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ON THE MECHANISM OF NITRATION OF 4-METHYL-2,6-DITERTIARYBUTYLPHENOL BY NITROGEN DIOXIDE IN THE LIQUID PHASE

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The reaction of nitrogen dioxide (NO_2) with phenol and cresols in the liquid phase is known[1] to result in polynitration of the aromatic ring. However, the nitration of sterically hindered phenols by nitrogen dioxide has received little attention. In this note we report on the reaction of nitrogen dioxide with 4-methyl-2,6-di-t-butylphenol (1), as part of a wider study of the kinetics and mechanism of the reactions of NO_2 in the liquid phase.

Passage of NO_2 through a stirred solution of (1), (5 g in 40 ml of 60/80 petroleum spirit) for two hours at room temperature in the absence of air, resulted in complete reaction of (1), as determined by t.l.c. Removal of the solvent gave a yellow, solid material which was recrystallized from methanol: m.p. 96-7°C; %C,67.6; %H,9.0; %N,5.5; (calculated for $C_{15}H_{23}NO_3$: %C,67.9; %H,8.7; %N,5.3). I.R.(C_2Cl_4): 1550,1570,1650,1670 cm^{-1}; ^1H n.m.r. ($CDCl_3$-DMSO-d6): δ,1.25(18H); δ,1.86(3H); δ,6.81(2H). The physical and spectroscopic properties of this material are consistent with the structure 4-nitro-4-methyl-2,6-di-t-butylcyclohexadieneone (2). This assignment was confirmed by synthesis of (2) by the action of nitric acid on (1).[2]

As NO_2 is a free-radical species we propose that the most likely initial reaction with the phenol (in a non-polar solvent) is abstraction of the labile phenolic hydrogen to form a phenoxyl radical and nitrous acid. In support of this proposal we have detected nitrous acid in the effluent gas stream and have observed the 4-methyl-2,6-di-t-butylphenoxyl radical (3) by e.s.r. spectroscopy. Compound (2) is formed by subsequent reaction of this radical with NO_2. This reaction is known to occur for the 2,4,6-tri-t-butylphenoxyl radical.[3]

When the time of reaction between NO_2 and (1) was increased to 6 h a white precipitate was formed. After filtration, removal of the solvent from the filtrate yielded a small amount (6%) of (2). The precipitate was recrystallized from propan-2-ol: m.p.124-6°C dec; %C,54.7; %H,7.4; %N,9.7; (calculated for $C_{15}H_{24}N_2O_6$: %C,54.9; %H,7.3; %N,8.5). I.R. medicinal white oil 1565, 1695,3540 cm^{-1}; ^1H n.m.r. ($CDCl_3$): δ,1.02(9H); δ,1.24(9H); δ,1.95(3H); δ,3.82(1H exchanges with D_2O); δ,5.30(1H); δ,6.28(1H). On the basis of its spectroscopic properties and for the reasons outlined below, the material is assigned the structure 2,6-di-t-butyl-6-hydroxy-4,5-dinitro-2,3-cyclohexenone (4). The same product was isolated after reaction of NO_2 with (2).

We propose that (4) is formed by addition of NO_2 to one of the double bonds of (2). Reaction of NO_2 with alkenes is well-established[1,4] and the products are dinitro-compounds, nitro-nitrites, and nitro-alcohols (the latter presumably formed as a result of decomposition of the nitro-nitrite structure).[5] Free-radical addition of NO_2 to one of the unsaturated carbon-carbon bonds of (2) would be expected to form the radical intermediate (5), as this radical will be stabilized by delocalization of the unpaired electron onto the oxygen atom. Radical (5) then reacts with NO_2 to produce the nitrite (6), which subsequently decomposes to form the product (4). Formation of the nitrite (6) rather than a nitro-compound is favoured because of steric hindrance by the t-butyl group.

Thus the products isolated are consistent with a free-radical mechanism for the reaction between NO_2 and the sterically hindered phenol (1).

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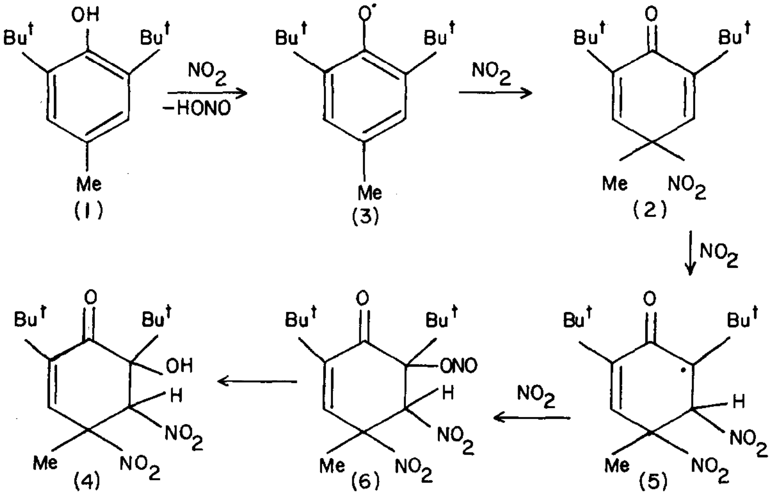

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