Formation of Hydroxy/Trinitromethyl Adducts in the Photochemical Reaction between Benzene and Tetranitromethane

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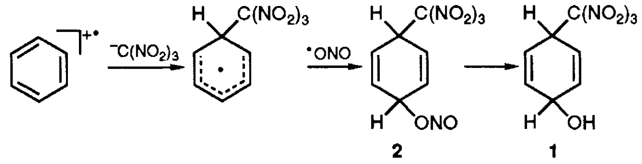
The photolysis of tetranitromethane/benzene in dichloromethane afforded the adducts, *cis*- and *trans*-1-hydroxy-4-trinitromethylcyclohexa-2,5-diene in low yields, showing that the aromaticity of even benzene can be broken in this type of reaction.

The photochemical reaction between aromatics (ArH) and tetranitromethane (TNM) leads predominantly to nitro/trinitromethyl adducts of the aromatic system for a number of poly- and mono-cyclic systems.[1–5] Sometimes nitrito/trinitromethyl adducts are also formed and detected as the corresponding hydroxy/trinitromethyl adducts.[2,3,5b] From studies of the stability of the adducts toward elimination of nitroform,[2,3] it was concluded that even benzene might give relatively stable adducts under suitable conditions. We now report the results of such a study.

A solution of benzene (0.4 mol dm^{-3}) and TNM (0.8 mol dm^{-3}) in dichloromethane has a very faint yellow colour due to the presence of a charge transfer (CT) complex. Irradiation of this solution with filtered light ($\lambda > 435$ nm) at



Scheme 1

−20 °C for 56 h, followed by careful workup at ≤0 °C, gave a mixture of nitrobenzene (2.8% absolute yield), *cis*- and *trans*-1-hydroxy-4-trinitromethylcyclohexa-2,5-diene (**1**, ratio ≈1 : 1, 5.2% absolute yield) and other minor adducts (total 2.5% absolute yield). The adduct structures **1** were deduced from the analysis of NMR spectra of the crude mixture in $CDCl_3$.†

In acetonitrile solution the reaction gave qualitatively similar results, nitrobenzene (1.0% absolute yield), adducts **1** (ratio **1a : 1b** ≈ 1.7, 2.1% absolute yield) and minor adducts (0.6% yield) being formed.

By analogy with earlier work,[1–3] we suggest that the triad formed upon irradiation of the CT band gives initially the trinitromethylcyclohexadienyl radical which is trapped by NO_2 (Scheme 1). The adducts **1** identified in this work could be formed from the intermediate nitrito/trinitromethyl adducts **2** either by the photochemical Barton reaction[6] or simply by hydrolysis during the workup procedure.

Received, 16th July 1992; Com. 2/03793J

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† NMR data for **1a**: ^1H NMR (300 MHz) δ 6.59, ddd, $J_{3,2}$ 10.4 $J_{3,4}$ 3.9, $J_{3,1}$ 1.9 Hz, 3H (5-H); 6.22, ddd, $J_{2,3}$ 10.4, $J_{2,1}$ 3.4, $J_{2,4}$ 1.6 Hz, 2H (6-H); ≈5.48, m, 4H; ≈4.64, m, 1H. **1b**: ^1H NMR (300 MHz) δ 6.62, ddd, $J_{3,2}$ 10.4, $J_{3,4}$ 3.1, $J_{3,1}$ 2.1 Hz, 3H (5-H); 6.24, ddd, $J_{2,3}$ 10.4, $J_{2,1}$ 3.5, $J_{2,4}$ 2.2 Hz, 2H (6-H); ≈5.48, m, 4H; ≈4.64, m, 1H. NMR spectral assignments were confirmed by double irradiation and two-dimensional heteronuclear correlation spectroscopy (HETCOR) experiments.