Anomalous Products Obtained by Nitration of Some Polyalkylnaphthalenes

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(Received November 16, 1970)

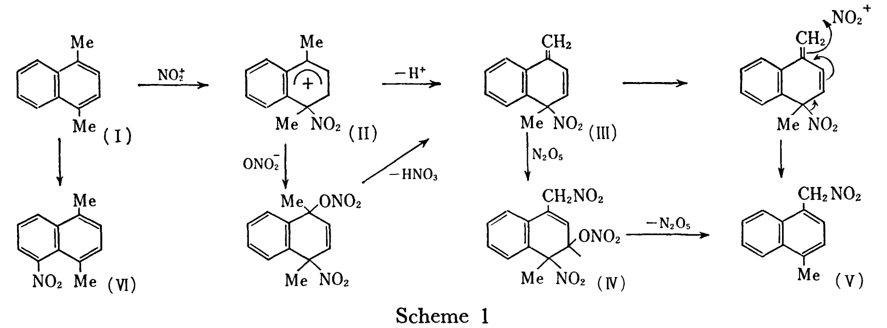
Polyalkylbenzenes react with fuming nitric acid in an unusual way to yield benzyl nitrate as the main product. The reaction has an electrophilic feature and is characterized for its peculiar orientation and high positional selectivity.$^{1)}$ Our studies on the anomalous nitration are now extended to include naphthalene series. Among various polyalkylnaphthalenes investigated, anomaly was observed only with those systems in which both 1 and 4 positions were occupied by alkyl groups. In contrast to the results obtained with polyalkylbenzene derivatives, the major product in this case was not nitrooxymethylnaphthalene but nitromethylnaphthalene.

1,4-Dimethylnaphthalene (I) was treated with fuming nitric acid in dilute methylene chloride solution at −5—0°C for 0.5 hr to give a pale yellow oily mixture, which was found to contain besides 4-methyl-1-nitromethylnaphthalene (V) some amounts of a methylene compound, presumably 1-methylene-4-nitro-4-methyl-1,4-dihydronaphthalene (III), and addition products on the basis of infrared, ultraviolet and PMR spectra as well as by spectral comparison with the anomalous nitration product from 9,10-dimethylanthracene.$^{2)}$ Our result differs somewhat from both an earlier report by Robinson and Thompson$^{3)}$ who isolated V, and from the recent comment by Davies and Warren$^{4)}$ who obtained 1,4-dimethyl-5-nitronaphthalene (VI).

With the use of excess of nitric acid, 1,2,4-trimethylnaphthalene readily underwent side-chain nitration at less hindered methyl group to give 3,4-dimethyl-1-nitromethylnaphthalene (mp 92—95°C) as the principal product. However, 1,2,3-trimethylnaphthalene was only nitrated at ring position to give 1,2,3-trimethyl-4-nitronaphthalene (mp 148—149°C) in good yield. No side-chain attack was observed. 1,2,3,4-Tetramethylnaphthalene showed a similar anomaly to give 2,3,4-trimethyl-1-nitromethylnaphthalene (mp 99.5—101.5°C). The orientation of these side-chain substituted products has been established by treatment of the corresponding polymethylnaphthylmethyl chlorides with silver nitrite in acetonitrile, followed by purification of the resulting nitro compounds through repeated precipitations from alkaline solution.

Davies and Warren$^{4)}$ recently suggested that the nitromethyl compound V can be derived from an acid-catalysed rearrangement of VI. Although the nitro group at the hindered position is known to be subjected to migration in some cases,$^{5)}$ there seems so far to be no analogy of such rearrangement. More probable reaction sequences which account for side-chain nitration might be as shown in Scheme 1

Nitronium ion attaches to 1-position of the higher alkylated ring to form arenonium ion II, in which steric strain due to the interaction between alkyl group and peri-hydrogen is partly relieved and the positive charge is more effectively delocalized when the alkyl groups are located at 1- and 4-positions. Loss of proton from the alkyl side-chain, followed by electrophilic attack of nitronium ion at the terminal methylene group of III, redistribution of electrons to regain the naphthalene ring system, and the concomitant departure of the nitro group from the ring will lead to the formation of side-chain nitro compound. An alternative reaction scheme involves intermediate formation of addition product. The methylene compound III may undergo 1,4-addition of dinitrogen pentoxide to form IV which, on further removal of dinitrogen pentoxide from the ring, will lead to side-chain nitration.



Scheme 1

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1) H. Suzuki and K. Nakamura, This Bulletin, **43**, 473 (1970); H. Suzuki, *ibid.*, **43**, 481 (1970); H. Suzuki, *ibid.*, **43**, 879 (1970); K. Nakamura, *ibid.*, **44**, 133 (1971); K. Nakamura and H. Suzuki, *ibid.*, **44**, 227 (1971).

2) Unpublished result.

3) R. Robinson and H. W. Thompson, *J. Chem. Soc.*, **1932**, 2015.

4) G. Davies and K. D. Warren, *ibid.*, *B*, **1969**, 873.

5) K. H. Pausacker and J. G. Scroggie, *ibid.*, **1955**, 1897; P. H. Gore, *ibid.*, **1957**, 1436.