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Photo-induced Cycloaddition of 1-Nitrocyclooctene and Cyclopentadiene

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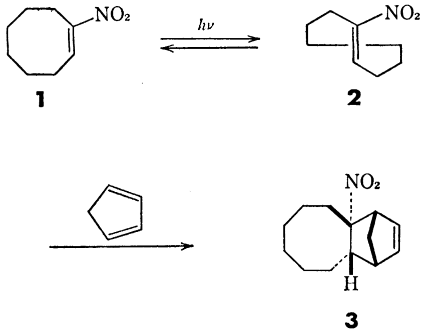
Synopsis. Irradiation of 1-nitrocyclooctene produces first the strained *trans* isomer, which in turn undergoes thermal Diels-Alder reaction with cyclopentadiene affording the tricyclic adduct.

As a part of our investigation of the photochemical behavior of medium-sized cycloalkene derivatives,[1] a reaction of 1-nitrocyclooctene (**1**) has been examined.[2]

In the dark and below room temperature, no appreciable reaction took place between the nitro olefin **1** and cyclopentadiene. However, when the mixture immersed in a Dry Ice bath was irradiated by a high-pressure mercury arc through a Pyrex filter (n-π^* excitation), smooth reaction occurred and after 4 h the 1: 1 cycloadduct **3** was obtained in *ca.* 40% yield. The norbornene type structure as well as the endo stereochemistry of the nitro group was deduced from the NMR signals of the vinylic protons;[3] both proton signals appeared as a doublet of doublets with $J=6$ and 3 Hz with a rather great chemical shift difference, $\Delta\delta$ 0.42 ppm, due to the presence of anisotropic influence of the neighboring nitro group.[4] Unlike photoreaction of 1-acetylcyclooctene[1f,g] or 1-carbomethoxycyclooctene,[5] no double-bond migration was observed with this eight-membered olefin.



Apparently the cycloaddition forming **3** involves the initial photo-induced *cis* to *trans* isomerization of the nitro olefin, **1**→**2**,[6] followed by thermal Diels-Alder reaction with cyclopentadiene.[7] The evidence for the intermediacy of the strained ground-state molecule **2** was obtained by a standard technique. Thus a solution of **1** in methylcyclohexane was first irradiated at −78 °C for 3 h. After the light source was removed, an excess of cold cyclopentadiene was added and the mixture was allowed to warm up to ambient temperature, which produced the cycloadduct **3**. The product to recovered **1** ratio indicated that the *trans* olefin **2** exists in rather high concentration (at least 28%) in the photo-equilibrium mixture produced by the photolysis of **1**.

Experimental

Photolysis of 1-Nitrocyclooctene (1) in Cyclopentadiene. The nitro olefin **1** was prepared by the known procedure,[8] bp 87—88 °C (3 Torr). The UV spectrum in hexane solution exhibited absorption maxima at 257 (ε 8470) and 345 nm (weak). A solution of **1** (550 mg, 3.54 mmol) in freshly distilled cyclopentadiene (50 ml) was placed in three Pyrex tubes (15×180 mm), flushed with nitrogen, and immersed in a Dry Ice–CH_3OH bath. Then irradiation was effected externally with a 200 W hign-pressure mercury arc for 4 h. The photolysate was concentrated at room temperature under reduced pressure and the residue was chromatographed on a silica gel plate (Merck Kieselgel GF_{254}, 10: 1 hexane–ether). The fraction slightly less polar than **1** was extracted to give 2α-nitro-(1β, 2α,9β,10β)-tricyclo[8.2.1.$0^{2,9}$]tridec-11-ene (**3**) (236 mg; 32%). The yield based on the unrecovered starting olefin was *ca.* 40%. In addition, several unidentified products were produced.[2] A sample of **3** for analysis was obtained by recrystallization from hexane, mp 76.0—76.5 °C (uncorrected). IR (CCl_4) 1610 (C=C), 1534, 1354, 1335 cm^{-1} (NO_2); NMR (CCl_4 containing tetramethylsilane as internal standard) δ 1.2—3.2 (broad signal with four envelopes), 5.88 (dd, $J=6$ and 3 Hz, vinylic proton at C_{11}), and 6.30 (dd, $J=6$ and 3 Hz, vinylic proton at C_{12}); MS (70 eV) *m/e* 221 (M^+), 190, 175, 147, 91, and 66 ($M^+ - C_5H_6$, *retro*-Diels-Alder process).

Found: C, 70.45; H, 8.74; N, 6.24%. Calcd for $C_{13}H_{19}O_2N$: C, 70.55; N, 8.65; N, 6.33%.

Dark Reaction of the Trans *Isomer of 1 and Cyclopentadiene.* A methylcyclohexane solution (25 ml) of **1** (256.6 mg, 1.66 mmol) in Pyrex tubes was cooled in a Dry Ice–CH_3OH bath and irradiated under nitrogen for 3 h. After the lamp had been turned off, to the photolysate was added cyclopentadiene (*ca.* 20 ml) and the mixture was warmed up spontaneously to room temperature with stirring. The volatile substances were removed by evaporation. TLC separation of the residual mixture afforded **3** (77 mg; 22% yield) and unchanged **1** (141 mg; 55% recovery).

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