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NUCLEOPHILIC ATTACK LEADING TO ADDITION OF ALKYLLITHIUM REAGENTS TO AROMATIC HYDROCARBONS

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Although a few investigators[1,2,3,4] have suggested or observed nucleophilic attack on, and addition to, aromatic hydrocarbons by organosodium or organopotassium reagents, it has been considered[5,6,7] that, generally, either of these are unlikely reaction paths. However, evidence has now been obtained in this Laboratory that alkyllithium compounds, presumably the least reactive of the organoalkali reagents, add to aromatic hydrocarbons at temperatures of 60°C and below, and further, that the addition

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[1] H. Pines and V. Mark, J. Amer. Chem. Soc. 78, 4316 (1956).

[2] L. Schaap and H. Pines, J. Amer. Chem. Soc. 79, 4967 (1957).

[3] A. A. Morton and E. J. Lanpher, J. Org. Chem. 23, 1639 (1958).

[4] K. Hafner, et.al., Ann. Chem. 650, 35, 80 (1961) have observed addition of alkyllithium reagents to azulene.

[5] A. A. Morton, Chem. Rev. 35, 1 (1944).

[6] J. D. Roberts and D. Y. Curtin, J. Amer. Chem. Soc. 68, 1658 (1946).

[7] D. Bryce-Smith, J. Chem. Soc. 1079 (1954).

proceeds via nucleophilic attack of a carbanion on an aromatic carbon.

It was recently observed[8] that alkyllithium reagents react with aromatic hydrocarbons at elevated temperatures in hydrocarbon solvents to yield mono- and dialkylated aromatic systems. While further studying this reaction, it was found that an isolable intermediate is formed if the aromatic hydrocarbon reactant is naphthalene or biphenyl. As the reaction proceeds, the intermediate is consumed and the alkylaromatic hydrocarbon and lithium hydride are produced.

In a typical reaction commercial[9] t-butyllithium in pentane was mixed with decahydronaphthalene, and the solution was allowed to react with naphthalene at 60°C for 28 hours. After hydrolysis, the organic products were separated and subjected to efficient fractional distillation. In addition to naphthalene and α- and β- t-butylnaphthalene, a 17 per cent yield of material boiling between these two products was isolated. By carbon and hydrogen analysis, quantitative hydrogenation and infrared spectra this was shown to be a mixture of t-butyldihydronaphthalenes. When the intermediate (I, II and III) was hydrolyzed with D_2O, a deuterium-containing t-butyldihydronaphthalene product was obtained. The n.m.r.[10] and infrared spectra of the products obtained upon hydrolysis with H_2O and D_2O indicated that 1-t-butyl-1,4-dihydronaphthalene, I, and 1-t-butyl-1,2-dihydronaphthalene, II, in the ratio 1/2 were the isomers

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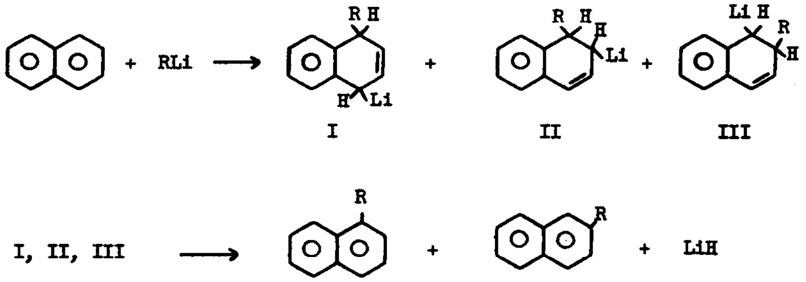
[8] J. A. Dixon and D. H. Fishman, J. Amer. Chem. Soc. **85**, 1356 (1963).

[9] Lithium Corporation of America.

[10] We are indebted to Dr. John Y. Beach of the California Research Corporation for the analysis of the n.m.r. spectra.

principally present. There was a much lesser amount of 2-t-butyl-1,2-dihydronaphthalene, III.



That this relatively facile addition occurs via nucleophilic attack of the carbanion is indicated by at least two observations. (1) The rate of alkylation is a function of aromatic substrate structure with biphenyl >> benzene > toluene > t-butylbenzene. From this series it is seen that inductive effects appear to be important, and that electron-withdrawing groups accelerate and electron-donating groups retard the reaction. (2) The rate of alkylation is a function of the alkyllithium reagent structure with t-butyl > sec-butyl > n-butyl. This series is just that which would be predicted from the limited data available[11,12] and our perhaps-primitive notions concerning the stabilities (or reactivities) of alkyl carbanions as a function of the structure of the alkyl group. Since the cation is in all cases lithium, it is believed

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[11] D. E. Applequist and D. F. O'Brien, J. Amer. Chem. Soc. 85, 743 (1963).

[12] P. D. Bartlett, S. Friedman and M. Stiles, J. Amer. Chem. Soc. 75, 1771 (1953).

that this series reflects the role of the anion as the attacking species. Further, inasmuch as the alkylation reaction proceeds via addition, rather than substitution, the nucleophilic attack is on carbon rather than on hydrogen. Protophilic attack has been suggested by Roberts[6] and Bryce-Smith[7] as the reaction path in metalation of aromatic compounds by alkylmetallic reagents.

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