Bromination of Some Substituted 9-Methylanthracenes

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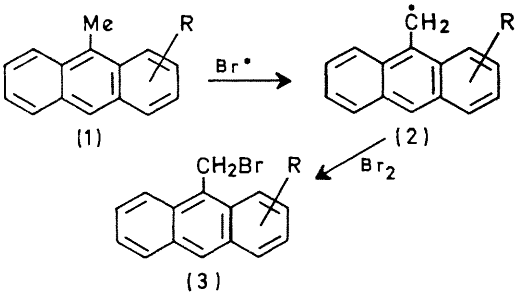
Summary The bromination of a series of 9-methylanthracenes with substituents in the side rings has been investigated under both radical and ionic conditions.

BROMINATION of 2,9- and 3,9-dimethylanthracenes with bromine in carbon disulphide has been reported to take place in the 9-methyl group to give the 9-bromomethylanthracenes.[1] This behaviour is in marked contrast to that of 9-methylanthracene which affords 9-bromo-10-methylanthracene under the same conditions.[2] These reactions have been re-examined and a systematic survey made of the influence of substituents in the side rings on the bromination product under various conditions.

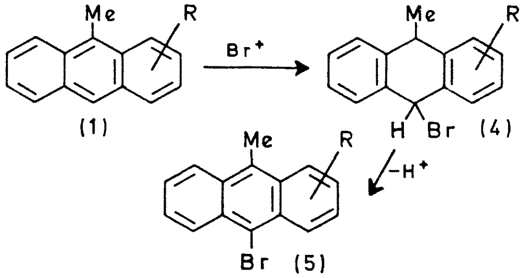
Bromination of 2,9-dimethylanthracene with bromine in carbon tetrachloride gave exclusively 9-bromomethyl-2-methylanthracene. The formation of this compound undoubtedly occurs by a free-radical mechanism (Scheme 1).



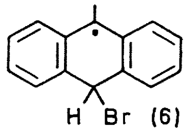
SCHEME 1

It was considered that if the reactions were carried out under conditions to vitiate against the formation of free radicals, then nuclear attack by Br^+ might occur (Scheme 2). Accordingly, the bromination of 2,9-dimethylanthracene was carried out in acetic acid in the dark in an atmosphere of nitrogen and found to give exclusively 10-bromo-2,9-dimethylanthracene. Unless there were vigorous exclusion of both oxygen and light a substantial amount of 9-bromomethyl-2-methylanthracene was obtained, indicative of the high propensity that the substrate has to undergo reaction by a radical pathway.

3,9-Dimethylanthracene and 2-chloro- and 3-chloro-9-methylanthracenes were found to react in the same manner as 2,9-dimethylanthracene giving the 9-bromomethyl compound in carbon tetrachloride and the 10-brominated derivative in acetic acid in the dark under nitrogen. In contrast to the behaviour of these compounds, 9-methylanthracene underwent bromination under both radical and ionic conditions to give only 9-bromo-10-methylanthracene. This would suggest that the radical (**2**; R = H) is less stable than the radical (**6**) resulting from addition of atomic bromine to the anthracene nucleus. No explanation can at present be advanced as to why substitution of the anthracene nucleus by both electron-donating methyl groups and electron-withdrawing chloro-groups apparently reverse the stabilities of these two radical types.



SCHEME 2



(6)

The work was extended to the study of 9-methyl anthracenes with substituents in the 1- and/or 4- or 5-positions. 1,5-Dichloroanthracene, which had previously been shown to undergo bromination in carbon disulphide to give 9-bromomethyl-1,5-dichloroanthracene,[3] was found to give only this compound on bromination both in carbon tetrachloride and in acetic acid in the dark in a nitrogen atmosphere. There was no evidence whatsoever for any nuclear bromination having occurred. Similar results were also obtained for 1,4,9-trimethylanthracene and 1-chloro-10-methylanthracene. The formation of these bromomethyl compounds, which can only be readily accounted for by a radical mechanism, under conditions which would generally be considered prejudicial to the generation of free radicals, is postulated to involve a molecule-induced homolysis of the bromine by the anthracene.[4] The non-intervention of the ionic reaction leading to nuclear substitution is probably because the substituent adjacent to the 10-position sterically inhibits attack at this position.

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[1] E. de B. Barnett and N. F. Goodway, *J. Chem. Soc.*, 1929, 1754.
[2] E. de B. Barnett and M. A. Matthews, *Ber.*, 1926, **59**, 1426.
[3] E. de. B. Barnett, J. W. Cook, and M. A. Matthews, *Ber.*, 1926, **59**, 2863.
[4] W. A. Pryor, "Free Radicals," McGraw-Hill, New York, 1966, p. 119.