for an additional 3 hr at room temperature, then concentrated *in vacuo* and distilled to give 3 g of starting material and 32 g (84%) of pure 2-chloro-2-carbomethoxycyclohexanone (**7**): bp 74° (0.1 mm); ir ($CHCl_3$) 2955, 1725, and 1440 cm^{-1}; nmr (CCl_4) δ 3.80 (3 H, s) and 1.4–3.0 (8 H, m).

Anal. Calcd for $C_8H_{11}ClO_3$: C, 50.42; H, 5.81. Found: C, 50.51; H, 5.71.

1-Carbomethoxycyclopentene (9).—Glass beads (50 g) were added to a flask containing 19.0 g (0.1 mol) of 2-chloro-2-carbomethoxycyclohexanone (**7**), 11.0 g (0.105 mol) of anhydrous sodium carbonate, and 150 ml of dry xylene. The resulting mixture was stirred at reflux for 14 hr and was then cooled, filtered, and passed through a dry column of 200 g of silica gel. After elution of the xylene with hexane, the product was washed out with chloroform. Evaporation and distillation yielded 9.0 g (71%) of 1-carbomethoxycyclopentene (**9**): bp 57° (10 mm) [lit.[12] bp 63–65° (10 mm)]; ir ($CHCl_3$) 1700 and 1620 cm^{-1}; nmr (CCl_4) δ 6.6 (1 H, s, br), 3.6 (3 H, s), and 2.7–1.7 (6 H, m); uv (EtOH) 224 nm (ϵ 9800); mass spectrum (70 eV) *m/e* (rel intensity) M^+ (32), 95 (48), 64 (100).

Methyl 2,4-diphenylacetoacetate was prepared in 78% yield according to ref 13: mp 61–63° (lit.[13] mp 59–60°); ir 1750, 1710, 1640, and 1600 cm^{-1}; nmr ($CDCl_3$) δ 3.7 (3 H, s), 3.8 (2 H, s), 4.8 (1 H, s), and 7.0–7.5 (10 H, m).

Chlorination of the Keto Ester.—To a stirred solution of 13.4 g (0.05 mol) of the above keto ester in 150 ml of dry chloroform was added dropwise under nitrogen 65 g (0.06 mol) of *tert*-butyl hypochlorite at a temperature of −10° over a 30-min period. The reaction mixture was stored for 7 days in a refrigerator and was then concentrated *in vacuo*, and the residue was diluted with an equal amount of methanol to afford 11 g (73%) of **10**, mp 50–60°. A small sample was recrystallized from methanol: mp 64–65°; ir ($CHCl_3$) 1720 and 1740 cm^{-1}; nmr (CCl_4) δ 3.7 (3 H, s), 3.8 (2 H, s), and 6.9–7.5 (10 H, m); mass spectrum *m/e* (rel intensity) M^+ (1), 184 (26), 91 (100).

Anal. Calcd for $C_{17}H_{15}O_3Cl$: C, 67.44; H, 4.99. Found: C, 67.43; H, 4.98.

"Decarbonylation" of the Chloride 10.—A flask, equipped with a Dean-Stark trap, was charged with 20 g of glass beads, 3.3 g (0.031 mol) of anhydrous sodium carbonate, and 150 ml of dry xylene. After the contents had been refluxed for 1 hr, 9.0 g (0.03 mol) of the chloride **10** was added and stirring was continued at reflux under nitrogen for 6 hr. The reaction mixture was then cooled, filtered, and concentrated *in vacuo*. The dark brown residue was chromatographed on 150 g of silica gel, using a 1:1 mixture of benzene–chloroform as eluent. Early fractions gave 2.9 g of a mixture of **23** and **19** which was rechromatographed *under argon* on silica gel (0.05–0.2 mm, 30 g) using a 4:1 mixture of hexane–ether to afford 400 mg (6%) of **23**: bp 150° (0.5 mm, Kugelrohr oven); ir ($CHCl_3$) 1720 and 1600 cm^{-1}; nmr (CCl_4) δ 3.6 (3 H, s), 6.9 (1 H, s), and 7.1–7.6 (10 H, m); uv (EtOH) 221 nm (ϵ 15,700) and 287 (22,000); mass spectrum (70 eV) *m/e* (rel intensity) M^+ (100), 177 (77), 121 (86). Hydrolysis with aqueous potassium hydroxide gave (*E*)-2-phenylcinnamic acid, mp 175° (lit.[14] mp 173°). The following fraction (1.5 g, 21% yield) consisted of a slightly yellow, exceedingly air-sensitive liquid which crystallized at −5°. Sublimation at 40° in a high vacuum gave pure **19**: mp 50° (lit.[15] mp 49–50°); ir (CCl_4) 1760 cm^{-1}; nmr (CCl_4) δ 3.5 (2 H, s), 4.6 (1 H, s), and 6.9–7.3 (9 H, m); mass spectrum (70 eV) *m/e* (rel intensity) M^+ (30), 179 (80), 178 (100), 177 (48), 165 (25), 89 (10).

