lowed here using isobutyl bromide to give a colorless crystalline product in a 60% yield, mp 46–47° (lit.[25] mp 38–40°).

**Di-*sec*-butylphosphinic Acid (5).**—The same procedure as was reported above for making di-*n*-butylphosphinic acid (**3**) was followed here for making **5** by using *sec*-butyl chloride to give product in a 60% yield. The final recrystallization step was omitted since the product is a liquid at room temperature. This is the first time a pure sample of this compound has been reported, the only other report being that of a crude sample.[26]

*Anal.* Calcd for $C_8H_{19}O_2P$: C, 53.92; H, 10.75; P, 17.38. Found: C, 54.10; H, 10.84; P, 17.51.

**Di-*n*-butylmethylphosphine Oxide (8).**—To a stirred Grignard solution prepared from 411 g (3.0 mol) of *n*-butyl bromide and 73 g (3.0 mol) of magnesium in 1 l. of diethyl ether was added dropwise (over a period of 1 hr) 194 g (1.0 mol) of di-*n*-butyl phosphite. A total of 142 g (1.0 mol) of methyl iodide was added and the mixture heated under reflux for 1.5 hr. The cooled solution was stirred with 500 ml of concentrated HCl and the organic phase (upper layer) was separated. The organic phase was washed successively with two 250-ml portions of water, one 250-ml portion of 1 *M* NaOH, and one 250-ml portion of water. The ether, *n*-butyl alcohol, and water were removed from the organic phase (the latter two under high vacuum since they were quite difficult to remove) to give 128.7 g (73%) of colorless solid product, mp 34–35° (lit.[27] mp 35°).

**Di-*tert*-butylmethylphosphine Oxide (10).**—The same procedure as was reported above for making di-*n*-butylmethylphosphine oxide (**8**) was used here for making **10** by using *tert*-butyl chloride in place of *n*-butyl bromide. The final product was purified by fractional distillation, and the purified product was obtained in a 25% yield. This is a vastly improved yield over the 2% yield of product reported from the reaction of *tert*-butylmagnesium chloride with methylphosphonic dichloride.[28]

**Registry No.**—**1**, 35210-25-4; **2**, 3283-12-3; **3**, 866-32-0; **4**, 15924-57-9; **5**, 35210-27-6; **6**, 677-76-9; **7**, 676-96-0; **8**, 14062-37-4; **9**, 16083-94-6; **10**, 18351-81-0.

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[25] K. A. Petrov, N. K. Bliznyuk, and V. P. Korotkova, *J. Gen. Chem. USSR*, **30**, 2967 (1960).

[26] P. J. Christen and L. M. van der Linde, *Rec. Trav. Chim. Pays-Bas*, **78**, 543 (1959).

[27] G. M. Kosolapoff and R. F. Struck, *Proc. Chem. Soc., London*, 351 (1960).

[28] A. D. Brown, Jr., and G. M. Kosolapoff, *J. Chem. Soc. C*, 839 (1968).

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# *Notes*

## Birch Reduction of Biphenylene. Formation of 4,5-Benzobicyclo[4.2.0]octa-2,4-diene

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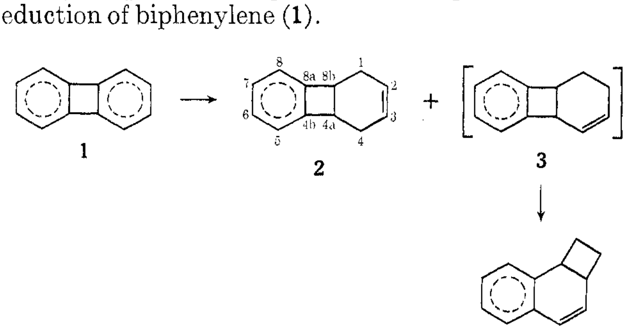
*Received March 3, 1972*

Braun's report[1] of the characterization of the products from the reaction of benzyne and 1,3-cyclohexadiene prompts us to report our findings in the Birch reduction of biphenylene (**1**).



Baker reported[2] that reduction of **1** by sodium in liquid ammonia yielded 30% biphenyl plus unsaturated oil. Atkinson[3] found that the mixture of products obtained by alkali metal reduction in liquid ammonia underwent disproportionation during distillation, reforming a small amount of biphenylene (**1**). Barton[4] found reduction with lithium in ethylamine–diethylamine (1:4 ratio) at 0° to give 85% biphenyl plus small amounts of 1-phenylcyclohexene and a tetrahydrobiphenylene.

Our results differ from those cited. Reduction of **1** using sodium or lithium in liquid ammonia plus anhydrous ether plus ethanol yielded a mixture which glc indicated was composed of unreacted **1**, 1,4,4a,8b-tetrahydrobiphenylene (**2**), and 4,5-benzobicyclo[4.2.0]-octa-2,4-diene (**4**), with the latter two in a ratio of about 4:1. Biphenyl was specifically sought by nmr and glc, but none was found.

