

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.<sup>31</sup> 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 approximately 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 response 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 isopropoxide-isopropyl alcohol was prepared and equilibrated as above. At 100°, the initial *cis* and *trans* rich mixtures gave equilibrium constants of  $4.83 \pm 0.14$  and  $4.75 \pm 0.13$ , respectively. At 154°, the initial *trans* rich mixture gave an equilibrium constant of  $3.62 \pm 0.07$ .

**Equilibration of Ethyl 3-*t*-Butylcyclobutanecarboxylate.**—The procedure used to equilibrate the esters was described previously.<sup>1</sup> 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.<sup>1</sup> 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 chromatographic 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.

**Acknowledgment.**—This work was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

## Studies of Benzonorbornene and Derivatives. IV.<sup>1</sup> Bridgehead and 1-Carbonyl Derivatives<sup>2,3</sup>

JAMES W. WILT, HENRY F. DABEK, JR., JORDAN P. BERLINER, AND CHARLES A. SCHNEIDER

*Department of Chemistry, Loyola University of Chicago, Chicago, Illinois 60626*

*Received November 26, 1969*

Benzonorbornenyl-1-carbonyl tosylate (1) is investigated as a possible model for a non- $\pi$ -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-1-carbinol (8) still failed to allow aromatic migration, although both methano and ethano bridge-migrated products were detected. Benzonorbornenyl-1-carbonyl radical, produced by radical-promoted decarbonylation of the aldehyde 22, did not rearrange. The absence of rearrangement illustrates the necessity of twist in the aromatic ring during rearrangement. From benzonorbornene-1-carboxylic acid (2) synthetic procedures to a number of the title compounds are described.

Recently our interest in benzonorbornene chemistry coincided with other interests in homoallylic  $\pi$ -electron systems<sup>4</sup> and ring-size effects in the neophyl rearrangements.<sup>5</sup> All three of these interests led to the present investigation of benzonorbornenyl-1-carbonyl deriva-

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

(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.

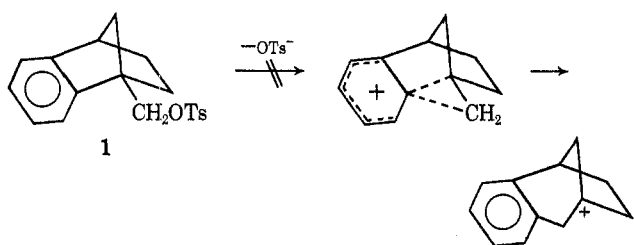
(3) Some of the material has appeared in preliminary form: J. W. Wilt and C. A. Schneider, *Chem. Ind.* (London), 951 (1963); J. W. Wilt, C. A. Schneider, J. P. Berliner, and H. F. Dabek, Jr., *Tetrahedron Lett.*, 4073 (1966).

(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).

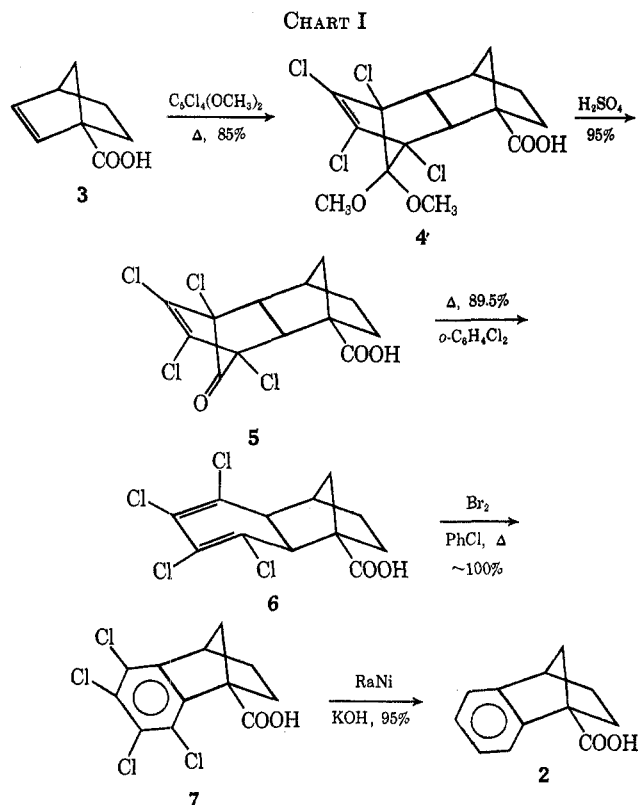
(6) Of the known synthetic routes to benzonorbornene and derivatives which follow, we felt only one<sup>6a</sup> could be developed for bridgehead substitution: (a) G. Wittig and E. Knauss, *Chem. Ber.*, **91**, 895 (1958); (b) J. Meinwald and G. A. Wiley, *J. Amer. Chem. Soc.*, **80**, 3667 (1958); (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. Abstr.*, **57**, 58166 (1962); (h) K. Alder and M. Fremery, *Tetrahedron*, **14**, 1960 (1961); (i) P. Bruck, *Tetrahedron Lett.*, 449 (1962); (j) H. Tanida, *Accounts Chem. Res.*, **1**, 239 (1968). See also ref 1.

