

Letter to the Editor

Adduct Formation in the Photochemical Reaction of 1,2,3,4-Tetramethylbenzene and Tetranitromethane

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The photochemical addition of tetranitromethane to aromatic compounds (ArH) is now a well established reaction, leading to nitro–trinitromethyl or nitrito–trinitromethyl addition across 1,2- or 1,4-bonds of ArH (anthracene and derivatives thereof,¹ naphthalene,^{2,3} a variety of dimethylnaphthalenes,^{4–7} 1-methylnaphthalene,⁸ 1,4,5,8-tetramethylnaphthalene,⁹ dibenzofuran,¹⁰ 4-chloroanisole,¹¹ fluoranthene¹² and benzene¹³). In contrast a variety of methylbenzenes, including mesitylene and pentamethylbenzene, have been reported to yield only products of side-chain and nuclear *substitution* on photolysis with tetranitromethane, with no indication of the formation of intermediate adducts from these substrates.¹⁴ We now report the isolation of *addition* products in >60% yield on photolysis of 1,2,3,4-tetramethylbenzene with tetranitromethane. This compound was selected in the hope that a possibly thermally labile 1,2-nitro–trinitromethyl adduct might be converted into a more stable product of intramolecular nitro–alkene cycloaddition.^{4–6,8,15} This type of reaction would be maximally favoured by a 1,2-dimethyl-substituted double-bond arrangement.

A solution of tetranitromethane (0.8 mol dm⁻³) and 1,2,3,4-tetramethylbenzene (0.4 mol dm⁻³) in dichloromethane (8 ml) was irradiated for 4 h at 20 °C by filtered light (cut-off < 435 nm). The volatile material was removed under reduced pressure at ≤ 0 °C, and the product composition was determined by NMR spectral analysis. Adducts comprised > 60% of the products, including the epimeric 1,4-nitro–trinitromethyl adducts **1** (17%) and **2** (12%), the *trans*-1,2-nitro–trinitromethyl adduct **3** (7%),

and the nitro cycloadduct **4** (17%) which arises as the product of an intramolecular nitro–alkene cycloaddition of adduct **2** (cf. Refs. 4–6, 8 and 15). Adducts **1**, **2** and **4** were isolated by HPLC, identified by spectroscopic means, and the structure of the nitro cycloadduct **4**, m.p. 137 °C (decomp.), confirmed by an X-ray crystal-

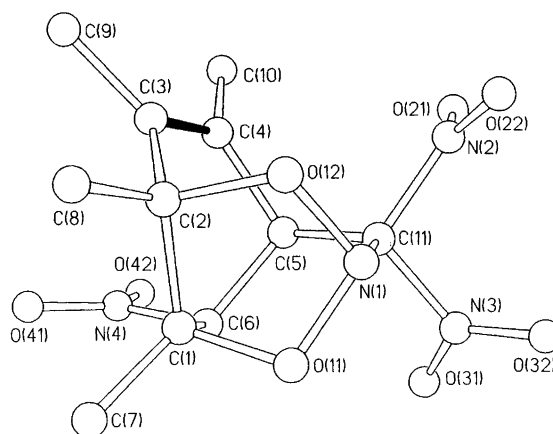
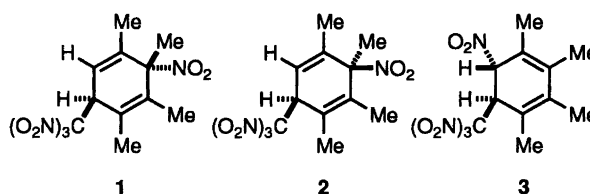


Fig. 1. Perspective view of the structure of **4**. The double bond is shown in black.



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lographic study (Fig. 1).[†] From the variation of product composition with time, it was clear that the *trans*-1,2-nitro-trinitromethyl adduct **3** was the precursor of **4**.

The isolation of nitro-trinitromethyl adducts **1–4** from the photolysis of 1,2,3,4-tetramethylbenzene with tetranitromethane is a clear indication that adducts can form in such reactions with methylbenzene derivatives. The further transformation of nitro-trinitromethyl adducts into secondary side-chain and nuclear substitution products remains to be explored, as well as the propensity of other polymethylbenzenes to yield adducts.

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[†] *Crystal data:* C₁₁H₁₄N₄O₈, *M* = 330.26, triclinic, space group *P*1, *a* = 6.628(1), *b* = 8.637(2), *c* = 12.691(3) Å, α = 99.37(3), β = 103.13(3), γ = 103.37(3)°, *V* = 668.5 Å³, *Z* = 2, μ (*M* *K* α) = 1.42 cm⁻¹, Mo*K* α radiation (λ = 0.71073 Å). Data were collected at 130 K using a Siemens R3m/V four-circle diffractometer for a colourless crystal of dimensions 1.0 × 0.5 × 0.06 mm. All 2047 reflections were used in all calculations with SHELXL93 for refinements using intensities [*w*R₂ = 0.196 for all data; *R* 1(*I*) > 2 σ (*I*) 0.068]. Atomic coordinates, bond lengths, angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.