The Photo-addition of Indene and Acrylonitrile

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PREVIOUS work[1] on the photochemistry of indene has shown that while the compound undergoes efficient dimerization when photosensitized, extensive polymerization occurs on direct irradiation. We have investigated the photo-addition of indene and acrylonitrile, and report that the acetophenone-sensitized reaction yields cyclobutanes (I) and (II); on direct irradiation, however, the cyanoethylindenes (III) and (IV) and a third cyclobutane (V) are obtained.

The sensitized reaction was carried out by irradiating indene (5·0 g), acrylonitrile (15·0 g), and acetophenone (5·0 g) in ethanol (400 ml.) with a Hanovia Type L 450 w lamp, fitted with a Corex sleeve. Gas chromatography† showed that two products were formed in about equal amounts. These were separated by chromatography on alumina, and have been assigned structures (I), m.p. 70°, and (II), m.p. 49°, for the following reasons.

Both products had a sharp peak at 2240 cm.$^{-1}$ in the infrared, and the mass spectra showed weak molecular ion peaks with *m/e* 169. The n.m.r. spectra‡ were difficult to interpret in detail, but they did not show any resonances at high field ($<2\cdot0$ p.p.m.) which would be expected from the isomeric benzonorbornenes.[2] (I) and (II) could be equilibrated by treatment with t-butoxide, showing that they are epimers.

Irradiation of indene and acrylonitrile as above,

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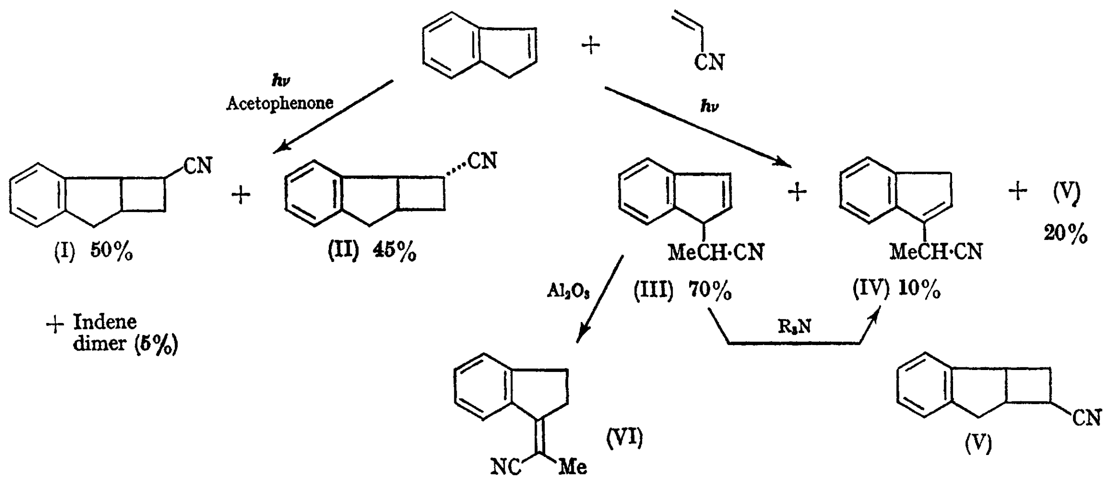
† Analysis was on 5 ft. × ¼ in. of Carbowax (15%) on Chromosorb W at 190°.

‡ Nuclear magnetic resonance spectra were measured on a Varian A-60 instrument in CCl_4 solution. Chemical shifts are given in p.p.m. downfield from tetramethylsilane, coupling constants are in c./sec.



in the absence of acetophenone, and with a Vycor sleeve led to the formation of three quite different adducts, which were separated on silica gel and are assigned structures (III), (IV), and (V) on the basis of the following evidence. The compounds all had infrared absorption at 2240 cm.$^{-1}$. The n.m.r. of (III) showed peaks at 1·10, doublet (J = 7·0), 3H (methyl); 3·0 and 3·6 multiplets, 1H per peak, (methines); 6·35 and 6·88 multiplets, 1H per peak, (vinylic); 7·25 and 7·59, multiplets, total 4H (aromatic). This the major product (70% by gas chromatography) was a liquid which isomerized cleanly to (IV), m.p. 80—82° on treatment with triethylamine.[3] Isomer (IV) had n.m.r. peaks at 1·56, doublet (J = 7·0) 3H (methyl); broad peak at 3·26, 2H (methylene); quartet at 3.52 (J = 7·0) 1H (methine); triplet at 6·44, 1H (vinylic); the aromatic protons gave a multiplet at 7·20, 4H.

On alumina, (IV) isomerized to the conjugated unsaturated nitrile (VI), m.p. 110—111°, which had infrared absorption at 2201 cm.$^{-1}$, and the ultraviolet spectrum had $\lambda_{\max}$ (EtOH) 274 mμ, log ϵ 4·20.[4] The n.m.r. of (VI) is of interest in that one proton of the aromatic system appears as a quartet (J = 6·5 and 3·0) at 8·28, well downfield[5] from the remaining three, which give a multiplet at 7·27.

The third product of the direct irradiation has been assigned structure (V), since its mass spectrum was almost identical with those of cyclobutanes (I) and (II). The n.m.r. was also similar to those of the sensitized addition products.

The structures and reactions described are shown in the Scheme.

Clearly the two photoadditions, sensitized and unsensitized, are proceeding by different mechanistic pathways. The triplet reaction gives cyclobutane products which are formed by ring closure of the more stable diradical.[6] In the case of the direct irradiation,[7] in which singlet indene is presumably involved, we propose that this species is sufficiently energetic (100 kcal.) to transfer a hydrogen atom[8] to acrylonitrile. A radical-pair would be formed which could collapse to form (III). The unsensitized photoaddition is of mechanistic interest and of some synthetic utility as a convenient route to indene derivatives, such as (VI).

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[4] *cis*-Cinnamonitrile has $\lambda_{\max}$ 273 mμ, log ϵ 4·22; W. E. Parham, W. N. Moulton, and A. Zuckerbraun, *J. Org. Chem.*, 1956, **21**, 72.

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[7] This reaction is formally analogous to a (sensitized) dimerization of cyclopentadiene reported by E. H. Gold and D. Ginsburg, *Angew. Chem. Internat. Edn.*, 1966, **5**, 246.

[8] C. P. Poole and R. S. Anderson, *J. Chem. Phys.*, 1959, **31**, 346, have reported e.s.r. evidence that unsaturated hydrocarbons can dissociate on photolysis to give free radicals.