Unusual Nitration of Some 1,2,3,4-Tetramethylbenzene Derivatives

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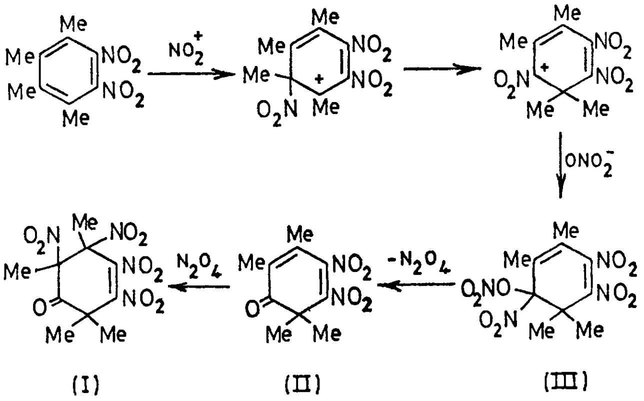
Summary Direct action of cold fuming nitric acid upon 1,2,3,4-tetramethyl-5,6-dinitrobenzene gave 2,3,6,6-tetramethyl-2,3,4,5-tetranitrocyclohex-4-en-1-one (I) in high yield; under mild conditions, 5,6-dihalogeno-1,2,3,4-tetramethylbenzenes were readily converted into a mixture of 5,6-dihalogeno-2,3,4-trimethylbenzyl nitrate and 6-halogeno-2,3,4,5-tetramethyl-4-nitrocyclohexa-2,5-dien-1-one.

Treatment of fully substituted derivatives of polyalkylbenzenes with fuming nitric acid at low temperature usually leads to either displacement of one of the substituent groups by a nitro group or substitution on the alkyl side-chain to yield benzylic compounds.[1] We report here an unusual nitration giving polynitrocyclohexenones or nitrocyclohexadienones in moderate to high yield.

When 1,2,3,4-tetramethyl-5,6-dinitrobenzene was dissolved in an excess of cold fuming nitric acid and the mixture set aside at room temperature for several days, there was a gentle liberation of nitrogen dioxide. Quenching with water, followed by crystallisation of the precipitate [dichloromethane–light petroleum (b.p. 40—50°)] gave nearly colourless prisms (I), (82—87%) m.p. 111—114° (decomp.), m/e 286 ($M^+ - NO_2$), 256 ($M^+ - NO_2 - NO$), and 240 ($M^+ - 2NO_2$); ν_{max} (Nujol) 1742 (C=O), 1674 (C=C), 1540—1580, and 1328—1337 cm^{-1} (NO_2); τ 8·71, 8·51, 8·11, and 7·67. No λ_{max} (MeOH) was observed above 220 nm. When compound (I) was heated gently in carbon tetrachloride it readily released nitrogen dioxide and was converted into a bright yellow substance (II), m.p. 94—96°, m/e 240 (M^+); ν_{max} 1684, 1644, and 1617 (conjugated C=O), and 1533—1543 and 1365 cm^{-1} (conjugated NO_2); λ_{max} (MeOH above 220 nm) 296—298 nm (log ϵ 3·66), its u.v. spectral pattern was typical of a cyclohexa-2,4-dien-1-one system; m/e 194 ($M^+ - Me - NO - H$), 166 ($M^+ - Me - NO - CHO$), 152 ($M^+ - 2Me - NO - CO$), 150 ($M^+ - 2Me - 2NO$), 148 ($M^+ - 2NO_2$), a peak cluster at 119—124, 108, 105, 93, 91, 79, 78, and 77; τ 8·56 (s), 7·94 (s), and 7·81 (s) (2:1:1). The signal at τ 8·56 was due to the geminal methyl groups at C-6, which must be located next to the vic-dinitro-grouping; otherwise it would absorb at around τ 8·7—8·9.[2] The vicinal disposition of the two nitro groups was confirmed by reduction, followed by condensation with 1,2-diketone. These spectral data are compatible only with the formulation of (I) and (II) as in the Scheme. The reaction seems to promise some synthetic utility, and a possible sequence for the formation of (I) is shown in the Scheme.

A similar treatment of 1,2,3,5-tetramethyl-4,6-dinitrobenzene gave 3,4,5-trimethyl-2,6-dinitrobenzaldehyde (m.p. 163—164°, 76—84%) as the major product, together with small amounts of 3,4,5-trimethyl-2,6-dinitrophenylnitromethane, 3,4,5-trimethyl-2,6-dinitrobenzoic acid, and 3,4,5-trimethyl-2,6-dinitrobenzyl alcohol. In contrast, 1,2,4,5-tetramethyl-3,6-dinitrobenzene was stable towards cold fuming nitric acid, in warm mixed acid it underwent a slow nitro-oxylation on the side-chain to give 2,4,5-trimethyl-3,6-dinitrobenzyl nitrate (m.p. 139—140°).

The product formed seems to be closely dependent on the orientation of the methyl groups, since the action of fuming nitric acid upon 5,6-dichloro-1,2,3,4-tetramethylbenzene in CH_2Cl_2 at -5 to 0° formed, as well as the expected 5,6-dichloro-2,3,4-trimethylbenzyl nitrate, appreciable amounts of a nitrocarbonyl compound, which after chromatography over alumina gave large prisms, m.p. 178—179°; i.r., n.m.r., u.v., and mass spectra identified the product as 6-chloro-4-hydroxy-2,3,4,5-tetramethylcyclohexa-2,5-dien-1-one. Similarly, 5,6-dibromo-1,2,3,4-tetramethylbenzene gave 6-bromo-4-hydroxy-2,3,4,5-tetramethylcyclohexa-2,5-dien-1-one, m.p. 190—191°. These p-quinols were no doubt derived from the initially formed 6-halogeno-2,3,4,5-tetramethyl-4-nitrocyclohexa-2,5-dien-1-one from hydrolysis during chromatography. However, 4,6-dihalogeno-1,2,3,5-tetramethylbenzene gave a mixture of 2,6-dihalogeno-3,4,5-trimethylbenzyl nitrate and 3,5-dihalogeno-2,4,6-trimethylbenzyl nitrate, while 3,6-dihalogeno-1,2,4,5-tetramethylbenzene yielded 3,6-dihalogeno-2,4,5-trimethylbenzyl nitrate or 1,2-bis(nitro-oxymethyl)-3,6-dihalogeno-4,5-dimethylbenzene depending on the reaction temperature and the amount of the nitrating agent employed.



Scheme

(*Received*, 30*th December* 1971; *Com.* 2205.)

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