules were removed at certain times, cooled, and opened. Water was added (so that the end point was sharper) and the excess collidine was titrated with standard 0.02 N hydrochloric acid to a bromophenol blue end point. The solvolyses were first order to over 80% completion and infinity titers (10 half-lives) were >97% of theory. Additional runs made with twice as much collidine showed essentially no rate effect, so the processes are believed to be true solvolyses with no SN2 component from the collidine.

Less satisfactory studies of 1 were done in acetic acid (distilled) containing 0.3% (v/v) acetic anhydride and sodium acetate (1.5 mmol/mmol of tosylate), again using the ampoule technique. Excess *p*-toluenesulfonic acid was added to each opened ampoule to react with the remaining sodium acetate. The excess acid was

then back-titrated with standard sodium acetate in acetic acid. Serious negative deviation from first-order kinetics occurred after ca. 60% reaction and the rate constants for 1 in acetolysis (Table I) are initial slopes. In contrast, 9 shows first-order kinetics to over 80% reaction and the infinity titer was 99% of theory. Both first order rate constants and activation parameters were calculated in both solvents by the usual methods, employing the Eyring equation for the latter. The errors given for these parameters are average deviations from the best (visual) straight line fit of the data.

Solvolysis Product Studies.—The solvolysis products from 9 in both aqueous acetone and acetic acid have been reported⁴ and they were not further investigated; nor were the products from 11. A larger scale solvolysis of 1 in 80% acetone at 150° for 4 days produced *ca*. 50% isolated product (there remained some unchanged 1), bp 103–105° at 0.5 mm. The material solidified on long standing. Preparative glpc on an SE-30 column (186°) separated the later eluting carbinol 8 (75%, confirmed with authentic material) from another alcohol (25%), to which was assigned the structure 6,7-benzobicyclo[3.2.1]oct-6-en-1-ol (13): viscous oil; δ^{CC1_4} 7.15 m (Ar–H), 3.21 m (bridgehead H), 2.27 m (*endo* C-3 proton), 2.25 s (OH), 1.32–1.87 m (other ring H's); λ^{neat} 3.0, 8.78, 8.90 (tertiary C–OH), 3.31, 3.45, 3.52, 6.9, 7.55, 7.82, 8.2, 9.4, 9.55, 9.81, 10.18, 10.7, 11.1, 11.2, 11.84, 12.3, 12.5, 13.3, 14.1, 14.8.²⁹

Anal. Calcd for C₁₂H₁₄O: C, 82.76; H, 8.05. Found: C, 82.36; H, 7.94.

Alcohol 13 (0.9 mmol) was converted into 6,7-benzobicyclo-[3.2.1]oct-6-en-1-yl acetate in standard fashion employing acetic anhydride and pyridine (10 mmol each). The acetate was collected as a colorless oil by distillation in a micro-Hickman distillation apparatus: 85%, δ^{CDCls} 7.35 m (Ar-H), 3.40 m (bridgehead H), 2.50 m (C-2 methylene), 2.20 m (endo C-3 H), 2.10 s (-OCOCH₈), 1.90-1.47 m (other ring H's); λ^{neat} 5.74, 7.95, 8.19, 13.2.

Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.74; H, 7.46. Found: C, 78.04; H, 7.42.

Attempts to prepare the tosylate of 13 were largely unsuccessful. Reaction of 13 with tosyl chloride in pyridine at 25° for 4 days led to an oily mixture of unchanged alcohol and the presumed tosylate 13-OTs. The small amount of material precluded isolation and analysis. However, after correction for the absorptions of 13, the ir spectrum of the presumed 13-OTs showed λ^{neat} 7.35, 8.36, 8.48, 8.52 (-OSO₂-), 9.09, 9.78, 10.20, 10.4-10.7 (broad), 11.32, 11.54, 12.00, 12.27, 13.24, 14.3-15.2 (broad).

The preparative acetolysis of 1 (1 g, 3 mmol) in glacial acetic acid (75 ml), acetic anhydride (1 ml), and sodium acetate trihydrate (0.61 g) was carried out under reflux for 330 hr. The solvolysis mixture was poured onto solid sodium carbonate, diluted with water, and extracted, with benzene. Removal of the benzene left an oil which was treated with petroleum ether causing a solid to precipitate (100 mg, 10% yield). Recrystallization of the solid from chloroform-petroleum ether afforded **benzobicyclo**-[2.2.2]oct-1-enyl tosylate (12-OTs): mp 99-100° (no decomposition), δ^{CC14} 7.85 d (downfield portion of Ar-H of tosyl group, A₂B₂), 7.5-6.9 m (rest of Ar-H of tosyl group and Ar-H of bicyclic), 2.90 m (bridgehead H), 2.73-2.21 m (C-6 exo and C-7 anti H's), 2.43 s (Ar-CH₃), 2.1-1.1 (other ring H's); λ^{KBr} 7.42, 7.50, 8.43, 8.55, (-OSO₂-), 10.10, 11.12, 11.59, 12.12, 12.22, 12.68, 13.18, 13.34, 14.60, 15.13.