**Synthesis and Solvolysis of Benzonorbornenyli-1-carbinyl Tosylate (1).**—Tosylate 1 has its aromatic ring so positioned that  $\pi$  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*  $\pi$  participation.<sup>7</sup> The calculated value of *ca.* eightfold given by Streitwieser<sup>8</sup> is commonly used for this effect, but little direct experimental evidence is available.<sup>9</sup>

Benzonorbornene-1-carboxylic acid (2) was synthesized from norbornene-1-carboxylic acid<sup>4</sup> *via* the sequence shown below in Chart I. The sequence was modeled after that of Mackenzie.<sup>6c</sup>



(7) E. Kosower, "An Introduction to Physical Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1968, p 125.

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

(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).

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  $\pi$ -assisted acetolysis,<sup>10</sup> it appears that  $\pi$  participation in 1 has been precluded. However,  $\sigma$  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 <sup>a,b</sup>	Temp, °C <sup>c</sup>	10 <sup>6</sup> k <sub>1</sub> , sec <sup>-1</sup>
1 <sup>d</sup>	132.0	1.18 ± 0.04
	139.0	2.07 ± 0.13
	156.0	6.66 ± 0.14
	25	(8.0 × 10 <sup>-11</sup> ) <sup>e</sup>
11	139.0	~0.3
	109.0	2.24 ± 0.10
9 <sup>f</sup>	120.0	6.30 ± 0.19
	130.0	14.0 ± 0.04
	25	(1.1 × 10 <sup>-9</sup> ) <sup>e</sup>
Tosylate <sup>a,g</sup>		
1 <sup>h</sup>	110.0	0.102 ± 0.01
	131.0	0.553 ± 0.04
	154.0	5.57 ± 0.48
9	99.5	1.13 ± 0.12 <sup>i</sup>
	133.0	27.0 ± 1.0
Neopentyl	133.0	6.8 <sup>e,j</sup>
Neophyl	133.0	470 <sup>e,k</sup>

<sup>a</sup> *Ca.* 0.03 M tosylate solutions were used, except for 11 which was 6 × 10<sup>-3</sup> M. <sup>b</sup> In 80% acetone–20% water (v/v) containing *ca.* 0.033 M *sym*-collidine. <sup>c</sup> ± 0.05°. <sup>d</sup>  $\Delta H^* = 25.8 \pm 0.2$  kcal mol<sup>-1</sup>,  $\Delta S^* = -17.9 \pm 0.2$  eu. <sup>e</sup> Extrapolated from data at other temperatures. <sup>f</sup>  $\Delta H^* = 26.0 \pm 0.3$  kcal mol<sup>-1</sup>,  $\Delta S^* = -12.4 \pm 0.3$  eu. <sup>g</sup>  $k_{rel}^{25^\circ}$  for 1, 1; 9, 14. <sup>h</sup> In glacial acetic acid containing acetic anhydride (0.3%) and excess sodium acetate (1.5 mmol/mmol of tosylate). <sup>i</sup>  $\Delta H^* = 27.9 \pm 0.2$  kcal mol<sup>-1</sup>,  $\Delta S^* = -13.7 \pm 0.5$  eu. <sup>j</sup>  $k_{rel}^{133^\circ}$  for 1, 1; neopentyl-OTs, 12; 9, 47; neophyl-OTs, 800. <sup>k</sup> Lit. value,  $1.17 \times 10^{-5}$  sec<sup>-1</sup> at 99.7°: R. L. Bixler and C. Niemann, *J. Org. Chem.*, **23**, 742 (1958). <sup>l</sup> S. Winstein and H. Marshall, *J. Amer. Chem. Soc.*, **74**, 1120 (1952). <sup>m</sup> S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *ibid.*, **74**, 1113 (1952).