Later fractions of the original chromatogram gave compound **22**, which crystallized from ether to afford 0.39 g (5%) of crystals: mp 150°; ir ($CHCl_3$) 1770 and 1650 cm^{-1}; nmr ($CDCl_3$) δ 3.7 (3 H, s), 6.2 (1 H, s), 7.2–7.6 (10 H, m); uv (EtOH) 295 nm (ϵ 10,800); mass spectrum (70 eV) *m/e* (rel intensity) M^+ (50), 238 (34), 178 (100).

Anal. Calcd for $C_{17}H_{14}O_3$: C, 76.67; H, 5.30. Found: C, 77.04; H, 5.35.

The last fraction afforded, after trituration with ether, 1.14 g (14%) of **16**: mp 111–112°; ir ($CHCl_3$) 1690, 1610, and 1590 cm^{-1}; nmr ($CDCl_3$) δ 4.2 (3 H, s), 5.6 (1 H, s), and 7.1–8.2 (10 H, m); uv (EtOH) 253 nm (ϵ 22,300) and 287 (9000); mass spectrum (70 eV) *m/e* (rel intensity) M^+ (51), 121 (100), 89 (27).

Anal. Calcd for $C_{17}H_{14}O_3$: C, 76.67; H, 5.30. Found: C, 76.63; H, 5.35.

Acknowledgments.—We are indebted to Firmenich SA, Geneva, for generous financial support.

Registry No.—**4**, 42367-18-0; **6**, 42367-19-1; **7**, 42367-20-4; **9**, 25662-28-6; **10**, 42367-22-6; **16**, 42367-23-7; **19**, 24017-08-1; **22**, 42367-25-9; **23**, 36854-27-0; 2-hydroxymethylenecyclododecanone, 949-07-5; 2-carbomethoxycyclohexanone, 41302-34-5; methyl 2,4-diphenylacetoacetate, 40195-49-1.

[12] S. J. Rhoads, J. K. Chattopadhyay, and E. E. Waali, *J. Org. Chem.*, **35**, 3352 (1970).

[13] J. B. Conant and A. H. Blatt, *J. Amer. Chem. Soc.*, **51**, 1227 (1929).

[14] R. Ketcham and D. Jambotkar, *J. Org. Chem.*, **28**, 1034 (1963).

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A Study of 1-Substituted Benzonorbornadienes[1]

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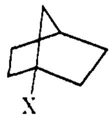
Work done on bridgehead carbinyl systems **1**,[2] **2**,[2,3] and **3**[4] has prompted us to study briefly the similar benzonorbornadiene system **4**, which has recently become available.[5–7]



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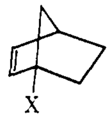

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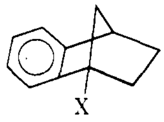

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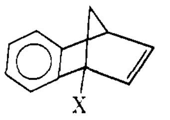


4

a, X = Br
b, X = COOH
c, X = CH_2OH
d, X = CH_2OAc
e, X = CH_2OTs
f, X = CH_2OBs

In the solvolysis of benzonorbornenyl-1-carbinyl tosylate (**3e**) Wilt and coworkers found that π participation is precluded geometrically because of the rigid nature of the bicyclic system, preventing the twist required of the aromatic ring to achieve a phenonium ion type of geometry in the transition state for this constrained neophyl-like tosylate. They showed that tosylate **1e** solvolyzed at 50 times the rate of **3e** at 131° in acetic acid. They attributed this to the electron-withdrawing, destabilizing $-I$ effect of the aromatic ring[4] and found no phenyl migration. Bly[3] has studied brosylate **2f** and showed that acetolysis of **1f** is at least 1.3 times as rapid as that of the unsaturated tosylate **2f** at 100°, demonstrating the $-I$ effect of the double bond. They found no double-bond migration either.

[1] This investigation was supported in part by a University of Wisconsin—Eau Claire University Research Grant.