Anal. Calcd for $C_{19}H_{20}O_3S$: C, 69.51; H, 6.10. Found: C, 69.52; H, 6.10.

While the structure assigned to 12-OTs must be considered provisional, three items support it. First, the bridgehead proton resonance at δ 2.90 is somewhat upfield from those found in benzonorbornene or 6,7-benzobicyclo[3.2.1]oct-6-ene derivatives (all > δ 3), but close to that of benzobicyclo[2.2.2]octene (δ 2.93). These differences possibly reflect the different percentage s character in these bridgehead C-H bonds. Second, the obvious inertness of the compound in acetolysis is in keeping with this

⁽²⁶⁾ N. D. Cheronis and J. B. Entrikin, "Semimicro Qualitative Organic Analysis," Interscience Publishers, Inc., New York, N. Y., 1957, p 353.
(27) R. S. Tipson, J. Org. Chem., 9, 235 (1944).

⁽²⁸⁾ For complete details, the dissertation of H. F. D., Jr., should be consulted.

⁽²⁹⁾ A mixture of alcohol **13** (69%) together with **8** (12%) and benzobicyclo[2.2.2]octen-1-ol (19%) was also prepared from *ar*-tetrachlorobenzonorbornenyl-1-carbinol. Reaction of the carbinol with fuming sulfuric acid (30% SOs) at 10° followed by solution in water led to the *ar*-tetrachloro derivatives of these alcohols. Dechlorination was then achieved with Raney nickel alloy in analogous fashion to the procedure described for acid **2**. The samples of alcohol **13** obtained by the solvolysis route from **1** and this route were identical (unpublished work).

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bridgehead derivative.¹³ Lastly, the presumed tosylate 13-OTs had a different ir spectrum from 12-OTs.

The petroleum ether mother liquor from which 12-OTs precipitated was evaporated to afford a mixture of acetates (400 mg, 62%). Analysis by glpc (SE-30, 170°) indicated two closely eluting fractions. A small first portion was possibly benzobicyclo[2.2.2] oct-2-en-1-yl acetate (12-OAc), although the small amount of material precluded positive identification. The major glpc fraction (97%) was an unresolved mixture of 8-OAc and 13-OAc, in the ratio of 37:63, respectively, as established by spectral comparison with mixtures of the authentic compounds.

Action of Carbinol 8 with Hydrobromic Acid-Zinc Bromide .-A mixture of hydrobromic acid (48%, 10 ml), zinc bromide (10 g), and carbinol 8 (0.5 g, 3 mmol) was heated at reflux with vigorous stirring for 40 hr.¹⁵ A 6.5-hr heating period was less effective, 4% unchanged 8 being left, while a 10-hr heating period at 100° effected little change in 8. The cooled material was diluted with water and extracted with hexane. The extracts were dried, freed of solvent, and distilled to afford a pale yellow oil (0.27 g, 47%, Hickmann microstill) and much residue. The distilled material showed no -OH in the ir spectrum, while the nmr spectrum was very complex, showing aromatic protons and a series of multiplets for the remaining protons from $\delta 3.4$ to 1.0. The 40-hr experiment showed no δ 3.97 singlet characteristic of carbinyl bromide 14 (-CH2Br), although some of this was observed in the 6.5-hr experiment.

To assist in product analysis, the bromides from the 6.5-hr experiment (0.5 g) were reduced in tetrahydrofuran (10 ml) and t-butyl alcohol (1.1 g) by addition of lithium shot (ca. 0.5 g).⁶ The exothermic reaction was selfsustaining for 2 hr, after which further refluxing was continued for 2 hr. Water was added to the cooled mixture and the hydrocarbon products were extracted with hexane. Preparative glpc (SE-30, 195°) of the dried extract produced a clear oil, shown by various analyses (see below) to be a mixture of hydrocarbons 17 (18%), 18 (70%), and 19 (12%).