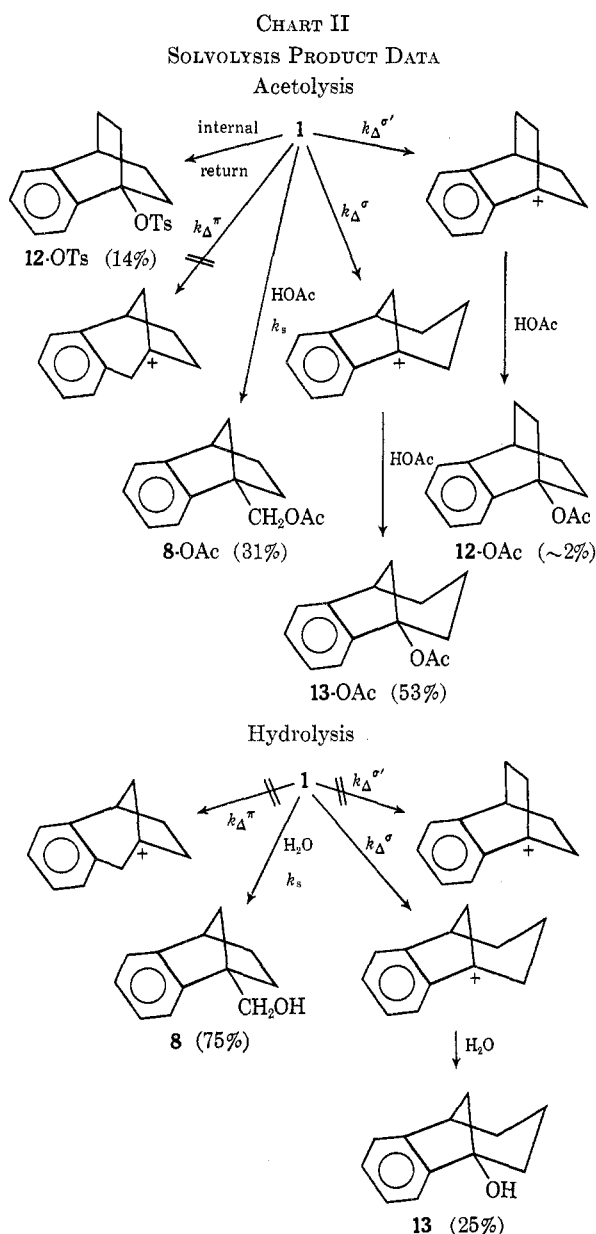
In 80% acetone at 25° the retardation observed with 1 is 14-fold relative to 9.<sup>11</sup> This 14-fold value compares well with the value of 16 obtained in an earlier study<sup>4</sup> in 60% acetone for the retardation caused by a homoallylic double bond. The comparison emphasizes the inductive similarity of the two  $\pi$  systems, the aromatic

(10) I. L. Reich, A. Diaz, and S. Winstein, *ibid.*, **91**, 5635, 5637 (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-1-carbinyl tosylate (**10**) and tosylate **1** solvolyzed at comparable rates in 80% acetone at 131°.<sup>12</sup> 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-

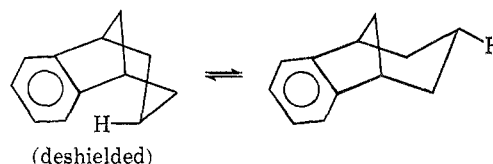


arranged tosylate (**12-OTs**) could be separated from the reaction material. Although its structure was not proved by independent synthesis, and must therefore be open to question, **12-OTs** is probably benzo-bicyclo[2.2.2]octen-1-yl tosylate. It was not **1** and it is unlikely that it could be benzo-bicyclo[3.2.1]oct-6-en-1-yl 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 coworkers<sup>13</sup> have demon-

