REACTION OF POLYALKYLBENZENES WITH NITRATING AGENTS IN HSO_3F

A. N. Detsina, V. I. Mamatyuk, and V. A. Koptyug

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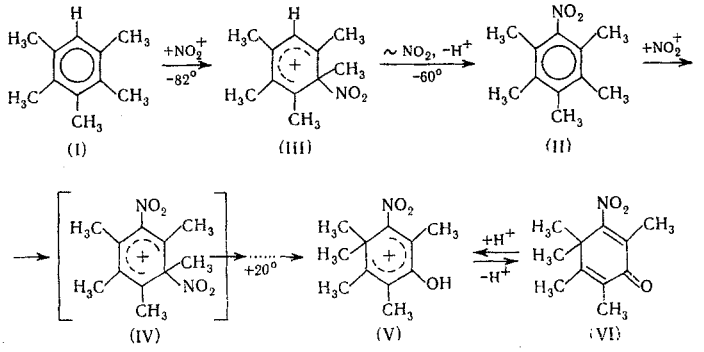
When polyalkylbenzenes are reacted with nitrating agents not only the insertion of the nitro group into the benzene ring is observed, but also various oxidative transformations [1-3]. For example, when pentamethylbenzene (I) is nitrated the maximum yield of pentamethylnitrobenzene (II) is a total of 30% [2, 3]. We established that when such reactions are run in HSO_3F at a sufficiently low temperature, with a subsequent "thawing" of the primary products by gradually raising the temperature, it becomes possible to follow the successive formation of the various particles employing NMR. Thus, when pentamethylbenzene (I) is reacted with either HNO_3 or $NO_2^+BF_4^-$ in HSO_3F the following transformations are observed:



Pentamethylnitrobenzene (II) (mp 155-157°) was obtained in 69% yield when 1 M of HNO_3 was used, while nitrodienone (VI) (mp 86-88°, after neutralization of the acid solution) was obtained in 60% yield when 2 M of HNO_3 were used. The formation of ions (III) and (V) was recorded via the NMR spectra. NMR spectrum of (III) (τ, ppm): 8.04 (1-CH_3), 7.68 (3-CH_3), 7.42 (2- and 6-CH_3), 7.02 (4-CH_3), and 2.36 (5-H) (cf. [4, 5]); NMR spectrum of (V): 8.33 (two groups, 1-CH_3), 7.89 and 7.69 (5- and 3-CH_3), 7.40 (6-CH_3). To prove the structure of these ions and of nitrodienone (VI) we also used the ^{13}C NMR method.

The transformation of (II) to ion (V) is a complicated process, and apparently proceeds with the intermediate formation of the unstable (IV) ion. Its rearrangement to the hydroxynitrobenzenonium ion resembles the previously described transformation of the 1-nitro-1, 2, 3, 4, 5, 6-hexamethylbenzenonium ion to the 6-hydroxy-1, 1, 2, 3, 4, 5-hexamethylbenzenonium ion [4], which is capable of rearranging further to the 4-hydroxy-1, 1, 2, 3, 5, 6-hexamethylbenzenonium ion [6].

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Novosibirsk Institute of Organic Chemistry, Siberian Branch of the Academy of Sciences of the USSR.
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