Anal. Calcd for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: 91.37; H, 8.88. С.

1-Methylbenzonorbornene (17).—Tosylate 1 (0.75 g, 2.3 mmol) was reduced in ether with lithium aluminum hydride (0.2 g) over a 4-day reflux period (a 15-hr period left 1 unchanged). The a 4-day redux period (a 13-m period let 1 direlatinged). The customary workup and distillation in micro-Hickman still produced 17 (45%) as a colorless oil. The residue was ca. 50% recovered 1. The analytical sample of 17 was collected by glpc on Reoplex 400 (polypropylene glycol adipate) at 185°: 7.0 s (Ar-H), 3.27 m (bridgehead H), 1.55 s (CH₃), 1.00-2.33 m (other ring H's); λ^{neat} 7.27 (C-CH₃), 13.34.

Anal. Calcd for C12H14: C, 91.08; H, 8.92. Found: C, 91.24; H, 8.92.

6,7-Benzobicyclo[3.2.1] oct-6-ene (18).--6,7-Benzobicyclo-[3.2.1]oct-6-en-3-one³⁰ [1.6 g, 9.3 mmol, mp 65-67°, δ^{CCl_4} 7.13 s (Ar-H), 3.35 (bridgehead H's), 1.80-2.53 m (other ring H); λ^{KBr} 5.9 (CO), 13.08–13.3] was reduced via the Huang-Minlon method to afford 18 as a colorless oil: 1.17 g, 80%, bp 95° at 3 mm, homogeneous on SE-30 at 190° for analytical sample; δ^{CCl_4} 7.1 s (Ar-H), 3.07 p (J = 2.5 cps, bridgehead H's), 2.25 p (endo C-3 H, J = 2.5 cps), 0.62–1.83 m (other ring H's); λ^{nest} 3.32, 3.36, 3.48, 3.55, 6.81, 6.90, 9.30, 10.72, 11.52, 12.81, 13.3–13.45, 14.5; lit.^{30b} δ (medium not given) 3.01 (bridgehead H's).

Anal. Calcd for C12H14: C, 91.08; H, 8.92. Found: C, 91.01; H, 8.94.

Benzobicyclo [2.2.2] octene (19) was available from an earlier study:³¹ mp 61-62°, δ^{CC1_4} 7.18 s (Ar-H), 2.93 m (bridgehead H's), 1.53 symmetrical m (other ring H's, A_2B_2); λ^{KBr} 7.52, 8.41, 9.70, 10.71, 11.6, 13.42; lit.³² mp 61-62°.

2,3-Benzobicyclo[3.2.1] oct-2-ene (20).—The literature⁸³ preparation of this hydrocarbon was followed (81%, bp 90-92° at 5 mm). Although the product was homogeneous on SE-30 or Reoplex 400 in glpc, nmr analysis of the product indicated that **20** was contaminated (*ca*. 30%) with the isomeric 1,2,3,3a,8,8a-hexahydrocyclopenta[*a*]indene.³⁴ The latter was evidenced by

 λ^{neat} 13.15 and by nmr resonances at δ 7.08 s (Ar–H) and 3.33– 3.83 dt (poorly resolved ArCH), in good agreement with values reported for this hydrocarbon.³⁴ Hydrocarbon 20 was a pleasant smelling oil: δ^{CO14} 6.97 s (Ar–H), with multiplets centered at 2.95, 2.67, 2.47, and 1.75 (other H's); λ^{neat} 12.93, 13.5, 13.82.

Study indicated that these hydrocarbons were resolved from 17, 18, and 19 on GE-XE-60 (silicone gum, nitrile) at 180° and that neither was present in the reduced reaction product from carbinol 8 mentioned above. On the other hand, individual coinjection of authentic 17, 18, and 19 with the reaction product enhanced the appropriate glpc peak. Infrared and nmr spectra of samples of three hydrocarbons made up in the aforementioned 18:70:12 ratio matched the reaction product.

