

Photochromic 1-Aryl-2-nitroalkenes

Sir:

In the course of our investigations of photochromic nitro compounds¹⁻⁴ we have observed that many *cis*-1-aryl-2-nitroalkenes are photochromic. Table I lists the compounds studied in the present investigation.

Table I

| Compound | R ₁ | R ₂ | R ₃ | R ₄ |
|----------|--|-------------------------------|------------------|----------------|
| I | H | H | H | H |
| II | Me | H | H | H |
| III | H | C ₆ H ₅ | H | H |
| IV | H | H | OCH ₃ | H |
| V | CH ₂ C ₆ H ₅ | C ₆ H ₅ | H | H |
| VI | NO ₂ | C ₆ H ₅ | H | H |
| VII | C ₆ H ₅ | H | H | H |
| VIII | C ₆ H ₅ | C ₆ H ₅ | H | H |
| IX | H | H | NO ₂ | H |
| X | H | H | Cl | Cl |
| XI | -CH ₂ CH ₂ CH ₂ CH ₂ - | | H | H |

trans- α -Methyl- β -nitrostyrene⁵ (II), the isomer which is isolated from the reaction of α -methylstyrene with nitric oxide,⁶ is not photochromic. The *cis* isomer was obtained by steady irradiation of the *trans* compound in ethanol solution, with ultraviolet light. Identification of the *cis* isomer was confirmed by elemental analysis, molecular weight, ultraviolet, infrared, and nuclear magnetic resonance measurements. The photochromic behavior of *cis*- α -methyl- β -nitrostyrene was determined by flashing an ethanol solution at room temperature and measuring the fading rate of the colored species at 420 m μ . The flash photolysis equipment has been previously described.⁷

To determine if the photochromic reaction is specific for only the *cis* form, other similar compounds were studied. Compounds I, III, IV, and V when initially flashed in ethanol solution did not show any photochromism. After a short irradiation period, either by exposure to several flashes or to constant ultraviolet light, they became photochromic. β -Nitrostyrene (I) and 1-*o*-methoxyphenyl-2-nitroethylene (IV) showed infrared absorption, before irradiation, at 10.34 μ , characteristic of the *trans* HC=CH configuration. No attempt was made to isolate the *cis* isomers in these cases.

1,2-Dinitro-1,2-diphenylethylene (VI) was isolated as the *cis* isomer,⁵ m.p. 184° (lit. m.p. 186°⁸) from the reaction of nitric oxides with diphenylacetylene and showed photochromic behavior on flashing, without any preliminary irradiation.

- (1) J. A. Sousa and J. Weinstein, *J. Org. Chem.*, **27**, 3155 (1962).
- (2) A. L. Bluhm, J. Weinstein, and J. A. Sousa, *ibid.*, **28**, 1989 (1963).
- (3) A. L. Bluhm, J. A. Sousa, and J. Weinstein, *ibid.*, **29**, 636 (1964).
- (4) J. Weinstein, J. A. Sousa, and A. L. Bluhm, *ibid.*, **29**, 1586 (1964).
- (5) The *cis* and *trans* designations in this report relate to the orientation of the nitro and phenyl groups.
- (6) C. A. Burkhard and J. F. Brown, Jr., U. S. Patent 2,867,669 (Jan. 6, 1959).
- (7) L. Lindquist, *Rev. Sci. Instr.* **35**, 993 (1964).
- (8) J. Schmidt, *Ber.*, **34**, 619 (1901).

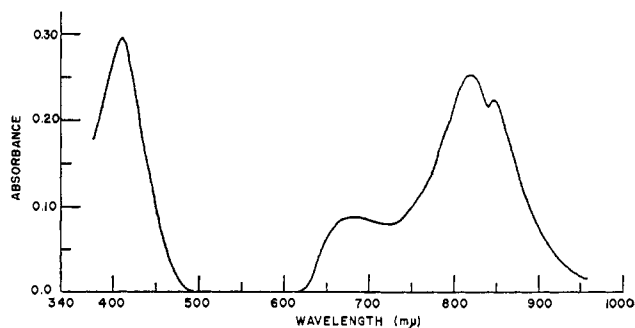


Figure 1. Visible spectrum of colored species of 1-phenyl-2-nitrocyclohexene in ethanol (5×10^{-4} M) at room temperature.

1,1-Diphenyl-2-nitroethylene (VII), triphenylnitroethylene (VIII), and 1-phenyl-2-nitrocyclohexene (XI) exist in only one configuration, in which the nitro and phenyl groups are *cis* to each other. These three compounds were photochromic on flashing without any preirradiation.

