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The photochemical reaction of I with acrylonitrile gave the cyclobutane adducts II and III, which on treatment with base afforded a novel polycyclic structure IV. Reduction of IV with LAH followed by Eschweiler-Clarke methylation yielded the polyheterocyclic structure VI.

J. Heterocyclic Chem., **16**, 205 (1979).

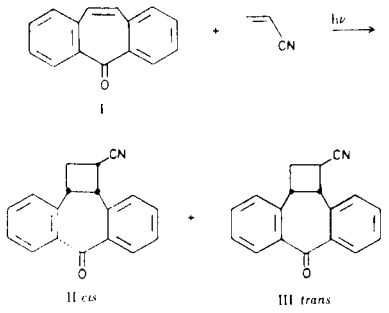
Sir:

Kopecky and Shields (1) have reported the first example of cyclobutane formation at the 10,11-position of dibenzo[*a*,*d*]cyclohepten-5-one (I) and we have recently reported on several cyclodimerizations of similar systems (2). Taking advantage of our photochemical results, we wished to study the effect which the special geometry of a cyclobutane ring would impart to the chemical and biological properties of this nucleus.

It is the purpose of this communication to report on some additional photochemical reactions of I and the subsequent chemical transformations which have led to a number of novel polycyclic structures.

When I is irradiated (Hanovia 450, Pyrex) in benzene with an excess of acrylonitrile, a high yield (95%) of *cis* and *trans* cyclobutane adducts in a 1:9 ratio is obtained.

Scheme I

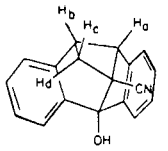


The predominant formation of the *trans isomer* is to be expected. The isomers II (*cis*), m.p. 167°, and III (*trans*), m.p. 90-92°, are easily separated by column chromatography. Nmr (220 MHz) provides confirmation of the proposed structures.

In an attempt to epimerize the *cis*-isomer using potassium *t*-butoxide in *t*-butanol, a quantitative yield of a new tetracyclic structure IV (m.p. 187-188°) was obtained. Treating the *trans* isomer in the same manner also led in quantitative yield to IV (See Scheme II).

The ir spectrum shows the disappearance of the carbonyl band, and the presence of an OH group at 3400, 3450 cm^{-1} and a cyano group at 2260 cm^{-1}. The mass spectrum shows the expected molecular ion (M^+ 259). The chemical shift/coupling constant matrix given below

Insert A

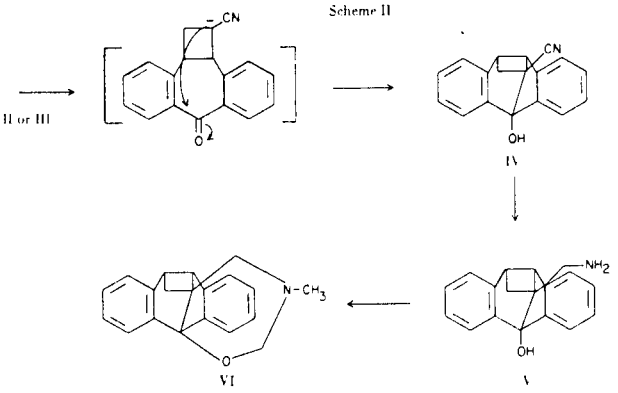


	H_a	H_b	H_c	H_d
H_a	4.3 δ	5.8 Hz	0	0
H_b	≈5.8 Hz	3.60 δ	≈6.3 Hz	≈0 Hz
H_c	0	≈6.3 Hz	2.80 δ	9.5 Hz
H_d	0	≈0 Hz	9.5 Hz	1.66 δ

for the cyclobutane protons is in good agreement with the proposed structure (220 MHz, deuteriochloroform).

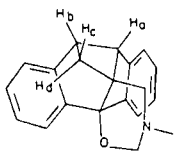
A Dreiding model shows that the cyclobutane ring is puckered, thus accounting for the zero or very small coupling constant observed between H_b and H_d. The aromatic protons appear as a multiplet (8H, δ 6.80-7.72).

Scheme II



Lithium aluminum hydride reduction of IV proceeded in 80% yield to V (m.p. 195-198°). When the latter was subjected to the Eschweiler-Clarke methylation procedure, a new polyheterocyclic compound (VI) was obtained in 80% yield, m.p. 117-118°. Mass spectral (M^+ 289), ir (lacks hydroxy and NH bands) and the following nmr data are in accordance with the proposed structure. The chemical shift/coupling constant matrix for the cyclobutane protons is as follows (220 MHz, deuteriochloroform).

