The Photo-addition of Naphthalene and Acrylonitrile

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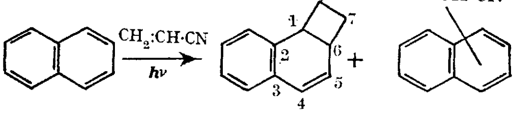
We have investigated the photo-addition of naphthalene and acrylonitrile, and report that on direct irradiation, cross-addition occurs and 8-cyano-2,3-benzobicyclo[4,2,0]octa-2,4-diene (I) is formed. Derivatives of this bicyclic system have not apparently been hitherto obtained in the photochemistry of naphthalene,[1] although the reaction type which leads to (I) is of course well known. The photo-addition is efficient, and is remarkably specific under certain conditions.

In the photolysis, naphthalene (0·1 g.), and acrylonitrile (2·0 g.) in t-butyl alcohol (80 ml.) were irradiated through Pyrex with a Hanovia Type L 450 w lamp for 40 min. The mixtures from five reactions were combined, the solvent was evaporated, and the residue was chromatographed on silica gel to afford (I), m.p. 98—99° (50 mg.; 30% based on unrecovered naphthalene).



(I) (II) and (III)

This product had i.r. absorption at 2235 $cm.^{-1}$, and the mass spectrum showed a molecular ion of *m/e* 181. The u.v. absorption had λ_{max} (EtOH) 269 mμ, log ε 3·91, with some absorption above 300 mμ, showing that the benzene ring and double bond were conjugated.[2]

The n.m.r. spectrum‡ ($CDCl_3$) of (I) showed a 4H multiplet at 714 c./sec. (aromatics), a 3H multiplet at 354 c./sec. (methines), and a 2H multiplet at 265 c./sec. (methylenes). Each of the vinyl protons gave a doublet (*J* 5 c./sec.), one centred at 663 and the other at 593 c./sec.; the

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† A satisfactory elemental analysis was obtained for (I), by the Spang Microanalytical Laboratory, Ann Arbor, Michigan.

‡ The n.m.r. spectrum was recorded at 100 M.c./sec. on a Varian HA-100 instrument. Chemical shifts are given in c./sec. downfield from tetramethylsilane.

doublet at higher field, assigned to the vinyl proton at C-5, showed some further splitting, part of which was a result of coupling to one of the methylene protons.[3] Thus, irradiation of the 2H multiplet at 265 c./sec. caused the higher-field doublet to become much sharper. This shows that the methylene group is at C-7, since negligible coupling would be expected between protons at C-8 and the vinyl protons.

In the above irradiation substituted naphthalenes, (II) and (III) (8%)§, were also obtained; on irradiation in quartz apparatus at 253·7 mμ with a Hanovia 60 w low pressure mercury lamp the fraction of these latter products increased to 12%. Irradiation of (I) at 253·7 mμ gave a quantitative yield of naphthalene.

In view of the specificity of the reaction leading to (I), it seemed worthwhile to determine the stereochemistry of the cyano-group, and an *X*-ray structure determination was undertaken. The crystals have monoclinic symmetry with lattice parameters, $a = 8{\cdot}81(1)$ Å, $b = 5{\cdot}676(6)$ Å, $c = 18{\cdot}89(2)$ Å and $\beta = 107{\cdot}7(2)^\circ$. The space group is uniquely determined to be $P2_1/c$ since the extinctions observed were $h0l$ (l odd) and $0k0$ (k odd); $D_m = 1{\cdot}2$, $D_c = 1{\cdot}3$ gm. cm.$^{-3}$ for $Z = 4$. Steric considerations suggest that the molecule cannot have the *cis*-configuration with a translational symmetry length as short as the *b* axis length found. The shortest molecular vector distance, that between the nitrogen atom and either the C-1 or C-2 of the aromatic ring was 3·7 Å based upon a model using well-known interatomic separations. Thus, if the distance between carbons on different molecules is 3·6 Å as suggested by Kitaigorodskii[4] and one assumes a similar intermolecular contact distance for the nitrogen atom of the cyano-group, the molecular size is found to be too large by about 0·6 Å. On the other hand, the *trans*-molecular configuration is not at all restricted by these unit-cell dimensions.

The cyano-group in (I) was not epimerized by treatment with potassium t-butoxide in t-butyl alcohol[5] at 60° for 20 hr., a result consistent with the more stable, *trans*-structure for (I).

We thank Mr. J. Z. Ozog for help in obtaining the *X*-ray data, and The National Research Council of Canada and The Imperial Oil Co. Ltd. for financial support.

(*Received, July* 15*th*, 1968; *Com.* 941.)

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§ Product ratios were measured by gas chromatography on a 5′ × $\frac{1}{8}$″ column of 5% SE 30 on Chromosorb W at 180°.

[1] Derivatives of this system have been proposed as reasonable intermediates in cross-additions of naphthalenes and tolan; W. H. F. Sasse, P. J. Collin, and G. Sugowdz, *Tetrahedron Letters*, 1965, 3373.

[2] The spectrum of 1,2-dihydronaphthalene has λ_{max} (EtOH) 259 mμ, log ε 3·98; W. Hückel, E. Vevera, and U. Wörfel, *Chem. Ber.*, 1957, **90**, 901.

[3] E. I. Snyder and B. Franzus, *J. Amer. Chem. Soc.*, 1964, **86**, 1166, report 4-bond coupling between the olefinic and *anti*-7-proton in 7-substituted norbornenes ($J \sim 0{\cdot}8$ c./sec.).

[4] A. I. Kitaigorodskii, "Organic Chemical Crystallography," english translation. Consultants Bureau Enterprises, New York, 1961, p. 9.

[5] This reagent equilibrated the indene–acrylonitrile cyclobutane adducts in 1 hr. at 25°; J. J. McCullough and C. W. Huang, *Chem. Comm.*, 1967, 815.