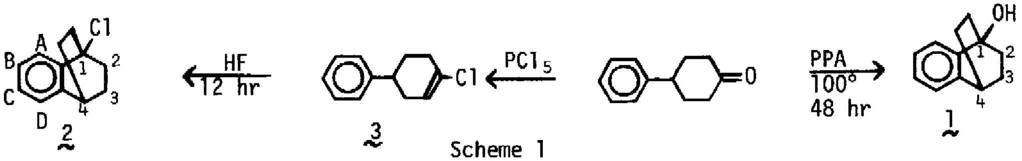
Tetrahedron Letters No. 51, pp 4669-4670, 1976. Pergamon Press. Printed in Great Britain.

GENERATION OF NOVEL BRIDGEHEAD SUBSTITUTED BENZOBICYCLO[2.2.2]OCTENES BY 1,4 ARYL PARTICIPATION

Virginia R. Haddon* and Han Chen, Department of Chemistry
Douglass College, Rutgers University, New Brunswick, New Jersey 08903

(Received in USA 21 June 1976; received in UK for publication 28 October 1976)

Bridgehead reactivity has been a subject of interest for many years.[1] As an extension of our interest in 1,4-aryl participation reactions,[2,3] we are currently investigating the application of such reactions to the synthesis of bridgehead substituted compounds. We now report the first synthesis of two novel bridgehead substituted benzobicyclo[2.2.2]octenes (1,2) from the readily available 4-phenylcyclohexanone using this approach (See Scheme 1).



Scheme 1

Thus, 4-phenylcyclohexanone[4] (100 mg) was converted to benzobicyclo[2.2.2]octen-1-ol, 1, by the action of polyphosphoric acid (5 ml, steam bath, 48 hrs). Following standard ether workup, a small amount of unreacted starting material was removed by its precipitation as the semicarbazone, affording the vpc-pure product alcohol as white crystals, m.p. 108.5-110°, 81% yield. All spectral data confirmed the structure of the product as benzobicyclo[2.2.2]octen-1-ol (1). High resolution mass spectrometry on the molecular ion of 1 gave a formula of $C_{12}H_{14}O$ (measured mass 174.0995, calculated 174.1045). Nmr (60 MHz, $CDCl_3$): δ7.6-7.0(c, 4H, Ar), 2.95(b, 1H, H_4), (c.f. δ2.93 for the bridgehead proton of benzobicyclo[2.2.2]octene), 2.1-1.2(c, 9H, including one D_2O-exchangeable proton at δ1.5). IR (nujol mull)3350 cm^{-1} (OH).

The synthesis of the chloro compound 2 (benzobicyclo[2.2.2]octen-1-yl chloride) proceeded via 1-chloro-4-phenylcyclohexene, 3, which was formed in 92% yield by reaction of 4-phenylcyclohexanone with phosphorus pentachloride. Recrystallization of the product from pentane afforded colorless crystals of 3 (92% yield), m.p. 50.8-51.5°. Analysis: calculated for $C_{12}H_{13}Cl$: C, 74.78; H, 6.80; Cl, 18.41. Found: C, 75.05; H, 6.74; Cl, 18.51. Nmr (60 MHz, $CDCl_3$): δ7.4-7.0(c , 5H, Ar), 5.82(b , 1H, olefinic), 3.0-1.6(c, 7H, aliphatic.)

1-Chloro-4-phenylcyclohexene (10 g) was placed in a polyethylene bottle equipped with a teflon coated stirrer bar, and anhydrous hydrogen fluoride (12 ml) was concensed into the bottle. The reaction mixture was stirred overnight, during which time the hydrogen fluoride was allowed to evaporate. Standard pentane workup yielded a colorless oil (7.4 g) whose major component (88%) was isolated by preparative vpc (6' SE30,270°) to provide 2,b.p.148°,.07mm whose spectral data were wholly consistent with the structure given. High resolution mass spectrometry gave a formula of $C_{12}H_{13}Cl$ (measured 194.0673 and 192.0700, calculated 194.0676 and 192.0705).

U.V. $\lambda_{max}^{CHCl_3}$ 208 (ε9,270) and 260.5 (319). Nmr (60 MHz, CCl_4): δ7.5(*c* , 1H, H_A), 7.1(*c* , 3H, $H_{B,C,D}$), 2.9(*b* , 1H, H_4), 2.5-1.5(*c* , 8H, CH_2). At 200 MHz the aromatic region was sufficiently simplified to allow its complete analysis as an ABCD system. 30 assigned lines produced, after three iterations, a calculated spectrum whose R.M.S. deviation from the observed spectrum was 0.183. The final parameter sets thus derived were only compatible with an unsymmetrical *o*-disubstituted benzene: δ_A 7.540, δ_B 7.191, δ_C 7.133, δ_D 7.036, $J_{A,B}$ 7.42, $J_{A,C}$ 1.07, $J_{A,D}$ 0.22, $J_{B,C}$ 7.36, $J_{B,D}$ 1.13, $J_{C,D}$ 7.28.

Although benzobicyclo[2.2.2]octene itself has been known since 1938,[5] ours is the first synthesis of bridgehead substituted compounds in this series.[6] The mechanism of formation of **1** and **2** proceeds via a 1,4 aryl participation across a (boat) cyclohexane. It is not possible to differentiate between the Ar_1-5 and Ar_2-6 modes in this system, although such mechanistic elucidation has been accomplished in the 4-aryl-*n*-butyl *p*-bromobenzenesulfonate series.[2,3] To our knowledge such 1,4 aryl participation reactions have not previously been extended to the synthesis of bridgehead substituted compounds.

Compounds **1** and **2** are of considerable interest with respect to their stability and solvolytic behavior. The 1-position is both benzylic *and* a bridgehead position, and the effects of these factors on reactivity at that position is currently being studied in our laboratory.

Acknowledgement is made to the Donors of the Petroleum Research Fund (Grant #8500-G1) administered by the American Chemical Society and to the Rutgers Research Council for the support of this research.

REFERENCES

1. a) D. E. Applequist and J. D. Roberts, Chem. Rev. **54**, 1065 (1954); b) R. C. Fort, Jr. in "Carbonium Ions", Vol. IV, G. A. Olah and P. v. R. Schleyer, ed., Wiley, New York, New York, 1973, Chapter 32; c) R. C. Fort and P. v. R. Schleyer, Adv. Alicyclic Chem. **1**, 283 (1966).
2. V. R. Haddon and L. M. Jackman, J. Amer. Chem. Soc. **93**, 3832 (1971).
3. L. M. Jackman and V. R. Haddon, J. Amer. Chem. Soc. **96**, 5130 (1974).
4. H. E. Ungnade, J. Org. Chem. **13**, 361 (1948).
5. B. A. Kasanskii and L. J. Vol'fson, J. Gen. Chem. (USSR) **8**, 1685 (1938).
6. The bridgehead tosylate was suggested as a minor product in the acetolysis of benzonorbornenyl-1-carbinyl tosylate,[7] but its structure was not unambiguously determined.
7. J. W. Hill, H. F. Dubeck, Jr., J. P. Berliner and C. A. Schneider, J. Org. Chem. **35**, 2402 (1970).