strated 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  $\sigma$ -assisted processes ( $k_{\Delta}^{\sigma}$ ) and unassisted processes ( $k_s$ ), as indicated in Chart II. In light of the recent elucidation of  $\sigma$  assistance in acetolysis of neopentyl tosylate,<sup>10</sup> this formulation is probably preferable to another view involving completely unassisted ionization followed by skeletal rearrangement.<sup>14</sup> It should be noted, however, that no product of aromatic migration was observed, so  $\pi$  assistance ( $k_{\Delta}^{\pi}$ ), 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,<sup>4</sup> and by the proton resonance at  $\delta$  2.27, ascribed to the *endo* C-3 proton. This resonance, also observed in **13-OAc** at  $\delta$  2.20, was prominent in the *bona fide* parent hydrocarbon **18** ( $\delta$  2.25) but was absent in the benzonorbornenyl-1-carbinyl and benzo-bicyclo[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.<sup>4</sup> 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.  $-1.6$ ),<sup>15</sup> 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  $k_{\Delta}$  processes relative to acetolysis. Unassisted ( $k_s$ ) processes proceed without rearrangement;<sup>10</sup> hence **8** predominates in the aqueous acetone.

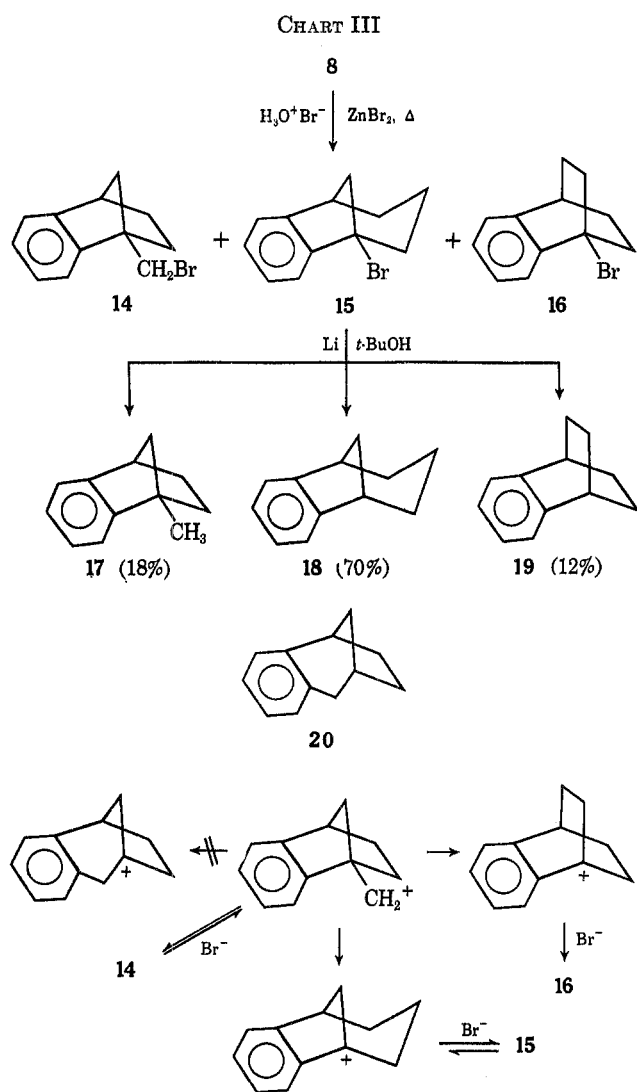
**Cationic Rearrangement of Benzonorbornenyl-1-carbinol (8).**—Carbinol **8** was subjected to vigorous treatment in hydrobromic acid containing zinc bromide

(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. Harper, and R. D. Nicholas, *J. Amer. Chem. Soc.*, **88**, 4475 (1966).

(15) Reference 7, p 311.



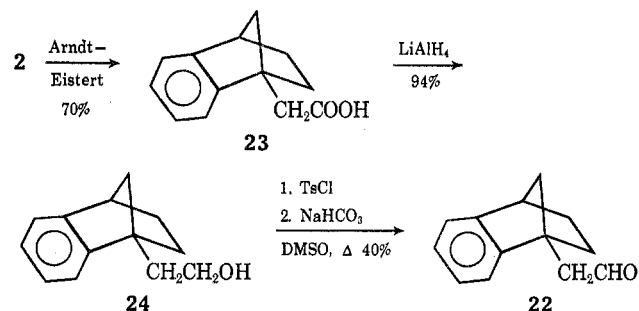
as shown in Chart III. The bromide isomers were best identified as their parent hydrocarbons formed by reduction. Again the principal rearrangement was *via* ethano bridge migration (as in solvolysis) although the exact product composition was time dependent. But now an increased percentage of methano 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 hr<sup>16</sup>). 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.<sup>17</sup> Similar but more detailed reasoning has been advanced

