OXIDATION OF TRIS(p-NITROPHENYL)METHANE BY OXYGEN IN THE PRESENCE OF KOH IN DIMETHOXYETHANE

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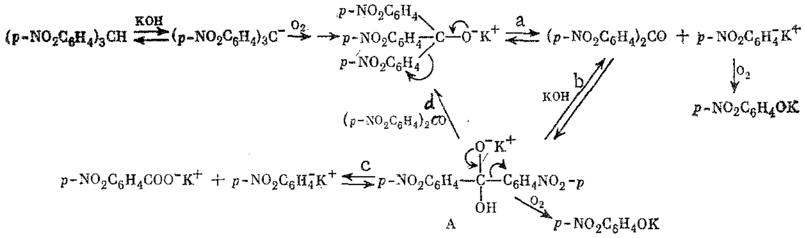
We have shown that the carbanion obtained in situ from tris(p-nitrophenyl)methane in a system consisting of solid KOH and dimethoxyethane with an excess of alkali is oxidized by O_2 at ~20°C for 1 h to give tris(p-nitrophenyl)carbinol in 60-70% yield. Subsequent oxidation over 15-20 h leads to p-nitrophenol and p-nitrobenzoic acid in 1.5-2 : 1 ratio (30-50% yield relative to starting hydrocarbon) and traces of nitrobenzene.

Possible pathways are the decomposition of the alcoholate $(p\text{-}NO_2C_6H_4)_3COK$ into $p\text{-}NO_2C_6H_4^-K^+$ and the ketone $(p\text{-}NO_2C_6H_4)_2CO$ (equilibrium *a*), and the generation of $p\text{-}NO_2C_6H_4^-K^+$ by the action of alkali from the ketone (equilibrium c):



We are unable to confirm that $p\text{-}NO_2C_6H_4^-K^+$ is formed in the free state. The attack of oxygen and the ketone may occur on a cryptocarbanion in complex A which forms in equilibrium step (b).

The possibility of step d was indicated by the high-yield transformation of benzophenone into Ph_3COH and $PhCO_2H$ in the KOH–dimethoxyethane system.

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