[2] J. W. Wilt, C. F. Parsons, C. A. Schneider, D. G. Schultenover, and W. J. Wagner, *J. Org. Chem.*, **33**, 694 (1968).

[3] (a) R. S. Bly and Q. E. Cooke, Abstracts, 148 National Meeting of the American Chemical Society, Chicago, Ill., Sept., 1964, Paper 80-S; (b) R. S. Bly and E. K. Quinn, Abstracts, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, Paper 91-O.

[4] J. W. Wilt, H. F. Dabek, Jr., J. P. Berliner, and C. A. Schneider, *J. Org. Chem.*, **35**, 2402 (1970).

[5] J. W. Wilt and P. J. Chenier, *J. Amer. Chem. Soc.*, **90**, 7366 (1968).

[6] J. W. Wilt and P. J. Chenier, *J. Org. Chem.*, **35**, 1562, 1571 (1970).

[7] Certain derivatives of this system have been synthesized by an entirely different route: (a) K. Wiesner and A. Philipp, *Tetrahedron Lett.*, 1467 (1966); (b) A. H. Philipp, Ph.D. Dissertation, University of New Brunswick, 1967. We thank Professor Wiesner for this information.

The present study of tosylate **4e** was undertaken for two reasons: (1) to determine if **4e**, containing both an aromatic ring and a double bond, solvolyzes slower than both **2e** and **3e** by the $-I$ effect and (2) to find if any rearrangement occurs in the absence of the easily rearranged ethano bridge of tosylates **1e**, **2e**, and **3e**.

We chose to synthesize **4e** from 1-bromobenzonorbornadiene (**4a**), previously reported.[6] Bromide **4a** was converted into benzonorbornadiene-1-carboxylic acid (**4b**) not without difficulty. Unsuccessful carbonations of organometallic reagents, including those formed from magnesium in ether, lithium in cyclohexane, and lithium in tetrahydrofuran, were followed by a successful carbonation in tetrahydrofuran of the Grignard reagent of **4a**. Reduction to benzonorbornadienyl-1-carbinol (**4c**) with lithium aluminum hydride in ether in the usual manner,[8] followed by reaction with tosyl chloride in pyridine,[9] gave tosylate **4e** in good yield. Acetate **4d** was also made from alcohol **4c**.[10]

The acetolysis of **4e** was performed at 132.5° in glacial acetic acid with 0.04 M sodium acetate buffer, 0.025 M tosylate, and 0.3% acetic anhydride. Neopentyl tosylate was solvolyzed in similar fashion at 133.5° and its solvolytic rate constant compares well with the literature value, as shown in Table I. Note that, although the temperatures for the different studies cited vary over 2°, creating an error of about 20% in k_{rel}, good qualitative conclusions can still be drawn from these values.

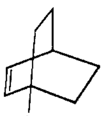
TABLE I

ACETOLYSIS STUDIES

Tosylate	Temp, °C	Ref	10^5k, sec^{-1}	k_{rel}
Neopentyl	133.5 ± 0.5		6.15	28
Neopentyl	133.0	*a, b*	6.8	31
Neophyl	133.0	*a, c*	470	2200
Norbornyl-1-carbinyl (**1e**)	133.0	*d*	27.0	120
Norbornenyl-1-carbinyl (**2e**)	132.5	*a, e*	7.3	34
Benzonorbornenyl-1-carbinyl (**3e**)	131.0	*d*	0.553	2.6
Benzonorbornadienyl-1-carbinyl (**4e**)	132.5 ± 0.5		0.217	1.0

[a] Extrapolated from data at other temperatures. [b] S. Winstein and H. Marshall, *J. Amer. Chem. Soc.*, **74**, 1120 (1952). [c] S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *ibid.*, **74**, 1113 (1952). [d] Reference 4. [e] Reference 3: the rate constant for the brosylate was assumed to be 2.9 times the rate of the corresponding tosylate.

The benzonorbornadienyl-1-carbinyl system is an excellent example of the inductive electron-withdrawing effect of both a double bond and an aromatic ring. Tosylate **4e** solvolyzes less than $^1/_{100}$ as fast as its saturated analog **1e**, less than $^1/_{30}$ as fast as **2e** (with only the double bond), and less than $^1/_2$ as fast as **3e** (with only the aromatic ring). It is also interesting to note that tosylate **4e** behaves like norbornenyl-1-carbinyl tosylate (**2e**): a drift in rate is noticed toward the end of the acetolysis, colored side products are formed, and addition to the highly reactive double bond occurs as in the study of **2e** by Wilt. Bly[3] has shown that the drift in the rate of solvolysis of **2f** is due to the formation of the relatively unreactive brosylate **5** by methano migration and ion-pair return. He isolated **5** from the product mixture in 18% yield. Solvolysis of **3e** also gives a similar tosylate (**6**) isolated in 14% yield.[4] In our study all attempts to identify any tosylate (such as **7**) in the crude product mixture failed, but it is possible that a small amount of **7** may have been missed.