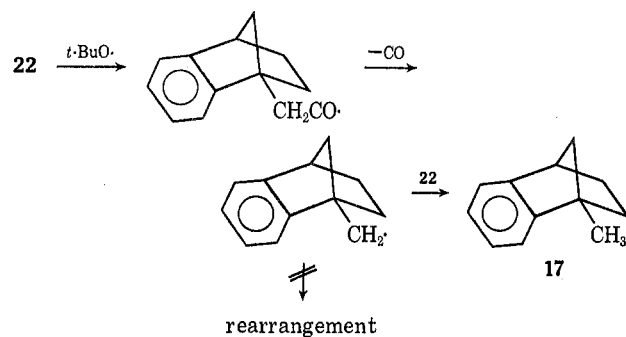
for the analogous transformations of the related tosylates **9** and **10**.<sup>4</sup>

**Decarbonylation of Benzonorbornenyl-1-acetaldehyde (22).**—The decarbonylation of aldehyde **22** was investigated because past work<sup>18</sup> 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-methylnorbornene (**17**).



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.<sup>5</sup>

**Acidity Constants.**—As a final demonstration of the inductive effect of the aromatic ring in acid **2**, its  $\text{p}K_a$  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 homomally positioned vinyl and aromatic functions, *ca.* 0.4–0.5  $\text{p}K$  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.

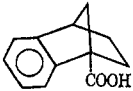
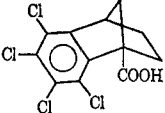
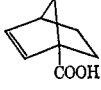
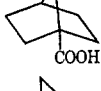
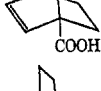
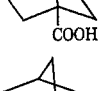
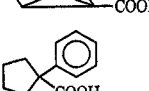
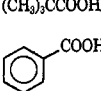
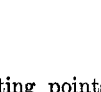
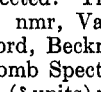
**Synthesis of Various Bridgehead-Substituted Benzonorbornenes.**—To illustrate its utility as a precursor to the heretofore unknown 1-substituted benzonorbornenes, acid **2** or its acid chloride was converted into a number of these as given in Chart IV. Experimental details are available upon request,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

(16) W. P. Whelan, Jr., Dissertation, Columbia University, 1952, pp 61–62.

(17) G. S. Hammond, *J. Amer. Chem. Soc.*, **77**, 334 (1955).

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

TABLE II  
ACIDITY CONSTANTS, 25°

	$pK_a$	
	50% EtOH-H <sub>2</sub> O (v/v)	75% acetone- H <sub>2</sub> O (v/v)
	5.88	7.09
		6.56
	5.98	7.61
	6.37	
	6.20	
	6.62	
	6.35	
	6.28	
	6.48	7.64
	5.50	6.71

## 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 ( $\delta$  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 ( $\lambda$ ) absorptions are listed, in microns ( $\mu$ ). Ultraviolet maxima ( $\lambda^{\max}$ ) are given in millimicrons ( $m\mu$ ). Gas-liquid 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-1,2,3,4,5,8a-octahydronaphthalene-1-carboxylic Acid (4).**—Norbornene-1-carboxylic acid<sup>4</sup> (3, 50 g, 0.362 mol) was heated at 165° under nitrogen for 6 hr with 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene<sup>19</sup> (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°;  $\delta^{\text{CDCl}_3}$  10.23 br s (COOH), 3.60 s, 3.55 s (2 OCH<sub>3</sub>), 2.77 q (5a,8a-H's, AB,  $J = 8$  cps), 2.33 m (4-H), 1.15–1.9 m (all other H's);  $\lambda^{\text{Nujol}}$  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 C<sub>15</sub>H<sub>16</sub>O<sub>4</sub>Cl<sub>4</sub>: 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),  $n_D^{20}$  1.5379;  $\delta^{\text{CCl}_4}$  essentially same as that of 4 minus the acid proton and with 3.63 s, 3.57 s, 3.47 s (3 OCH<sub>3</sub>);  $\lambda^{\text{neat}}$  5.72 (C=O), 6.21 (C=C).