The rate constants, k , of the fading reactions are shown in Table II for some of the compounds. All

Table II. Values of k for the Fading Reaction in Ethanol at Room Temperature

| Compound | k , sec. ⁻¹ | λ , m μ |
|-----------------|--------------------------|---------------------|
| I ^a | 1486 | 415 |
| II | 7600 | 425 |
| VIII | 578 | 440 |
| IX ^a | 115,891 | 430 |
| XI | 564 | 420 |
| XI | 570 | 850 |
| XI | 1294 ^b | 420 |

^a Solution is a mixture of *trans* and *cis* isomers. ^b In cyclohexane.

followed first-order kinetics. There are two rates shown for 1-(*o*-nitrophenyl)-2-nitroethylene (IX). This compound was obtained as the *trans* isomer, and on initial flashes showed only one rate of fading, corresponding to the slower rate constant. After a short preirradiation, the color-fading process showed a characteristic fast rate superimposed on the slow fading process. The slow rate observed on initial flashes may be due to *aci*-nitro \rightarrow nitro tautomerization. In this compound formation of the *aci*-nitro isomer by irradiation is possible since there is a CH group *ortho* to an aromatic nitro group.¹⁻⁴

The visible spectrum observed after flash irradiation of 1-phenyl-2-nitrocyclohexene (XI) in ethanol is shown in Figure 1. It was obtained by point-by-point measurement over the range 350-950 m μ . All absorption bands decayed at the same rate, and activation energies (E_{exp})¹ determined at 420 and 850 m μ were the same, 12.4 kcal./mole. The entropy of activation (ΔS^*)¹ was calculated to be -6.8 e.u.

From the foregoing observations it appears that the photochromism in these compounds requires that the nitro and phenyl groups be *cis* with respect to each other. Replacing one of the *ortho* positions on the phenyl ring (e.g., compound IV) did not prevent the photochromic reaction. When both *ortho* hydrogens were replaced by chlorine (X) no photochromism was observed. *o*-Nitrobiphenyl, which might be con-

sidered analogous to this group of compounds, did not show photochromic behavior under the conditions of these experiments.

Details of the scope and mechanism of this photochromic reaction are being further investigated in these laboratories.

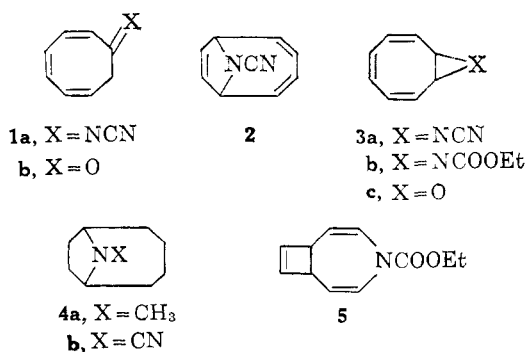
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Reaction of Cyanonitrene with Cyclooctatetraene. 1,4 and 1,2 Adducts

Sir:

We wish to report a case of 1,4 addition of a nitrene to a polyene.¹ Treatment of a dilute solution of cyclooctatetraene (COT) in ethyl acetate (*ca.* 12%) with cyanogen azide (N₃CN) at 78° results in evolution of 1 mole equiv. of nitrogen and the formation of two products in 31% yield. The predominant component² (68% of the mixture) is an orange, viscous liquid purified by high vacuum distillation and identified as **1a**: $\lambda_{\text{max}}^{\text{CH}_3\text{ON}}$ 243 m μ (ϵ 16,000) and 331 (6900), $\nu_{\text{max}}^{\text{nat}}$ 2180 (C \equiv N) and 1540 cm.⁻¹ (C=N) and n.m.r. (neat) multiplets centered at τ 3.5 (5 H), 4.5 (1 H), and 7.2 (2 H). Chemical proof for structure **1a** derives from its hydrolysis with moist alumina to the known³ ketone **1b** in 75% yield. The less abundant component² (32% of the mixture) is a white, sublimable solid (m.p. 102–103°) identified as the 1,4 adduct **2**: $\lambda_{\text{max}}^{\text{CH}_3\text{CN}}$ 255 m μ (ϵ 4500), $\nu_{\text{max}}^{\text{KBr}}$ 2220 cm.⁻¹ (C \equiv N), and n.m.r. (CDCl₃), narrow multiplets at τ 3.7 (4 H), 4.6 (2 H), and a broader peak at τ 5.3 (2 H; width at half-height = 5 c.p.s.). On catalytic hydrogenation over rhodium at room temperature and atmospheric pressure, **2** took up 3 mole equiv. of hydrogen to yield N-cyano-9-azabicyclo[4.2.1]nonane (**4b**) ($\nu_{\text{max}}^{\text{KBr}}$ 2210 cm.⁻¹, n.m.r. (CDCl₃) multiplets at τ 5.9 (2 H) and



(1) For equivocal reports of 1,4 addition see: R. Appel and O. Buchner, *Angew. Chem.*, **74**, 430 (1962); K. Hafner and W. Kaiser, *Tetrahedron Letters*, No. 32, 2185 (1964). The ambiguity in these reports arises from failure to observe 1,2 addition products, which could conceivably be the progenitors of the 1,4 adducts.

