The Mechanism of Addition of Benzyne to Cyclopentadienyl- and Indenyl-magnesium Bromide

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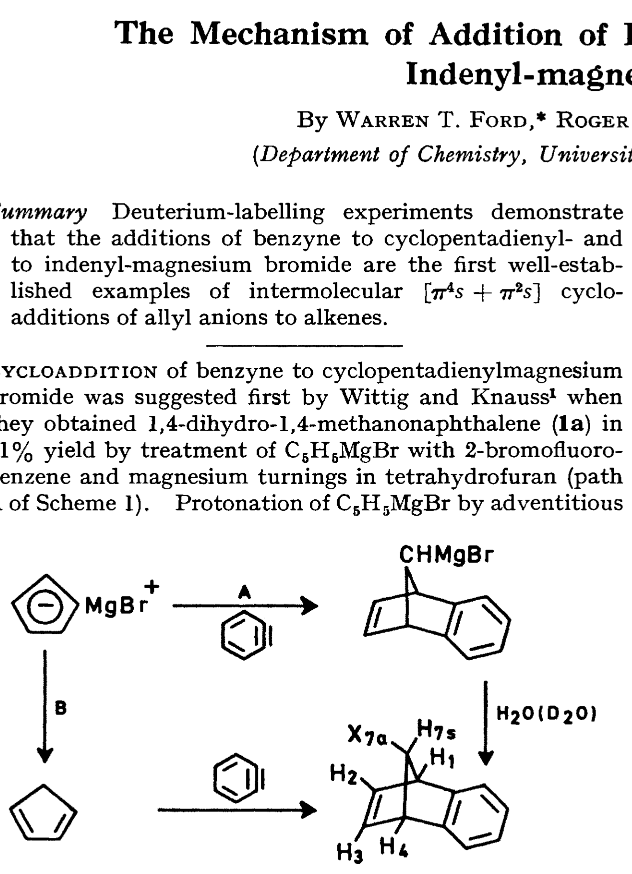
Summary Deuterium-labelling experiments demonstrate that the additions of benzyne to cyclopentadienyl- and to indenyl-magnesium bromide are the first well-established examples of intermolecular $[\pi^4s + \pi^2s]$ cycloadditions of allyl anions to alkenes.

CYCLOADDITION of benzyne to cyclopentadienylmagnesium bromide was suggested first by Wittig and Knauss[1] when they obtained 1,4-dihydro-1,4-methanonaphthalene (**1a**) in 21% yield by treatment of C_5H_5MgBr with 2-bromofluorobenzene and magnesium turnings in tetrahydrofuran (path A of Scheme 1). Protonation of C_5H_5MgBr by adventitious moisture to give cyclopentadiene (path B of Scheme 1), which adds to benzyne in 66·5% yield under similar conditions,[1] might also explain formation of (**1a**). We have prepared C_5H_5MgBr by heating a solution of cyclopentadiene (38 mmole) and ethylmagnesium bromide (40 mmole) under reflux in 25 ml of tetrahydrofuran over an excess of Mg until peaks due to vinyl hydrogens were entirely replaced by a single peak at δ 5·94 in the ^1H n.m.r. spectrum of the solution. Addition of 2-bromofluorobenzene (37 mmole) at reflux followed by hydrolysis with D_2O, work-up, and distillation gave a 29% yield of (**1b**) which contained a 0·91 atom excess of deuterium. Deuterium content was determined from comparison of the areas of ^1H n.m.r. signals of (**1b**) at δ 2·15 (7*s*-H and 7*a*-H) and δ 3·75 (1-H and 4-H) and from the 143/142 isotope ratio in its mass spectrum at low electron energy (Atlas CH-4). All of the deuterium ($\geqslant 95\%$) was incorporated *anti* to the benzene ring as determined from the ^1H n.m.r. spectrum of the diphenylisobenzofuran adduct of (**1b**).[2] Incorporation of deuterium during hydrolysis confirms path A and rules out path B for the mechanism of formation of (**1**).



(**1a**) X = H
(**1b**) X = D

SCHEME 1. *Mechanisms for addition of benzyne to cyclopentadienylmagnesium bromide.*

Addition of an equimolar mixture of cyclopentadiene and 2-bromofluorobenzene to a mixture of tetrahydrofuran and Mg followed by D_2O hydrolysis gave (**1**) containing a 0·05 atom excess of deuterium, indicating that the intermediate 2-fluorophenylmagnesium bromide produced benzyne much faster than it abstracted a proton from cyclopentadiene.

However, Huebner and Donoghue[3] reported that treatment of indene with a fourfold excess of 2-bromofluorobenzene and Mg in tetrahydrofuran led to 9,10-dihydro-9,10-methanoanthracene (**2a**) and 9,10-dihydro-9,10-methanoanthracen-11-ol (**2c**) in 22% and 9% yields, respectively. The (**2c**) was presumably formed by oxidation of the intermediate Grignard reagent (**2d**) in path A of Scheme 2. Thermal conversion of indene into isoindene proceeds readily only at >200°,[4] but base-catalysed formation of isoindene might account for production of (**2a**) *via* path B of Scheme 2. We have repeated their[3] preparation and were able to isolate only a 15% yield of (**2a**) and no (**2c**). Hydrolysis with D_2O produced (**2b**) containing a 0·90 atom excess of deuterium by the ^1H n.m.r. and mass spectral methods described for (**1**). Deuterium incorporation during hydrolysis confirms that (**2a**) is formed by cycloaddition of benzyne to C_9H_7MgBr rather than to isoindene.

