Stereochemistry and Orientation of the Addition of Alkyl-lithium to 9-Methylanthracene†

By DAVID J. SCHAEFFER, ROBERT LITMAN, and HERMAN E. ZIEGER*
(*Department of Chemistry, Brooklyn College of the City University of New York, Brooklyn, New York* 11210)

Summary Alkylaromatic radicals are proposed as plausible intermediates in the radical-anion-initiated alkylation of aromatic hydrocarbons by alkyl-lithium reagents.

ALTHOUGH the addition of lithium alkyls to phenyl-conjugated olefins and dienes has been known for many years,[1] additions to alternate aromatic hydrocarbons have been reported only recently.[2,3] The reaction produces an alkyldihydroaromatic lithium compound and is thought to be best understood in terms of an ionic addition of lithium alkyl to the aromatic hydrocarbon.[4]

Anthracene[5] and perylene[3] react readily in tetrahydrofuran (THF) or benzene solution, while naphthalene, biphenyl, and phenanthrene could not be alkylated to any significant extent in this laboratory with primary alkyllithiums.[6] The order of alkylation reactivity in aromatic hydrocarbons parallels their polarographic single-electron reduction potentials.[7] The reactivity sequence of the lithium alkyls is $\mathrm{Bu^t} > \mathrm{Bu^s} > \mathrm{Bu^n}$.[2] Methyl-lithium reacts slowly at higher temperatures in THF[8] or in the presence of *NNN'N'*-tetramethylethylenediamine.[9] A similar relative reactivity was observed in alkyl-lithium additions to ethylene.[10]

Recently, it was reported that the addition of alkyllithium to anthracene, followed by alkyl iodide quenching, stereospecifically produces *cis*-9,10-dialkyl-9,10-DHA[8] (DHA = dihydroanthracene), suggesting that two consecutive stereospecific reactions occur, (i) alkyl-lithium

---

† D. J. Schaeffer, Ph.D. Thesis, The City University of New York, 1970; *Diss. Abstracts*, 1970, **31** B, 131.

addition to anthracene and (ii) reaction of the intermediate 10-alkyl-9-lithio-9,10-DHA carbanion with alkyl halide to give a *cis*-9,10-dialkyl-9,10-DHA. This might be evidence for nucleophilic addition of alkyl-lithium reagents to aromatic hydrocarbons. In fact, it is in partial agreement with our early work[11] on reactions of 10-ethyl-9-lithio-9,10-DHA with methyl iodide, but not with our later results[12] on reactions of 10-isopropyl-9-lithio-9,10-DHA with methyl and isopropyl iodide.

If alkyl-lithium reagents add stereospecifically to anthracene, additions to 9-methylanthracene should produce only the *cis*-9,10-dialkyl-9,10-DHA stereoisomer together with some 9,9-dialkyl-9,10-DHA. In fact the addition of ethyl-lithium to 9-methylanthracene in THF at 0° for one h followed by hydrolysis with water gave both *cis*- and *trans*-9-ethyl-10-methyl-9,10-DHA in 25—30% yields together with 9-methyl-9,10-DHA and smaller amounts of a dimer (m.p. 226—230°) and a trimer (m.p. 326—328°). the addition of isopropyl-lithium to 9-methylanthracene is similarly regiospecific[13] in THF at $-60°$. The formation of both *cis*- and *trans*-9-isopropyl-10-methyl-9,10-DHA suggests that alkyl-lithium addition is neither concerted nor stereospecific.

Based on a study of the reaction of anthracene with a cyclohexane solution of ethyl-lithium-*NNN'N'*-tetramethyl-*o*-phenylenediamine complex,† we suggest that the actual reaction pathway involves homolytic cleavage of the carbon–lithium bond [equations (1)—(3)].

In the first step the alkyl-lithium transfers an electron to the aromatic hydrocarbon to form an aromatic radical anion (*cf.* ref. 14). In step (2), the alkyl radical adds to a new molecule of hydrocarbon to generate an alkylaromatic radical which is reduced in step (3) to an alkylaromatic carbanion with formation of a fresh alkyl radical. In equation (1) equilibrium is displaced to the left. That is, the amount of aromatic radical anion being formed is only sufficient to initiate the alkylation process. Alkyl radicals from (1) may couple with aromatic radical anions but such coupling is not indicated by experiments in which alkyl radicals are generated in the presence of radical anions.[15]

$$\text{RLi} + \text{ArH} \rightleftarrows \text{(complex)} \rightarrow \overset{-}{\text{ArH}}{}^{\bullet}\ \text{Li}^{+} + \text{R}\cdot \qquad (1)$$

$$\text{R}\cdot + \text{ArH} \rightleftarrows \text{R-ArH}\cdot \qquad (2)$$

$$\text{R-ArH}\cdot + \text{RLi} \rightarrow \text{R-Ar}\overset{\bullet}{\text{H}}{}^{-}\text{Li}^{+} + \text{R}\cdot \qquad (3)$$

Our basis for proposing (3) is a study of the reduction of the trityl radical with n-butyl-lithium in cyclohexane using visible spectroscopy. The yellow colour of the solution is rapidly and quantitatively converted into that of the trityl carbanion. Similarly, current research on the reaction of 9-methylanthracenyl-lithium with ethyl-lithium shows that the 9-methylanthracenyl dianion is formed.[15]

We thank the City University of New York for a Faculty Research grant.

(*Received, March 15th*, 1971; *Com.* 265.)

[1] K. Ziegler, F. Crossman, H. Kleiner, and O. Schafer, *Annalen*, 1929, **473**, 1.
[2] R. L. Eppley and J. A. Dixon, *J. Amer. Chem. Soc.*, 1968, **90**, 1606 and refs. therein.
[3] H. E. Zieger, *J. Org. Chem.*, 1966, **31**, 2977.
[4] J. A. Dixon, D. H. Fishman, and R. S. Dudinyak, *Tetrahedron Letters*, 1964, 613.
[5] D. Nichols and M. Szwarc, *Proc. Roy. Soc.*, 1967, *A* **301**, 231.
[6] H. E. Zieger and co-workers, unpublished observations.
[7] I. Bergman, *Trans. Faraday Soc.*, 1954, **50**, 829.
[8] R. G. Harvey and C. C. Davis, *J. Org. Chem*, 1969, **34**, 3806.
[9] H. E. Zieger and E. Laski, *Tetrahedron Letters*, 1966, 3801.
[10] P. D. Bartlett, S. J. Tauber, and W. P. Weber, *J. Amer. Chem. Soc.*, 1969, **91**, 6362.
[11] D. J. Schaeffer and H. E. Zieger, *J. Org. Chem.*, 1969, **34**, 3958.
[12] H. E. Zieger, D. J. Schaeffer, and R. M. Padronaggio, *Tetrahedron Letters*, 1969, 5027.
[13] A. Hassner, *J. Org. Chem.*, 1968, **33**, 2684.
[14] J. E. Mulvaney, S. Groen, L. J. Carr, Z. G. Garlund, and S. L. Gardlund, *J. Amer. Chem. Soc.*, 1969, **91**, 388.
[15] H. E. Zieger and I. Angres, in preparation.