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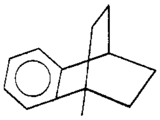

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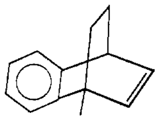

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Another difference between benzonorbornadienyl-1-carbinyl tosylate and the other previously studied systems is the lack of any rearrangement (with the possible exception of small amounts of **7**). Since the aromatic ring in **3e** and the double bond in **2e** do not migrate or participate, it is easily seen why neither the ring nor the double bond in **4e** undergo rearrangement. In view of the preference for ethano over methano migration in **2e** and **3e**,[3,4] it is not surprising that the methano bridge does not migrate in **4e**. Only unrearranged products were isolated from the acetolysis of tosylate **4e**. Depending on the temperature and time of solvolysis, either benzonorbornadienyl-1-carbinyl acetate (**4d**) or diacetates formed by addition to the strained double bond of **4d** were the only observed products. The diacetates were formed during a product study at 160°, whereas the rearranged monoacetate **4d** was formed in refluxing acetic acid (118°). The solvolytic rate was measured at 132.5°; so both competing reactions may be occurring at this temperature. The exact stereochemistry of the diacetates was not determined, but they are most probably *exo*-2-acetoxybenzonorbornadienyl-1-carbinyl acetate and the *exo*-3 isomer. Similar difficulties were found with tosylate **2e**.[11]

As a final proof for the strong inductive effect in the benzonorbornadienyl system, the pK_a of bridgehead acid **4b** was compared with those of the other three bicyclic structures in question. Table II summarizes the results obtained in 50% ethanol–water at 25°.

The general order of acidity is **4b** > **3b** > **2b** > **1b**; *i.e.*, as more unsaturated groups are placed on the

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(8) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Vol. 1, Wiley, New York, N. Y., 1967, pp 581–595.

(9) Reference 8, pp 1179–1185.

(10) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 5th ed, Wiley, New York, N. Y., 1964, p 247.

(11) Note also the addition of formic acid to norbornene by D. C. Kleinfelter and P. v. R. Schleyer, *Org. Syn.*, **42**, 79 (1962).

TABLE II

pK_a VALUES

Acid	Ref	pK_a
Benzoic	4	5.50
Benzoic		5.58
Norbornane-1-carboxylic (**1b**)	4	6.37
Norbornene-1-carboxylic (**2b**)	4	5.98
Benzonorbornene-1-carboxylic (**3b**)	4	5.88
Benzonorbornadiene-1-carboxylic (**4b**)		5.46

[2.2.1] skeleton, the acidity of the bridgehead acid increases because the carboxylate anion becomes more stable owing to greater electron withdrawal.

Experimental Section[12]

1-Bromobenzonorbornadiene (4a).—2-Bromobenzonorbornadiene[6] (17.5 g, 0.0800 mol) was refluxed and stirred magnetically with 48% hydrobromic acid (200 ml) for 12 hr. The mixture was diluted with water (200 ml) and extracted with petroleum ether (bp 30–60°) (4 × 50 ml). The extracts were washed with 10% sodium bicarbonate (100 ml) and water (2 × 100 ml), dried over magnesium sulfate, and rotary evaporated to a reddish-brown oil, crude 1,2-dibromobenzonorbornene (17.0 g, 0.0550 mol, 69%). The dehydrobromination with excess potassium *tert*-butoxide in *tert*-butyl alcohol was performed as described previously[6] and the product was distilled to give pure 1-bromobenzonorbornadiene (7.2 g, 0.033 mol, 41% overall from 2-bromobenzonorbornadiene) as a colorless oil, bp 90–93° (1.5 mm), identical in spectral properties with those published and free of any 2 isomer by glc.

