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THE SYNTHESIS AND PHOTODIMERISATION OF 4-NITRO-1-PHENYLPENTA-1,3-DIENE.[1]

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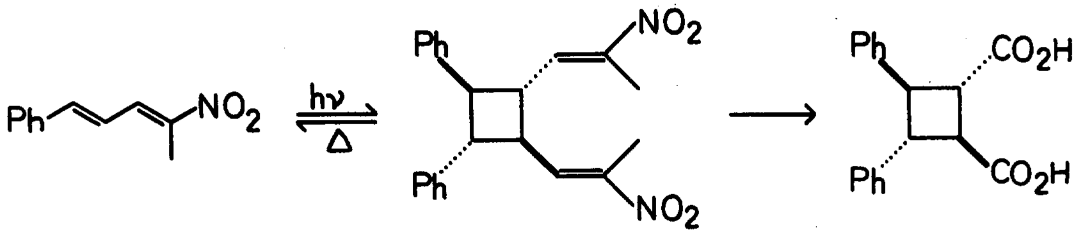
Recent interest in the photochemistry of α,β-unsaturated nitro-compounds has resulted in the discovery[2-5] of a number of reaction pathways available to the excited molecule. The study of conjugated nitro-dienes has, however, been limited to an examination of 6-nitrocholesta-3,5-diene which, on irradiation in acetone[2] or ethanol,[3] yields 3-oximinocholest-4-en-6-one. In this paper, we report the synthesis and photodimerisation of another nitro-diene, 4-nitro-1-phenylpenta-1,3-diene (I).

Attempts to obtain the nitro-diene (I) by base-catalysed condensation of cinnamaldehyde with nitroethane using ammonium acetate, 1-butylamine or triethylamine in refluxing toluene, or sodium hydroxide in methanol at 0°C, led to explosive decomposition on attempted distillation of the crude reaction mixture. A more successful approach was made through 4-nitro-1-phenylpent-1-en-3-ol, which was obtained in good yield by treatment[6] of a solution of cinnamaldehyde and nitroethane in methanol with Permutit Deacidite FF-1P (SRA 67) at 0-5°C. Acetylation of the nitro-alcohol with acetyl chloride in pyridine, followed by elimination with anhydrous sodium carbonate in reluxing xylene, gave on chromatography of the crude product on neutral alumina (Grade 1), 4-nitro-1-phenylpenta-1,3-diene; yellow crystals from cyclohexane had m.p. 92° (Found: C, 70.11; H, 5.63; N, 7.35. $C_{11}H_{11}NO_2$ requires C, 69.83; H, 5.86; N, 7.40%). ν_{max} (nujol) 3040, 1636, 1515, 1312, 975, 965, 879, 768, 729 and 696 cm^{-1}. λ_{max} (methanol) 239 nm (ε 12,000), 256 nm (ε 10,000), 349 nm (ε 37,000); λ_{max} (n-decane) 234 and

239 nm (ε 8,500), 337 nm (ε 29,000). τ($CDCl_3$), 2.47 (6H,m), 2.90 (2H, m) and 7.64 (3H, s).

A solution of 4-nitro-1-phenylpenta-1,3-diene (2.0 g) in methanol (1.1 l) under nitrogen was irradiated with a Hanovia medium pressure mercury arc (100 watt) surrounded by a water-cooled pyrex filter (wavelength > 280 nm) until a sample had no absorption at 349 nm or 1636 cm^{-1} (33 hours). Distillation of the solvent followed by chromatography of the residue on silica gel gave, on elution with 4:1-chloroform: 40-60° petrol, pale yellow crystals (1.56 g, 78%) with m.p. 188-9° from chloroform/methanol (Found: C, 70.25; H, 5.63; N, 7.48. $C_{11}H_{11}NO_2$ requires C, 69.83; H, 5.86; N, 7.40%). ν_{max} (nujol), 3030, 1670, 1603, 1510, 1330, 972, 770 and 705 cm^{-1} λ_{max} (methanol) 218 nm (ε 19,300), 263 and 268 nm (ε 14,200). τ($CDCl_3$), 2.65 (12H, m), 6.1 - 7.0 (4H, m) and 7.93 (6H, s).

The dimeric nature of this photoproduct was established by mass spectra, the molecular ion being at m/e 378; the monomer (I) was regenerated by heating the photoproduct to 230° _in vacuo_, a thermal reaction characteristic of many dimers formed by (2 + 2)π photocycloaddition. This together with the spectral evidence supports the assignment of a 1,2-di(2'-nitropropen-1'-yl)-3,4-diphenylcyclobutane structure (II) to the photoproduct, the 1,2-diphenyl relationship being indicated by the presence of a peak at m/e 180 in the mass spectrum.



I II III

The structure of the dimer II was confirmed and its stereochemistry established as _trans-anti-trans_ by oxidation of the dimer with potassium permanganate/sodium metaperiodate[7] to the known _trans-anti-trans_-truxinic acid[8] (III).

Interest in this photoreaction is to be found in the unusual specificity of the dimerisation; a single stereoisomer is obtained even in dilute solution (9.6×10^{-3} moles/litre), and there is no evidence for the occurrence of $(4 + 2)\pi$ or $(4 + 4)\pi$ cycloaddition, frequently observed for other dienes. It is notable too, that the dimerisation reaction is preferred to the previously described[2-5] photo-reactions of α,β-unsaturated nitro-alkenes. The dimerisation of β-nitrostyrene has been reported,[11] but only in the solid state where it leads to the formation of *cis*-*anti*-*cis*-1,3-dinitro-2,4-diphenylcyclobutane.

The yield of dimer II is solvent dependent, being considerably lower (24%) in acetone; no dimer was detected on irradiation of I in cyclohexane. Solvent effects have been reported in other dimerisations, and have been attributed[12] to solvation either of monomeric complexes or of the dimerisation transition state, or alternatively, to enhancement of inter-system crossing to a triplet state. Further investigations with this compound are in progress.

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