*Anal.* Calcd for C<sub>16</sub>H<sub>18</sub>O<sub>4</sub>Cl<sub>4</sub>: 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.<sup>20</sup>

**5,6,7,8-Tetrachloro-9-keto-1,4:5,8-dimethano-1,2,3,4,5,8a,8b-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°;  $\delta^{\text{CDCl}_3}$  10.23 br s (COOH), 2.92 q (upfield pair obscured, 5a,8a-H's, AB,  $J \approx 8$  cps), 2.65 m (4-H), 1.3–2.0 m (all other H's);  $\lambda^{\text{Nujol}}$  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 C<sub>15</sub>H<sub>10</sub>O<sub>3</sub>Cl<sub>4</sub>: 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).<sup>20a,b</sup> Evolution of carbon monoxide<sup>21</sup> 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°,  $\delta^{\text{pyridine}}$  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);  $\lambda^{\text{Nujol}}$  3.4–4.4, 5.96 (COOH), 6.23 (C=C);  $\lambda^{\text{CHCl}_3}$  282 ( $\epsilon$  3267), 293 (3367), 306 (3367), 319 (3233).<sup>22</sup>

*Anal.* Calcd for C<sub>15</sub>H<sub>10</sub>O<sub>2</sub>Cl<sub>4</sub>: C, 43.94; H, 3.07. Found: C, 44.12; H, 2.69.

***ar*-Tetrachlorobenzonornbornene-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°,  $\delta^{\text{pyridine}}$  3.7 m (bridgehead H), 1.0–2.9 m (other ring H's);  $\lambda^{\text{Nujol}}$  3.2–4.0, 5.90 (COOH) 13.15;  $\lambda^{\text{CHCl}_3}$  247 ( $\epsilon$  3217), 284 (1283), 295 (1300).<sup>22</sup>

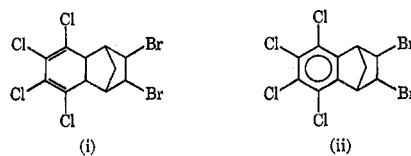
*Anal.* Calcd for C<sub>12</sub>H<sub>8</sub>O<sub>2</sub>Cl<sub>4</sub>: C, 44.20; H, 2.48. Found: C, 44.11; H, 2.51.

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°,  $\delta^{\text{CCl}_4}$  3.90 s

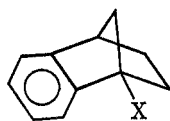
(20) (a) S. B. Soloway, Dissertation, University of Colorado, 1955; J. G. Martin and R. K. Hill, *Chem. Rev.*, **61**, 537 (1961); (b) C. F. H. Allen and J. Van Allan, *J. Amer. Chem. Soc.*, **64**, 1260 (1942).

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

(22) MacKenzie<sup>20</sup> 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  $\lambda^{\max}$  are: 279, 290,



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

CHART IV  
 1-SUBSTITUTED BENZONORBORNENES


X	Mp, bp (mm), °C	Analyses, % <sup>a</sup>		X spectra <sup>b</sup>	Lit. ref
		C	H		
CONH <sub>2</sub>	156-157... (from benzene)	76.98	7.00	5.7-7.0 m 3.00, 3.15, 6.0-6.2	c
		77.26	6.99		
CN	... <sup>d</sup>	85.17	6.55	4.5	e
		85.04	6.58		
CHO <sup>f</sup>	... <sup>d</sup>	83.68	7.03	10.15 s	g
		83.67	7.09		
COOCH <sub>3</sub>	106-110 (0.2)	77.20	6.98	3.67 s	h
		77.00	7.18		
COCH <sub>3</sub> <sup>i,j</sup>	90-93 (0.1)	83.83	7.58	2.25 s	k
		83.72	7.68		
OCOCH <sub>3</sub> <sup>l</sup>	82-84 (0.2)	77.2	6.980	2.10 s	m
		77.31	7.14		
OH	... <sup>d</sup>	82.46	7.55	6.0 s <sup>n</sup>	o
		82.29	7.43		
Br	68-70 (0.1)	59.21	4.97	... <sup>p</sup>	q
		59.42	5.13		
NH <sub>3</sub> <sup>+</sup> Cl <sup>-</sup> r,s	240-245 dec (from ether-butanol)	Cl <sup>t</sup> 18.12,		7.0-8.5	m
		18.21			
Cl	... <sup>d</sup>	73.95	6.21	... <sup>p</sup>	u
		74.10	6.30		