Benzonorbornadiene-1-carboxylic Acid (4b).—Bromide **4a** (8.5 g, 0.038 mol) and magnesium (1.0 g, 0.041 g-atom) were mixed in dry tetrahydrofuran (40 ml). An iodine crystal and a few drops of dibromoethane were added and the mixture was refluxed and mechanically stirred for 5 hr. The mixture was cooled in an ice bath and dry carbon dioxide was bubbled through for 1 hr, followed by addition of Dry Ice. Sulfuric acid (10%, 300 ml) was cautiously added and the mixture was extracted with ether (3 × 75 ml). The separated ether layers were then extracted with 10% sodium hydroxide (2 × 100 ml) and the aqueous layers were acidified with 6 *N* hydrochloric acid (100 ml) to produce a white solid. The precipitate was filtered and dried to give crude benzonorbornadiene-1-carboxylic acid (4.1 g, 0.022 mol, 58%), mp 119–123°. Five recrystallizations from ligroin gave a white, crystalline solid: mp 122.2–123.0° (lit.[7b] mp 124–126°); ir (KBr) 3–4 (OH), 5.96 (C=O), 7.09, 7.72, 8.45, 10.80, 13.25, 13.90 μ; nmr ($CDCl_3$) δ 11.82 (s, 1, COOH), 6.6–7.6 (m, 6, ArH and HC=CH), 3.95 (br s, 1, CH), 2.63 (br s, 2, CH_2).

Anal. Calcd. for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41. Found: C, 77.45; H, 5.43.

Benzonorbornadienyl-1-carbinol (4c).—Acid **4b** (4.5 g, 0.024 mol) in anhydrous ether (100 ml) was reduced with lithium aluminum hydride (2.0 g) in ether (100 ml) in normal fashion[8] to give alcohol **4c** (3.3 g, 0.019 mol, 80%), which was recrystallized once from petroleum ether: mp 54–55° (lit.[7b] mp 60°); ir (neat) 2.95 (OH), 3.24 (ArH), 3.37, 3.46 (CH), 5.80 (impurity), 6.84, 8.00, 9.5–9.9 (CO), 13.35, 13.75, 14.45 μ; nmr ($CDCl_3$) δ 6.3–7.3 (m, 6, ArH and HC=CH), 4.26 (s, 2, CH_2O), 3.26 (br s, 1, CH), 3.30 (s, 1 OH), 2.35 (d of m, 1, J = 9 Hz, anti H), 2.12 (d of m, 1, J = 9 Hz, syn H). The alcohol was used to make the tosylate and acetate.

Benzonorboranadienyl-1-carbinyl Acetate (4d).—Alcohol **4c** (1.10 g, 0.00640 mol) and acetic anhydride (4.40 g, 0.0432 mol) in pyridine (10 ml) were treated in normal fashion[10] to give acetate **4d** (1.13 g, 0.00528 mol, 83%), bp 120–140° (1 mm). The acetate was distilled twice more to obtain a pure sample: ir (neat) 3.27 (ArH), 3.4 (CH), 3.50, 5.74 (C=O), 6.90, 7.30, 8.10 (CO), 9.70 (CO), 13.35, 13.75, 14.50 μ; nmr (CCl_4) δ 6.7–7.3 (m, 5, ArH and C=CH), 6.55 (d of m, 1, C=CH, J = 6 Hz), 4.72 (s, 2, CH_2OAc), 3.7–4.0 (m, 1, CH), 2.1–2.4 (m, 2, CCH_2C), 2.03 (s, 3, CH_3).

Anal. Calcd for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.29; H, 6.76.

Benzonorbornadienyl-1-carbinyl Tosylate (4e).—Alcohol **4c** (5.74 g, 0.0334 mol) and purified tosyl chloride (12.7 g, 0.0666 mol) in pyridine (65 ml) by the usual method[9] yielded crude tosylate **4e** quantitatively. One recrystallization from petroleum ether gave mp 70–72°. Five recrystallizations gave a pure sample as white crystals: mp 71.0–71.5°; ir (melt) 3.25 (ArH), 3.35, 3.47 (CH), 6.20 (C=C), 6.80, 7.26 (S=O), 8.49 (S=O), 9.11, 10.45, 10.90, 12.40, 13.18, 13.70, 14.40 μ; nmr ($CDCl_3$) δ 7.3–8.1 (AA'BB', 4, ArH), 6.8–7.4 (m, 5, ArH and C=CH), 6.58 (d of m, 1, C=CH, J = 5 Hz), 4.71 (s, 2, CH_2OSO_2), 3.8–4.0 (m, 1, CH), 2.47 (s, 3, CH_3), 2.33 (d of m, 1, J = 8 Hz, anti H), 2.15 (d of m, 1, J = 8 Hz, syn H).

Anal. Calcd for $C_{19}H_{18}O_3S$: C, 69.91; H, 5.56. Found: C, 69.70; H, 5.65.