(2) Satisfactory elemental analysis was obtained for this material.

(3) A. C. Cope and B. D. Tiffany, *J. Am. Chem. Soc.*, **73**, 4158 (1951).

7.5–8.4 (12 H)), identical (n.m.r., infrared) with an authentic sample (m.p. 114–116°) prepared from homotropene⁴ (**4a**) and cyanogen bromide.

At room temperature a mixture of cyanogen azide and COT slowly evolves 1 mole equiv. of nitrogen and gives exclusively **1a**⁵ in 73% yield.

The absence of **2** when the reaction was carried out at room temperature coupled with the temperature (*ca.* 40°) at which cyanogen azide is known to fragment to nitrogen and cyanonitrene⁶ (NCN) indicates⁷ that **2** is the product not of cyanogen azide but of NCN.

When the reaction of N₃CN with COT at 78° in the presence of a large excess of ethyl acetate was interrupted prior to completion, aziridine **3a** was observed in addition to **1a** and **2**. The relative amounts⁸ of **1a**, **2**, and **3a** were found to be essentially constant (38:14:48) from 10% reaction (4 min.) to 75% reaction (40 min.), whereas in the later stages of the reaction the amount of **3a** in the mixture decreases and when the reaction is 91% complete (130 min.) **1a**, **2**, and **3a** are present in ratios of 56:33:11, respectively. Compound **3a** could not be obtained in the pure state on account of its low thermal stability, and the structural assignment derives from its n.m.r. spectrum (in the mixture), which is virtually identical with those of **3b**⁹ and **3c**³; n.m.r. (CDCl₃), unsymmetrical doublet centered at τ 3.9 (6 H) and a sharp singlet at τ 6.6 (2 H; width at half-height = 1.5 c.p.s.).

More information concerning the origin of the products was obtained from the results of a control experiment in which a known mixture of **1a**, **2**, **3a** and a standard¹⁰ (2.0:0.9:1.7:1.0) in ethyl acetate was maintained at 78° for 30 min. Under these conditions **1a** and **3a** decreased by 10 and 24%, respectively,¹¹ whereas the amount of **2** remained unaltered.¹⁰

The constant ratio in which the three products are formed in the first 75% of the reaction coupled with the failure of either **1a** or **3a** to isomerize to **2** when maintained at the reaction temperature for 0.5 hr. and the presence of **2** in the first 4 min. of the reaction indicates that the 1,4 adduct **2** is primarily a direct product of NCN and COT and does not arise to any appreciable extent from isomerization of **1a** or **3a**.¹²

Although the detailed mechanism for the formation of the 1,4 adduct is now known, it appears likely that it is formed in a nonconcerted fashion from triplet NCN.^{13,14} On the basis of the data presented here, the following

(4) A. C. Cope, H. R. Nace, and L. L. Estes, Jr., *ibid.*, **72**, 1134 (1950).

(5) The reaction of cyanogen azide with olefins leads to N-cyanoaziridines and/or alkylidene cyanamides: F. D. Marsh and M. E. Hermes, *ibid.*, **86**, 4506 (1964).

(6) A. G. Anastassiou, H. E. Simmons, and F. D. Marsh, *ibid.*, **87**, 2296 (1965).

(7) Compound **1a** does not isomerize to **2** at 80° in ethyl acetate.

(8) These were determined from the n.m.r. spectra of the crude mixtures using the signals due to the allylic hydrogens.

(9) S. Masamune and N. T. Castellucci, *Angew. Chem.*, **76**, 569 (1964).

(10) Dimethyl phthalate was used as the standard. The composition was determined by n.m.r. using the allylic hydrogens of the three products and the aromatic as well as aliphatic hydrogens of the standard.

(11) The predominant product of the thermal decomposition is an insoluble, high-melting (>300°) amorphous solid.

(12) The structurally related aziridine **3b** is known⁹ to isomerize to **5** at 80°.

(13) The ground state of NCN is ³ Σ_g^- : G. Herzberg and D. N. Travis, *Can. J. Phys.*, **42**, 1658 (1964); G. J. Pontrelli and A. G. Anastassiou, *J. Chem. Phys.*, **42**, 3755 (1965); E. Wasserman, L. Barash, and W. A. Yager, *J. Am. Chem. Soc.*, **87**, 2075 (1965).

(14) The addition of α -cyanoisopropyl radicals to COT occurs in a 1,4 fashion: J. L. Kice and T. S. Cantrell, *J. Am. Chem. Soc.*, **85**, 2298 (1963).