Two-step ionic mechanisms for addition of C_5H_5MgBr and C_9H_7MgBr to benzyne are highly unlikely because they would require conversion of aryl Grignard reagents into the less stable (**1**; X = MgBr) and (**2d**). Nucleophilic addition would be expected to produce after hydrolysis phenylcyclopentadiene and 3-phenylindene. We have not been able to isolate either of these compounds in our preparations. We have isolated, however, unchanged starting materials (dicyclopentadiene, indene, and 2-bromofluorobenzene) and normal benzyne products (biphenylene, triphenylene, and 2-fluorobiphenyl).

Analogous cycloadditions of benzyne[5] and halogenated benzynes[6] to neutral, instead of anionic, aromatic compounds are known to produce substituted benzobicyclo-[2,2,2]octatrienes. Tetrafluorobenzyne is known to give two cycloadducts with nickelocene.[7] Benzyne is generally considered to be a symmetric singlet in its ground state.[8]

The additions of benzyne to C_5H_5MgBr and to C_9H_7MgBr are the first well-established examples of intermolecular $[\pi^4 s + \pi^2 s]$ cycloadditions of allyl anions to alkenes.[9] Many examples of isoelectronic 1,3-dipolar cycloadditions are known.[9,10] A possible $[\pi^6 s + \pi^4 s]$ cycloaddition of a pentadienyl anion to a diene was reported recently.[11] Although additions of benzyne to aromatic carbanions are special cases, carbanion cycloadditions should soon be common.

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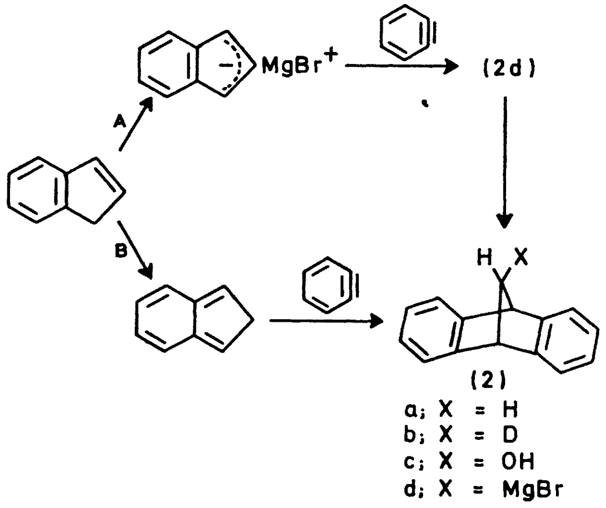

Scheme 2. *Mechanisms for addition of benzyne to indene.*

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[1] G. Wittig and E. Knauss, *Chem. Ber.*, 1958, **91**, 895.

[2] S. J. Cristol and A. L. Noreen, *J. Amer. Chem. Soc.*, 1969, **91**, 3969.

[3] C. F. Huebner and E. M. Donoghue, *J. Org. Chem.*, 1968, **33**, 1678.

[4] W. R. Roth, *Tetrahedron Letters*, 1964, 1009; L. L. Miller, R. Greisinger, and R. F. Boyer, *J. Amer. Chem. Soc.*, 1969, **91**, 1578.

[5] R. G. Miller and M. Stiles, *J. Amer. Chem. Soc.*, 1963, **85**, 1792; M. Stiles, U. Burckhardt, and G. Freund, *J. Org. Chem.*, 1967, **32**, 3718; L. Friedman, *J. Amer. Chem. Soc.*, 1967, **89**, 3071; L. Friedman and D. F. Lindow, *ibid.*, 1968, **90**, 2329.

[6] D. D. Callander, P. L. Coe, J. C. Tatlow, and A. J. Uff, *Tetrahedron*, 1969, **25**, 25; H. Heaney and J. M. Jablonski, *J. Chem. Soc.* (*C*), 1968, 1895; D. J. Berry and B. J. Wakefield, *ibid.*, 1969, 2342; D. M. Roe and A. G. Massey, *J. Organometallic Chem.*, 1969, **17**, 429.

[7] D. M. Roe and A. G. Massey, *J. Organometallic Chem.*, 1969, **20**, P1.

[8] H. E. Simmons and R. W. Hoffmann in R. W. Hoffmann, "Dehydrobenzene and Cycloalkynes," Academic Press, New York, 1967, p. 264.

[9] R. B. Woodward and R. Hoffmann, *Angew. Chem. Internat. Edn.*, 1969, **8**, 781.

[10] For reviews see R. Huisgen, R. Grashey, and J. Sauer, in "The Chemistry of Alkenes," ed. S. Patai, Interscience, New York, 1964, p. 739; R. Huisgen, *J. Org. Chem.*, 1968, **33**, 2291.

[11] C. Cottrell, R. C. Dougherty, G. Fraenkel, and E. Pecchold, *J. Amer. Chem. Soc.*, 1969, **91**, 7545.