Kinetic Studies.—Standard procedures were followed for the acetolysis studies. Standardized 0.04 *M* sodium acetate in redistilled glacial acetic acid containing 0.3% acetic anhydride was the solvent, with a tosylate concentration of 0.025 *M*. Aliquots (2 ml) were sealed in ampoules and heated at 133 ± 0.5°. The excess sodium acetate was back-titrated in the ampoule with standard 0.014 *M p*-toluenesulfonic acid in acetic acid using bromophenol blue indicator (yellow to colorless end point). The first-order plot of tosylate **4e** was linear to 65% completion.

Solvolysis Products.—Two separate acetolysis product studies were performed. Tosylate **4e** (3.0 g) and sodium acetate trihydrate (1.8 g) were refluxed in acetic acid (225 ml) and acetic anhydride (3 ml) for 7 weeks. The solvent was distilled, and the solution was concentrated to 50 ml and added to solid sodium carbonate. Water was added, the products were extracted with ether, and the ether was washed with 10% sodium carbonate solution and water, dried with magnesium sulfate, and rotary evaporated to give an oil. Infrared and nmr analysis on the crude oil gave indication of only unrearranged acetate **4d**. No evidence of a tosylate was found. Glc analysis confirmed the presence of only the one acetate, **4d**.

In a second study, tosylate **4e** (2.28 g, 0.00700 mol) and anhydrous sodium acetate (1.15 g, 0.0140 mol) were dissolved in redistilled acetic acid (30 ml) containing 0.3% acetic anhydride. The mixture was heated in a pressure bottle at 160° for 10 days. The solution was diluted with water (350 ml), extracted with ether (4 × 100 ml), washed with 10% sodium bicarbonate cautiously (2 × 150 ml), water (2 × 200 ml), and brine, dried with magnesium sulfate, and rotary evaporated to a dark, viscous oil which did not resemble the acetate product above. The product was vacuum distilled to give a pale yellow oil: bp 134–138° (0.10 mm); ir (neat) 3.3–3.5 (CH), 5.81 (C=O), 6.85, 7.35, 8.20 (CO), 9.52 (CO), 10.31, 13.34 μ; nmr (CCl_4) δ 7.0–7.4 (m, 4, ArH), 4.66 (AB, 2, CH_2O, J = 20 Hz), 4.4–4.8 (m, 1, CHO), 3.3–3.5 (m, 1, CH), 2.07 (s, 3, CH_3), 2.05 (s, 3, CH_3), 1.7–2.2 (m, 4, two CH_2C). Two peaks in a ratio of 84:16 were observed by glc. They were collected together and analyzed as diacetates. Infrared, nmr, and glc data showed no indication of rearrangement.

Anal. Calcd for $C_{16}H_{18}O_4$: C, 70.05; H, 6.61. Found: C, 70.01; H, 6.55.

pK_a of Benzonorbornadiene-1-carboxylic Acid (4b).—The acid (0.0558 g, 0.000300 mol) was dissolved in 50% ethanol (50 ml, 1:1 absolute ethanol–distilled water by volume) and titrated with 0.0525 *N* aqueous sodium hydroxide at 24.6° while the pH was measured with a Corning Model 7 pH Meter. The pK_a was obtained from the pH at the half-neutralization point by use of a computer program designed for this purpose. Analytical reagent benzoic acid was used for a control, and its pK_a value agreed well with the literature.[4]

Registry No.—**4a**, 23537-80-6; **4b**, 5890-15-3; **4c**, 19648-23-8; **4d**, 42272-74-2; **4e**, 42272-75-3; *exo*-2-acetoxybenzonorbornadienyl-1-carbinyl acetate, 42272-76-4; *exo*-3-acetoxybenzonorbornadienyl-1-carbinyl acetate, 42272-78-6; 2-bromobenzonorbornadiene, 23537-79-3.

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[12] Melting and boiling points are uncorrected. The following instruments were used: Varian T-60 nmr spectrometer, Beckman IR 8 infrared spectrophotometer, Beckman Microspec Model 1325 infrared spectrophotometer, and a Varian Aerograph Model 700 Autoprep gas chromatograph. Nmr data are given in parts per million (δ) relative to internal TMS, with the usual splitting abbreviations followed by number of protons and interpretation. Only significant ir absorptions are listed in microns (μ). Gas chromatography was performed on an SE-30 column with helium gas as carrier. Microanalyses were performed by Ilse Beetz Microanalytisches Laboratorium, West Germany, and Micro-Tech Laboratories, Skokie, Ill.