<sup>a</sup> Microanalyses were performed by Micro-Tech Laboratories, Skokie, Ill. The italicized values are the calculated figures. <sup>b</sup> The italicized spectra are nmr  $\delta$  values indicative of the group X. Solutions in CCl<sub>4</sub> or CDCl<sub>3</sub> were used. The spectra were determined at 60 MHz relative to TMS. The other ( $\lambda$ ) spectral data are infrared maxima indicative of the group X. Spectra were determined on neat liquids or on KBr disks of solids. <sup>c</sup> 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. <sup>d</sup> Not determined. The material was collected by gas-liquid partition chromatography or by molecular distillation. <sup>e</sup> J. Thurman, *Chem. Ind.* (London), 752 (1964). <sup>f</sup> 2,4-Dinitrophenylhydrazones, mp 173.5-175° from ethyl acetate. *Anal.* Calcd for C<sub>18</sub>H<sub>16</sub>O<sub>4</sub>N<sub>4</sub>: N, 15.91. Found: N, 16.19. <sup>g</sup> H. C. Brown and R. F. McFarlin, *J. Amer. Chem. Soc.*, **80**, 5372 (1958). <sup>h</sup> From the acid 2 and diazomethane. <sup>i</sup> 2,4-Dinitrophenylhydrazones, mp 161-162° from ethyl acetate. *Anal.* Calcd for C<sub>19</sub>H<sub>18</sub>O<sub>4</sub>N<sub>4</sub>: N, 15.29. Found: N, 15.14. <sup>j</sup> Oxime, mp 120.5-129° from aqueous methanol. It is a mixture of stereoisomers. *Anal.* Calcd for C<sub>13</sub>H<sub>15</sub>ON: N, 6.96. Found: N, 7.13. <sup>k</sup> C. DePuy, G. Dappen, K. Eilers, and R. Klein, *J. Org. Chem.*, **29**, 2813 (1964). <sup>l</sup> Other methods of synthesis were also employed. The best is referenced. <sup>m</sup> J. W. Wilt, C. F. Parsons, C. A. Schneider, D. G. Schultenover, and W. J. Wagner, *J. Org. Chem.*, **33**, 694 (1968). <sup>n</sup> Varies with concentration and temperature. <sup>o</sup> Saponification of the acetate with alkali. <sup>p</sup> No characteristic spectra. <sup>q</sup> C. Grob, M. Ohta, R. Renk, and A. Weiss, *Helv. Chim. Acta*, **41**, 1191 (1959). <sup>r</sup> Acetamide, mp 156.5-157.5° from aqueous methanol. *Anal.* Calcd for C<sub>13</sub>H<sub>15</sub>ON: C, 77.58; H, 7.51. Found: C, 77.62; H, 7.55. <sup>s</sup> Benzamide, mp 150.5-151.5° from aqueous methanol. *Anal.* Calcd for C<sub>13</sub>H<sub>17</sub>ON: C, 82.10; H, 6.51. Found: C, 81.96; H, 6.45. <sup>t</sup> Volhard determination of ionic chloride. <sup>u</sup> J. Kochi, *J. Org. Chem.*, **30**, 3265 (1965); *J. Amer. Chem. Soc.*, **87**, 2500 (1965).

(COOCH<sub>3</sub>), 3.81 m (bridgehead H), 2.5-1.2 series of multiplets (other ring H's);  $\lambda_{\text{CCl}_4}$  5.83, 8.0 (-COOCH<sub>3</sub>).

*Anal.* Calcd for C<sub>13</sub>H<sub>15</sub>O<sub>2</sub>Cl<sub>4</sub>: 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 catalyst<sup>23</sup> (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 g, 95%, mp 88-90°). The acid could be recrystallized from heptane or hexane as colorless prisms [mp 93-94°,  $\delta_{\text{CCl}_4}$  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);  $\lambda_{\text{Nujol}}$  3.3-4.0, 5.95 (COOH), 6.32, 13.3 (Ar-H);  $\lambda_{\text{CHCl}_3}^{\text{max}}$  264 ( $\epsilon$  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 C<sub>12</sub>H<sub>12</sub>O<sub>2</sub>: 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°).<sup>24</sup>

*Anal.* Calcd for C<sub>20</sub>H<sub>22</sub>O<sub>2</sub>N<sub>2</sub>S: 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%).<sup>25</sup> The acid was sublimed, recrystallized from heptane, and resublimed: white crystalline solid, mp 124.5-126°, neut equiv 205,  $\delta_{\text{CCl}_4}$  12.4 s (COOH), 1.0-2.2 m (all other H's);  $\lambda_{\text{Nujol}}$  3.3-4.0, 5.92 (COOH), 13.7; blank in uv.