Braun[1] isolated **4** from the reaction of benzyne and 1,3-cyclohexadiene and proposed its formation by the rearrangement of 1,2,4a,8b-tetrahydrobiphenylene (**3**), which was the expected minor 1,2 addition product. Thus, our obtaining **4** instead of **3** by a different route supports Braun's proposed rearrangement of **3**. However, neither we nor Braun have isolated **3** or established whether the rearrangement occurs spontaneously or is caused by the glc work-up. It may be significant that two tetrabromo compounds with the same skeletal structure as **3** have been reported[5] and seem stable.

Braun[1] characterized **4**, which exhibits a uv absorption spectrum typical of styrene derivatives rather than benzocyclobutene derivatives.[6] Previously unreported **2** exhibits the uv spectrum (ETOH) typical of a benzocyclobutene derivative and a molecular

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[1] A. M. Braun, *J. Org. Chem.*, **35**, 1208 (1970).

[2] W. Baker, M. P. V. Boarland, and J. F. W. McOmie, *J. Chem. Soc.*, 1476 (1954).

[3] E. R. Atkinson and F. E. Granchelli, private communication cited in M. P. Cava and M. J. Mitchell, "Cyclobutadiene and Related Compounds," Academic Press, New York, N. Y., 1967, pp 267 and 283.

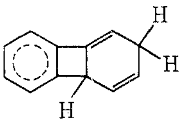
[4] J. W. Barton and D. J. Walsh, unpublished work mentioned by Barton in "Nonbenzenoid Aromatics," Vol. I, J. P. Snyder, Ed., Academic Press, New York, N. Y., 1969, pp 56–57.

[5] J. W. Barton and K. E. Whitaker, *J. Chem. Soc. C*, 28 (1968).

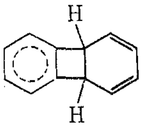
[6] M. P. Cava, R. J. Pohl, and M. J. Mitchell, *J. Amer. Chem. Soc.*, **85**, 2080 (1963).

weight of 156 by mass spectral analysis. Nmr ($CCl_4$) indicates the following protons: four aromatic, two vinyl, two benzylic methinyl, and four allylic methylene. The benzylic hydrogens (δ 3.65) are further downfield than usual[7] for benzylic hydrogens, which is in agreement with their location on a cyclobutene ring.[7,8] Equivalency of the benzylic hydrogens is indicated, as they have the same chemical shift and do not split one another (a $J$ of 6–10 magnitude[7] would be required). Also absence of mutual splitting and identical chemical shift indicate equivalency of the vinyl hydrogens. The absence of carbon-to-carbon double bond stretching in the 1600–1680-cm$^{-1}$ region of the ir spectrum, as well as the overall simplicity of the ir and nmr spectra, agrees with the symmetrical structure of **2**.

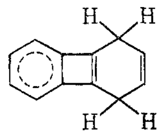
The most likely structures for the dihydro intermediate which must form first and then go on to tetrahydro products **2** and **4** are 2,4a-dihydrobiphenylene (**5**), 4a,8b-dihydrobiphenylene (**6**), and 1,4-dihydrobiphenylene (**7**). **5** is the product predicted[9] by Streitwieser, who used molecular orbital theory based on protonation at sites of highest electron density in the radical anion and anion intermediates. Further reduction of **5** would be expected to form **3**. Isomerization of **5** to 1,8b-dihydrobiphenylene (**8**) by the ethoxide ion present is reasonable and further reduction would lead to **2** and **3**.



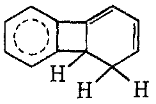
**5**



**6**



**7**



**8**

### Experimental Section[10]

**Biphenylene** (1) was prepared in 25% yield by the procedure of Friedman,[11] mp 108–110°.

**Reduction of Biphenylene** (1).—To a stirred, refluxing (−33°) mixture of 500 ml of liquid ammonia, 150 ml of anhydrous ether, and 2.00 g of 1 (0.0132 mol) was added 0.90 g of sodium (0.039 mol). The blue solution was stirred for 15 min and then 15 ml of absolute ethanol was added over a 5-min period. The blue color disappeared and the $NH_3$ was allowed to evaporate. The residue was mixed with 150 ml of water and extracted with ether. Evaporation of the ether from the dried extracts ($MgSO_4$) yielded 1.70 g of a mixture of solid and liquid. Glc analysis indicated that **1**, **2**, and **4** were present in the ratio of 11:4:1 and that biphenyl was absent. Nmr confirmed the absence of biphenyl. Preparative glc gave enough material for spectral and elemental analysis.

Use of lithium instead of sodium required no ethanol but gave the same results. When the amount of sodium was increased to 4.5 equiv, then no unreacted **1** remained and the amounts of **2** and **4** were increased proportionally.