Insert B



	H_a	H_b	H_c	H_d
H_a	≈3.60 δ	5.5 Hz	0	0
H_b	≈5.5 Hz	3.60 δ	5.0 Hz	≈0 Hz
H_c	0	≈5.0 Hz	2.41 δ	≈9.0 Hz
H_d	0	≈0 Hz	≈9.0 Hz	1.76 δ

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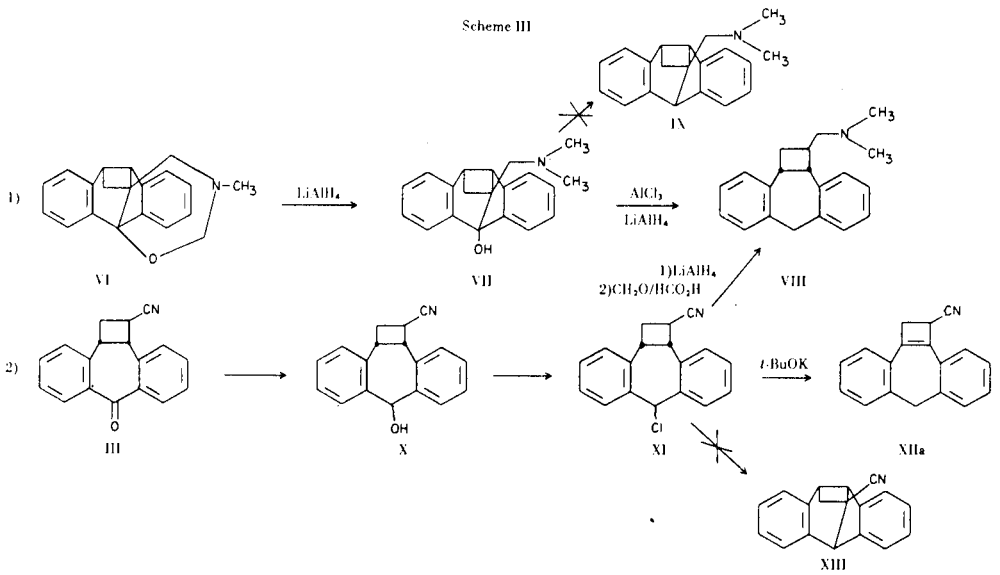
Scheme III



The other protons appear at: CH_2N- (s, 2H, δ 2.82), N-CH_3 (s, 3H, δ 2.50), O-CH_2N- (d, 1H, δ 4.56; d, 1H, δ 4.63; J_{Gem} = 10), aromatics (m, 8H, δ 6.75-7.70).

Hydride reductions of VI (Scheme III, equation 1) led interesting and unexpected ring cleavages.

Lithium aluminum hydride reduction of VI cleanly cleaves the 1,3-oxazine ring to give VII in 80% yield, m.p. 117-118°. In an attempt to remove the OH group in VII, the combination of lithium aluminum hydride/-aluminum chloride was tried, but instead of the expected compound IX, we obtained the reduced ring-opened compound VIII. The mechanism of this surprising reductive carbon-carbon ring cleavage is not clear at the present time.

To confirm the structure of VIII, an alternate synthesis was carried out (Scheme 3, equation 2). Compound III was reduced with sodium borohydride in 90% yield to X, m.p. 221-223°, followed by thionyl chloride treatment to compound XI in quantitative yield, m.p. 150-152°. Compound XI, upon lithium aluminum hydride reduction followed by Eschweiler-Clarke methylation, completed the synthesis of VIII, indicating at the same time that the stereochemistry of the dimethylaminomethyl is probably *trans*.

It was of interest to attempt the intramolecular cyclization of XI to obtain XIII in analogy to the formation of IV. However, on treatment with potassium *t*-butoxide, a 70% yield of XIIa was isolated, m.p. 132-134°. The formation of XIIa can be rationalized as follows. In structure XI, the hydrogen α to the cyano group is the most acidic one in the molecule and the anion will be formed there. The stereochemistry of the chlorine atom is not known. If it is *anti* to the cyclobutane ring, cyclization could occur to yield XIII. Compound XIII, if formed, should have been easily isolable in view of the stability of IV. If, however, the chlorine atom is *syn* to the cyclobutane ring, no cyclization can occur and one of the following courses may be operative: (a) Nucleophilic attack of the α-cyanocarbanion, XI, on the chlorine to yield XIVa, followed by elimination of hydrogen chloride and rearrangement to XIIa. In a closely related molecule, XIVb (prepared by phosphorus pentachloride chlorination of III, m.p. 154-156°), treatment with sodium hydroxide/-methanol leads in very good yield to XIIb, m.p. 137-140°.

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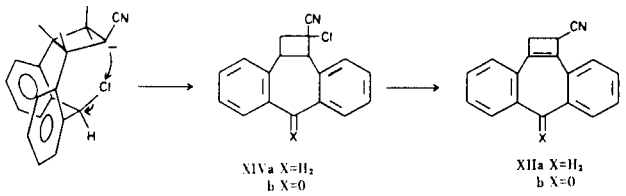

(b) Concerted hydrogen elimination followed by proton transfer.

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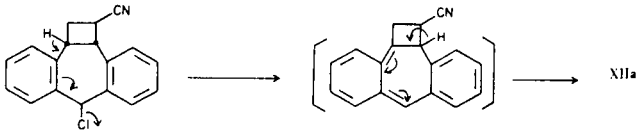

A similar 1,4 hydrogen chloride elimination under basic conditions has been observed recently in a related system (3).

Insert E

The chemistry and potential use of these polycycles are currently under investigation.

REFERENCES AND NOTES

(1) J. Kopecky and J. E. Shields, *Tetradedron Letters*, **24**, 2821 (1968); *Collect. Czech. Chem. Commun.*, 36, 3517 (1971).

(2) J. Rokach, Y. Girard and J. G. Atkinson, *Chem. Commun.*, 602 (1975).

(3) E. E. Galantay, R. Simpson, G. Corriveau, M. Denzer, D. C. Knorr, R. J. Strohschein, N. A. Paolella and Y. Vike, *J. Med. Chem.*, 17, 1316 (1974).