Benzonorbornenyl-1-acetic Acid (23).-Benzonorbornene-1carboxylic acid chloride (2A) was prepared from the acid and thionyl chloride (85%, bp 93-96° at 0.2 mm). The acid chloride (5.15 g, 0.025 mol) was converted at 0° into the diazoketone $(\lambda^{neat} 4.75, 6.15)$ by means of ethereal diazomethane (0.07 mol). Removal of the ether left a viscous oily product which was dissolved in dry methanol (200 ml), stirred, and treated portionwise with silver ion catalyst (silver benzoate in freshly distilled triethylamine) as described by Newman and Beal.⁸⁵ Gas evolution was vigorous after a short induction period and was complete in 15 min. After 3 more hr of stirring, the solvents were removed on a rotary evaporator, and the black residual oil was taken up in ether, washed successively with aqueous sodium bicarbonate (5%), dilute hydrochloric acid, water, and then brine, and dried and distilled. Methyl benzonorbornenyl-1-acetate was collected as a pale yellow oil (4.4 g, 81%, bp 112-117° at 0.2 mm). A sample was redistilled for analysis: bp 116° at 0.2 mm, n^{24} D 1.5327, δ^{neat} 7.05 m (Ar-H), 3.51 s (OCH₃), 3.18 m (bridgehead H), 2.90 s (-CH₂CO-), 0.95-2.11 (other ring H's); λ^{nest} 5.78, 8.40, 8.56 (-COOCH₃), 13.3.

Anal. Caled for C14H16O2: C, 77.75; H, 7.46. Found: C, 77.93; H, 7.41.

Glpc (SE-30, 180°) indicated about 1.5% contamination by methyl ester 28.

Saponification of the ester with sodium hydroxide in aqueous alcohol and acidification produced acid 23 as an oil which slowly solidified: 86%, white solid, mp 59-60° upon recrystallization from petroleum ether and sublimation (occasionally a sample had mp 64-65° but would remelt at 59-60°); δ^{CC1_4} 12.1 broad s (COOH), 7.03 sharp m (Ar-H), 3.27 m (bridgehead H), 2.97 s $(-CH_2CO-)$, 1.00-2.33 (other ring H's); λ^{Nujol} 2.9-4.0, 5.85 (COOH), 13.3.

Anal. Calcd for C₁₂H₁₄O₂: C, 77.23; H, 6.93. Found: C, 77.04; H, 7.05.

The aceto-p-toluidide derivative of 23 was prepared from the acid chloride (86% from 23 and thionyl chloride, bp 95-97° at 0.5 mm) and p-toluidine in benzene under reflux. Recrystallization from aqueous ethanol gave a microcrystalline white solid (mp 147-148°).

Ânal. Caled for C20H21ON: C, 82.44; H, 7.27. Found: C, 82.39; H, 7.27.

2-(Benzonorbornen-1-yl)ethanol (24).-Reduction of acid 23 (3.5 g, 17.3 mmol) with lithium aluminum hydride in ether in the normal fashion produced alcohol 24 as an oil that slowly solidified: 3.05 g, 94%, mp 52.5-53.5° when recrystallized from ben-zene and petroleum ether; δ^{cCl_4} 7.10 sharp m (Ar-H), 3.79 t (-CH₂CH₂OH), 3.28 m (bridgehead H), 3.22 s (OH shifted on dilution), 2.25 probable 12-line multiplet though not all observed, (AB portion of ABX₂, $-CH_2CH_2OH$, $J_{AB} = 15$ cps, $J_{AX(BX)} \cong 7$ cps), 0.90–2.03 m (other ring H's); $\lambda^{\text{neat}} 3.00-3.20$, 9.60 (-CH₂OH), 9.90, 13.3.

Anal. Calcd for C13H16O: C, 82.93; H, 8.57. Found: C, 82.90; H, 8.69.

The tosylate was prepared in pyridine in the usual way:²⁷ 80%, mp 60-61° from benzene-petroleum ether; $\delta^{\rm CC1_4}$ (partial) 4.33 t (-CH₂CH₂OTs), 3.40 m (bridgehead H), 2.53 s (Ar-CH₃); λ^{KBr} 7.38, 8.42, 8.50 (-OSO₂-).

Anal. Calcd for C₂₀H₂₂O₃S: C, 70.14; H, 6.48. Found: C, 70.27; H, 6.55.

Benzonorbornenyl-1-acetaldehyde (22) .-- Dry dimethyl sulfoxide (75 ml) was heated to 150° under nitrogen and then cooled. To this was added the tosylate of alcohol 24 (4 g, 11.7 mmol)

