Photochemical Addition of Methyl-lithium to Anthracene

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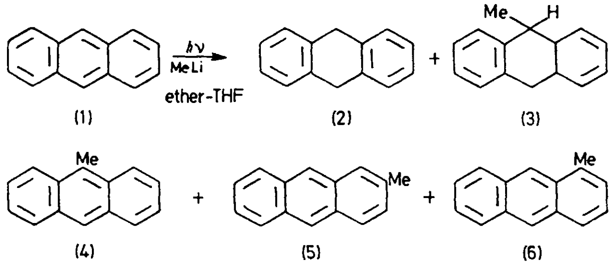
Summary Methyl-lithium adds photochemically to anthracene to give substantial amounts of the 2- and 9-methylated products.

The thermal addition of alkyl-lithium reagents to aromatic hydrocarbons has been studied by several groups.[1] Anthracene (**1**) is reported to give the 9-alkyl-9,10-dihydroanthracenes; a photochemical reaction of alkyl-lithium reagents with (**1**) (and other aromatic compounds) also occurs,[1g] producing from (**1**) the 9-alkylated products, except in the case of methyl-lithium, which was reported to give only 9,10-dihydroanthracene (**2**) in small amounts with ether as solvent and in somewhat greater amounts in tetrahydrofuran (THF).[1g] We have further investigated the photochemical reaction of (**1**) with MeLi (at higher concentrations of MeLi than previously used)[1g] and have found that alkylation does indeed occur. Furthermore, the isomer distribution of the methylanthracenes produced is strikingly different from that produced in the thermal addition of MeLi to (**1**) and from the isomer distributions reported for the photoadditions of other alkyl-lithiums to (**1**).[1g]



(1) (2) (3) (4) (5) (6)

A solution of (**1**) (0·013M) and MeLi (0·91M) in ether was irradiated (Pyrex filter) for 6·5 h. The reaction was monitored by g.l.c. of hydrolysed aliquot portions. The hydrolysed final reaction mixture contained 9-methyl-9,10-dihydroanthracene (**3**), 1-, 2-, and 9-methylanthracene, and other (1- and 2-) methyldihydroanthracenes† [but little (**2**)]. Oxidation of the mixture with Pd–C in xylene afforded‡ compounds (**4**) (19%), (**5**), (12%), and (**6**) (*ca.* 3%), in addition to 19% of recovered (**1**). With THF as cosolvent the reaction proceeds faster and gives substantial amounts of (**2**) and an increased ratio of 2-methyl- (**5**) relative to 9-methyl- (**4**) anthracene. Thus, after 2·5 h a solution of (**1**) (0·013 M) and MeLi (0·91 M) in THF–ether (6:5) pro-

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† The structures of these materials, which could not be obtained in pure form, are indicated by their n.m.r. spectra and by their disappearance upon treatment with Pd–C coincident with the appearance of (**5**) and (**6**).

‡ Product yields are based on unrecovered (**1**).

duced 23% of (**2**) and, after oxidation, 12% of (**4**), 13% of (**5**), and 4% of (**6**) in addition to 15% of recovered (**1**).

When a 0·013M-ether solution of (**1**) alone was irradiated, essentially all the (**1**) had disappeared (to dimer) after 0·5 h. Therefore, MeLi is an efficient quencher of (**1**).

Thermal addition of MeLi to (**1**) in THF–ether proceeded slowly at 50—55°. Reaction of a solution of (**1**) (0·14M) and MeLi (0·75M) in THF–ether (5:3) for 7 h gave *ca.* 20% conversion of (**1**). Analysis of the oxidized product mixture showed the alkylated anthracenes to consist of 92% of (**4**), *ca.* 7% of (**6**), and a trace (*ca.* 1—2%) of (**5**). In contrast, photolysis of an identical solution gave 21% of (**2**), 15% of (**4**), 21% of (**5**), and 4% of (**6**). Therefore, it is clear that (a) MeLi does add to (**1**) photochemically; (b) MeLi inhibits the photochemical dimerization of (**1**); and (c) the isomer distribution of methylanthracenes produced photochemically, where a large amount of 2-alkyl product is found, is radically different from that produced thermally and from that reported for other photoalkylations,[1] where exclusive or nearly exclusive 9-alkylation is the case.¶

The e.s.r. spectrum obtained after irradiation of (**1**) and MeLi in ether was similar to that after irradiation of (**1**) in the presence of PhLi.§ The latter reaction has been shown to produce the anthracene radical anion.[1h] Thus an electron transfer–alkyl transfer process is indicated. However, it is also possible that methylation is a separate reaction not proceeding *via* initial complete electron transfer but *via* a direct addition of a methyl carbanion instead. Either process would result in the formation of lithium salts of methyldihydroanthracenes. Loss of LiH apparently occurs to some extent (more so with the 1- and 2-methylated intermediates, as expected) to form methylanthracenes during the reaction. We note the analogy between the present reaction and the photoaddition of amines to (**1**).[2] The reason for the large amount of 2-alkyl product is presently unknown.

MeLi also adds photochemically to naphthalene and phenanthrene.

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¶ These conclusions hold even in the unlikely extreme event that the entire mass deficiency is a result of a photochemical destruction of only 9-alkylated material.

§ A slight difference (line broadening with PhLi) is attributed to a solvent effect; PhLi experiments were in 35% benzene–ether; MeLi in pure ether.

[1] (a) J. A. Dixon and D. H. Fishman, *J. Amer. Chem. Soc.*, 1963, **85**, 1356; (b) J. A. Dixon, D. H. Fishman, and R. S. Dudinyak, *Tetrahedron Letters*, 1964, 613; (c) D. Nicholls and M. Swarc, *J. Amer. Chem. Soc.*, 1966, **88**, 5757; *Proc. Roy. Soc.*, 1967, A**301**, 231; (d) R. G. Harvey and C. C. Davis, *J. Org. Chem.*, 1969, **34**, 3607; (e) R. G. Harvey, L. Nazareno, and H. Cho, *J. Amer. Chem. Soc.*, 1973, **95**, 2376; (*f*) E. J. Panek, *ibid.*, 1973, **95**, 8460; (g) H. J. S. Winkler, R. Bollinger, and H. Winkler, *J. Org. Chem.*, 1967, **32**, 1700; *Intra-Sci. Chem. Reports*, 1969, **3**, 261; (h) H. J. S. Winkler and H. Winkler, *J. Org. Chem.* 1967, **32**, 1695.

[2] N. C. Yang and J. Libman, *J. Amer. Chem. Soc.*, 1973, **95**, 5783, and references therein.