Lateral Nitroxylation of Penta-alkylbenzenes

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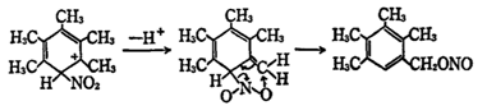
Nitrations of pentamethylbenzene have been reported to yield either nitropentamethylbenzene (I) or dinitroprehnitene (II).[1] However, the products were found not to be as simple as had generally been thought. Nitrations carried out at -10—$+5$°C by fuming nitric acid ($d=1.50$) in a variety of solvents, always gave, besides I, an appreciable amount of a non-crystallizable, syrupy substance, which, by careful chromatographic treatment on silica gel using light petroleum and benzene as eluants, could be separated into several side-chain substituted products. The main component (III) recrystallized from light petroleum melted at 45—46°C (Found: C, 63.06; H, 7.41; N, 6.69%. Calcd for $C_{11}H_{15}NO_3$: C, 63.14; H, 7.23; N, 6.69%) and showed strong infrared bands (in Nujol) at 1270 and 1636 cm^{-1} ($-ONO_2$); PMR peaks (in CCl_4) at 7.82 (2 CH_3), 7.77 (2 CH_3), 4.64 (CH_2) and 3.05 τ (aromatic H). The mixed acid converted III into II, so it was identified as 2,3,4,5-tetramethylbenzyl nitrate, the structure of which was further confirmed by synthesis from prehnitene through chloromethylation and by the subsequent treatment of the chloride with silver nitrate in acetonitrile. The other products were 2,3,4,5-tetramethylbenzyl alcohol, mp 81—82°C (Found: C, 79.76; H, 9.89%. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83%), probably formed by the hydrolysis of III; 6-nitro-2,3,4,5-tetramethylbenzyl nitrate, mp 100—101°C (Found: C, 52.03; H, 5.83; N, 10.94%. Calcd for $C_{11}H_{14}N_2O_5$: C, 51.96; H, 5.55; N, 11.02%), and 2,3,4,5-tetramethylbenzaldehyde (semicarbazone, mp 209—210 and 235—242°C*[1]; Found: C, 65.51; H, 7.88%. Calcd for $C_{12}H_{17}N_3O$: C, 65.72; H, 7.81%). The preferential attack by nitric acid on the side-chain rather than on the nuclear position becomes predominant with an increase in crowding around the ring. Thus, a similar treatment of pentaethylbenzene with fuming nitric acid gave a syrup, nearly half of which was found by means of a study of its PMR spectra to be composed of a nitrate. The chromatography of the syrup gave impure nitropentaethylbenzene (mp 86—90°C), a vinyltetraethylbenzene (IV), α-methyl-2,3,4,5-tetraethylbenzyl alcohol (mp 49—62°C), and a trace of a carbonyl compound. The last three compounds were doubtless the decomposition products of the unstable nitrate. The main product (IV), bp 103—104°C/2.5 mmHg (Found: C, 88.99; H, 11.22%. Calcd for $C_{16}H_{24}$: C, 88.82; H, 11.18%), had infrared bands at 888 (isolated ring H), 905, 989 and 1624 cm^{-1} ($-CH=CH_2$); PMR peaks at 8.69—9.02 (4 CH_3), 7.15—7.60 (4 CH_2), 4.83, 4.48 and 2.97 ($-CH=CH_2$; $J_{trans}=17.8$ cps; $J_{cis}=11.0$ cps; $J_{gem}=1.8$ cps), and 2.87 τ (aromatic H). Its structure was proved to be 2,3,4,5-tetraethylvinylbenzene by comparison with an authentic specimen prepared from 2,3,4,5-tetraethylacetophenone through the lithium aluminum hydride reduction and subsequent dehydration of the alcohol. This result differs from the earlier findings that the nitration of pentaethylbenzene mainly yielded *p*-dinitrotetraethylbenzene,[2] although the use of the mixed acid partly confirmed the latter results. The amounts of nitrous acid formed roughly paralleled the degree of side-chain substitution. Other mixed penta-alkylbenzenes were found to behave similarly.

The anomalous substitution may be explained by a process similar to that postulated for the side-chain chlorination of hexamethylbenzene;[3] *i. e.*, a process involving the initial attack of the nitronium ion on the open place of the ring, followed by the hyperconjugative release of a proton from the neighboring methyl group and the rearrangement of the unstable intermediate (V) to the benzyl nitrite, which may then further be transformed into the nitrate or decomposed into the aldehyde.[4]



1) L. I. Smith and S. A. Harris, *J. Am. Chem. Soc.*, **57**, 1289 (1935); P. Kreienbuhl and H. Zollinger, *Tetrahedron Letters*, **1965**, 1739.

*1 The semicarbazone melted at 209—210°C to a liquid, which quickly solidified and remelted at 235—242°C with decomposition.

2) L. I. Smith and C. O. Guss, *J. Am. Chem. Soc.*, **62**, 2635 (1940).

3) E. Baciocchi, A. Ciana, G. Illuminati and C. Pasini, *ibid.*, **87**, 3953 (1965); also *cf.* P. B. D. de la Mare and H. Suzuki, *J. Chem. Soc. (C)*, **1967**, 1586.

4) R. G. Gillis, *J. Org. Chem.*, **21**, 805 (1956); also *cf.* D. H. R. Barton, G. C. Ramsay and D. Wege, *J. Chem. Soc. (C)*, **1967**, 1916.