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and sodium bicarbonate (12 g). The heterogeneous mixture was heated at 150° with a nitrogen purge for 10 min and cooled.³⁶ Water was added and the material then was extracted with ether. Most of the ether was removed from the dried extracts by aspiration, and the residual oil was vigorously shaken with saturated aqueous sodium bisulfite to afford the bisulfite adduct (4.5 g). The sulfurous by-products in this adduct were removed by ether extraction in a Soxhlet apparatus for 40 hr. The purified bisulfite adduct was then mixed with aqueous sodium hydroxide (5%) and the liberated oil taken up in ether. Distillation of the neutral, dried extracts produced aldehyde 22 as a colorless oil with a slight floral odor: 0.87 g, 40%, bp 105–108° at 0.2 mm; $\delta^{\rm CCI}$ 10.0 t (-CHO, J = 2 cps), 7.10 sharp m (Ar-H), 3.33 m (bridge head H), 2.92 eight-line m (-CH₂CHO, AB portion of ABX, $J_{AB} = 15$ cps, $J_{AX} = 2$ cps, lines 1,2 and 7,8 very weak), 1.00–2.23 m (other ring H's); $\lambda^{\rm neat} 3.55$, 3.72, 5.83 (-CHO), 13.3. The analytical sample was collected by glpc (SE-30, 190°).

Anal. Calcd for C₁₃H₁₄O: C, 83.83; H, 7.57. Found: C, 83.60; H, 7.67.

The 2,4-dinitrophenylhydrazone derivative was routinely prepared (yellow needles from aqueous methanol, mp 129-131°). Anal. Calcd for C12H12O4N4: N, 15,29. Found: N, 15,45.

Anal. Calcd for $C_{19}H_{18}O_4N_4$: N, 15.29. Found: N, 15.45. Decarbonylation of Aldehyde 22.—A 1 *M* solution of 22 (2 mmol) in chlorobenzene (2 ml) was sparged with helium for 15 min and then treated at 140° with three successive 0.2-mmol portions of freshly distilled di-t-butyl peroxide equally spaced over 14 hr. Carbon monoxide (92% of theory, analyzed by glpc at 25° on a molecular sieve 5A column) was evolved steadily and the reaction half-time was ca. 260 min. The entire reaction contents were analyzed by glpc (SE-30) and showed only one product from 22, 1-methylbenzonorbornene (17), identical in retention time and spectra with authentic material. Some 5% of the unchanged 22 was also detected. The other possible hydro-

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Totes

Studies of Benzonorbornene and Derivatives. V. Adduction of Benzyne with 5,5-Dimethoxy-1,2,3,4-tetrachlorocyclopentadiene. A Convenient Synthesis of 1,2,3,4-Tetrachloronaphthalene¹

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The adduction of benzyne with cyclopentadiene³ is the method of choice for the synthesis of benzonorbornadiene. As part of a general research program in benzonorbornene chemistry, the addition of benzyne to 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene was achieved (76% based on diene). Of the numerous interesting reactions of the adduct $1,^4$ its conversion

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carbon products (18-20) were absent. On the scale employed, yield data were difficult to obtain but calibration studies indicated at least a 70% yield of 17.

Acidity Constants.—Ca. 0.3-mmol portions of the acids in Table II were dissolved in 50 ml of either 50% (v/v) aqueous ethanol or 75% (v/v) acetone-25% water. The acidic solutions were then titrated at 25° with sodium hydroxide (0.05 N) from a microburet using a Leeds and Northrup pH meter with a Beckman glass electrode and a Coleman saturated calomel electrode. The pK_a was obtained from the pH at the half-neutralization point.

Registry No.—1, 15642-38-3; 2, 13733-46-5; Sbenzylisothiuronium salt of 2, 24452-99-1; 1,4-methanodecahydronaphthalene-1-carboxylic acid, 24453-00-7; 1,4-methanodecahydronaphthalene-1-carboxamide, 24453-01-8; 4, 16166-88-4; methyl ester of 4, 15642-40-7; 5, 15642-39-4; 6, 13733-44-3; 7, 13733-45-4; methyl ester of 7, 24453-07-4; 8, 13733-48-7; 8-OAc, 24453-09-6; *ar*-tetrachlorobenzonorbornenyl-1-carbinol, 24453-10-9; 11, 24453-11-0; 13, 24453-12-1; 13-OAc, 24453-13-2; 12-OTs, 24453-14-3; 17, 24453-15-4; 18, 15391-62-5; methyl ester of 23, 24453-17-6; 22, 24453-18-7; 2,4-dinitrophenylhydrazone of 22, 24453-19-8; 23, 24453-20-1; aceto-*p*-toluidide derivative of 23, 24453-21-2; 24, 24453-22-3; tosylate of 24, 24453-23-4.

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into the rare 1,2,3,4-tetrachloronaphthalene (2) is particularly efficient (quantitative yield).

Syntheses of 2 are recorded.⁵ None of them has,

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