**1,4,4a,8b-Tetrahydrobiphenylene** (2): nmr ($CCl_4$) δ 2.35 ("filled-in" t, $J$ = <3 Hz, 4 H), 3.65 ("filled-in" t, $J$ = <3 Hz, 2 H), 5.60 ("filled-in" t, $J$ = <3 Hz, 2 H), 6.95 (m, 4); ir (neat) 3.3, 3.4, 3.5, 6.9, 13.5 (ortho-disubstituted benzene), and 14.8 μ (*cis*-HC=CH); uv max (ethanol) 214 (ε 5184), 261 (ε 1410), 266.5 (ε 2150), and 273 nm (ε 2570); mol wt 156 (mass spectrum).

*Anal.* Calcd for $C_{12}H_{12}$: C, 92.25; H, 7.74. Found: C, 92.10; H, 7.71.

The dibromide of **2** was prepared by addition of bromine in $CCl_4$, mp 87–88°, recrystallized from ethanol.

*Anal.* Calcd for $C_{12}H_{12}Br_2$: C, 45.60; H, 3.83; Br, 50.57. Found: C, 45.37; H, 3.98; Br, 50.50.

**4,5-Benzobicyclo[4.2.0]octa-2,4-diene** (4): nmr ($CCl_4$) same as published spectrum[1] δ 1.8–2.7 (m, 4, two $CH_2$), 2.9–3.9 (m, 2, methyl CH), 5.75 (double d, 1, $J_{AB}$ = 10 Hz, $J$ = 3 Hz, vinyl CH), 6.30 (d, 1, $J_{AB}$ = 10, vinyl CH), 6.93 (m, 4, aromatic CH); ir (neat) 13.2 μ; uv max (ethanol) 219.5 nm (ε 22,265), 226 (ε 17,877), 248.5 (ε 7801), 271 nm (ε 6825), lit.[1] max 248 nm (ε 8600); mol wt 156 (mass spectrum).

*Anal.* Calcd for $C_{12}H_{12}$: C, 92.25; H, 7.74. Found: C, 92.15; H, 7.55.

**Registry No.**—**1,** 259-79-0; **2,** 35031-03-9; **2** dibromide, 35031-04-0; **4**, 21367-71-5.

**Acknowledgment.**—The authors are indebted to the Research Corp. for a Frederick Gardner Cottrell grant, which purchased some of the equipment used, and to Dr. D. K. Wedegaertner and the University of Rochester, N. Y., for the nmr and mass spectra.

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[7] R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," 2nd ed, Wiley, New York, N. Y., 1967, pp 136–145.

[8] F. A. Bovey, "NMR Data Tables for Organic Compounds," Wiley, New York, N. Y., 1967, pp 353 and 416.

[9] (a) A. Streitwieser, Jr., "Molecular Orbital Theory," Wiley, New York, N. Y., 1961, p 429; (b) A. Streitwieser, Jr., and S. Suzuki, *Tetrahedron*, **16**, 153 (1961).

[10] Analyses were by Bernhardt Mikroanalytisches Laboratorium, Elbach uber Engelskirken, West Germany. Ir spectra were obtained on Perkin-Elmer 137B. Nmr spectra were obtained in $CCl_4$ on Joel JNM-C-60HL with tetramethylsilane as internal standard. Molecular weights were obtained using a Hitachi Perkin-Elmer RNV-6E mass spectrometer. Uv spectra were obtained on a Perkin-Elmer 202. Glc analysis and separations were done using Aerograph Model A-90-P instrument and a 1/4 in. × 10 ft column of 10% Carbowax on 80–100 mesh firebrick treated with HMDS at 190°. The ammonia for the reductions was distilled from its metal cylinder and condensed in the reduction flask, but not dried before use. The sodium was cut free of oxide and hydroxide just before use.

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## Hydrogenolysis of the Acetal 6,8-Dioxabicyclo[3.2.1]octane by Aluminum Chloride Hydride. Evidence for the Preferred Direction of Ring Cleavage in the Course of α-Bromination of This Acetal

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A recent report[2] has suggested that bromination of acetals is acid catalyzed and that the exclusive attack of bromine on the α position of the acetal 6,8-dioxabicyclo[3.2.1]octane (**1**) is the result of initial cleavage of the protonated acetal to give the oxocarbonium ion **2** and/or **6** (path A and/or B of Scheme I) which in turn would lose a proton to form an intermediate α,β-unsaturated ether **3** and/or **7**. Bromine attack on **3** and/or **7** would produce the species **4** and/or **8** which would then suffer intramolecular attack by the hydroxyl group to re-

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[1] Author to whom correspondence should be directed.

[2] T. P. Murray, C. S. Williams, and R. K. Brown, *J. Org. Chem.*, **36**, 1311 (1971).