*Anal.* Calcd for C<sub>12</sub>H<sub>15</sub>O<sub>2</sub>: 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 method<sup>25</sup> seems too vigorous, even under these milder conditions, for the production of unsaturated acids.







and sodium bicarbonate (12 g). The heterogeneous mixture was heated at 150° with a nitrogen purge for 10 min and cooled.<sup>36</sup> 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;  $\delta_{\text{C}^{14}}$  10.0 t (-CHO,  $J = 2$  cps), 7.10 sharp m (Ar-H), 3.33 m (bridgehead H), 2.92 eight-line m (-CH<sub>2</sub>CHO, AB portion of ABX,  $J_{\text{AB}} = 15$  cps,  $J_{\text{AX}} = 2$  cps, lines 1,2 and 7,8 very weak), 1.00–2.23 m (other ring H's);  $\lambda^{\text{neat}}$  3.55, 3.72, 5.83 (-CHO), 13.3. The analytical sample was collected by glpc (SE-30, 190°).

*Anal.* Calcd for C<sub>13</sub>H<sub>14</sub>O: 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 C<sub>19</sub>H<sub>15</sub>O<sub>4</sub>N<sub>4</sub>: 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-

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<sub>a</sub> was obtained from the pH at the half-neutralization point.

**Registry No.**—1, 15642-38-3; 2, 13733-46-5; S-benzylisothiuronium 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.

**Acknowledgment.**—We appreciate very much the support given to the early portion of this work by the National Science Foundation, Grant No. GP-1968.

(36) N. Kornblum, W. J. Jones, and G. J. Anderson, *J. Amer. Chem. Soc.*, **81**, 4113 (1959).

## Notes

### Studies of Benzenorbornene and Derivatives. V.

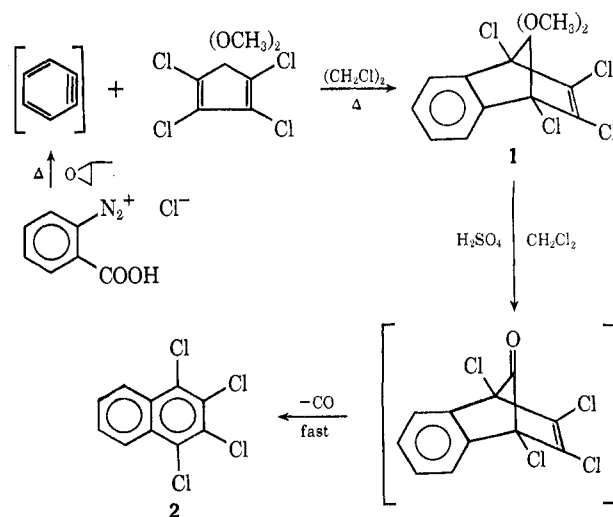
#### Adduction of Benzyne with 5,5-Dimethoxy-1,2,3,4-tetrachlorocyclopentadiene. A Convenient Synthesis of 1,2,3,4-Tetrachloronaphthalene<sup>1</sup>

JAMES W. WILT AND EDMUNDAS VASILIAUSKAS<sup>2</sup>

Department of Chemistry, Loyola University of Chicago, Chicago, Illinois 60626

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The adduction of benzyne with cyclopentadiene<sup>3</sup> is the method of choice for the synthesis of benzenorbornene. As part of a general research program in benzenorbornene 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**,<sup>4</sup> its conversion



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

Syntheses of **2** are recorded.<sup>5</sup> None of them has,

(1) Part IV: J. W. Wilt, H. F. Dabek, Jr., J. P. Berliner, and C. A. Schneider, *J. Org. Chem.*, **35**, 2402 (1970).

(2) National Defense Education Act Fellow, 1966–1968.

(3) G. Wittig and E. Knauss, *Chem. Ber.*, **91**, 895 (1958). For a convenient recent modification, cf. L. Friedman and F. M. Logullo, *J. Org. Chem.*, **34**, 3089 (1969).

(4) J. W. Wilt and E. Vasiliauskas, to be published.

(5) (a) From *ar*-tetrachlorotetralin, J. von Braun, *et al.*, *Ber.*, **56B**, 2332 (1923), and modified by W. P. Wynne, *J. Chem. Soc.*, **61**, (1946); (b) from naphthalene, A. A. Danish, M. Silverman, and Y. A. Tajima, *J. Amer. Chem. Soc.*, **76**, 6144 (1954); (c) from trichloroethylene, W. L. Howard and R. E. Gilbert, *J. Org. Chem.*, **27**, 2685 (1962).