γ-Pyran is extremely unstable at room temperature,[11] particularly when exposed to air, while a moderately slow decomposition takes place at −80° in an ethereal solution containing a small amount of hydroquinone. We are searching for an efficient inhibitor to preserve a sufficient quantity of I for the further investigation.[12]

(11) Within 10 minutes coloration of I is noticeable and it decomposes completely overnight. Accordingly, elementary analysis was not possible.

(12) We are indebted to Dr. B. L. Shapiro and Mr. J. J. Burke for the n.m.r. spectrometric measurement.

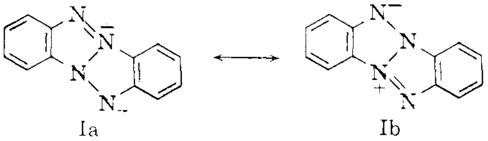
MELLON INSTITUTE
PITTSBURGH 13
PENNSYLVANIA
SATORU MASAMUNE
NICHOLAS T. CASTELLUCCI

RECEIVED MAY 23, 1962

DIBENZO-1,3a,4,6a-TETRAAZAPENTALENE—A NEW HETEROAROMATIC SYSTEM

Sir:

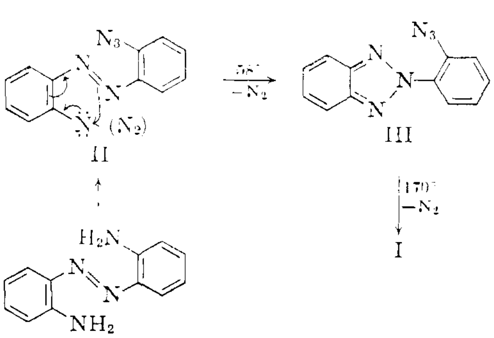
We wish to report the preparation of a stable, new heterocyclic system represented by dibenzo-1,3a,4,6a-tetraazapentalene (I).[1] This meso-ionic molecule can be represented as a hybrid of several dipolar resonance structures (two of which are Ia and Ib).



Ia Ib

The planar tetraazapentalene I can assume the electronic character of a pentalene dianion[2] molecule by virtue of a contribution to the π-electron system of six electrons by the four nitrogen atoms. This conjugation is reflected by the pronounced stability displayed by the molecule I. I is unaffected by heating in solvents above 300° and can be sublimed unchanged at atmospheric pressure. The solid dissolves in concentrated sulfuric acid and can be reprecipitated by diluting with water. An acetone solution of I is stable to potassium permanganate.

By contrast, dibenzopentalene is reported to exhibit distinct olefinic properties about the central pentalene nucleus.[3]



The dibenzo-1,3a,4,6a-tetraazapentalene was prepared in greater than 90% yield by thermal decomposition of *o,o'*-diazidoazobenzene (II).[4] Compound I also forms when a benzene solution of II is exposed to sunlight.

o,o'-Diaminoazobenzene[5] was tetrazotized, then treated with aqueous sodium azide to obtain *o,o'*-diazidoazobenzene (II), yield 93%, m.p. 116–117° (dec.).

Anal. Calcd. for $C_{12}H_8N_8$: C, 54.54; H, 3.05; N, 42.41. Found: C, 54.75; H, 3.31; N, 42.37.

When a solution of II in decalin was heated, decomposition proceeded in two stages with evolution of nitrogen. One mole of gas was released at the remarkably low temperature of 58° to yield 2-(*o*-azidophenyl)-2,1,3-benzotriazole (III), m.p. 78–79°, in good yield.

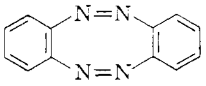
Anal. Calcd. for $C_{12}H_8N_6$: C, 61.01; H, 3.41; N, 35.58. Found: C, 61.04; H, 3.65; N, 35.94.

The structure of III was confirmed by independent synthesis. At 170°, another mole of nitrogen was evolved, and compound I was obtained as long, yellow needles, m.p. 237–238°.

Anal. Calcd. for $C_{12}H_8N_4$: C, 69.22; H, 3.87; N, 26.91; mol. wt., 208. Found: C, 69.06; H, 3.99; N, 26.96; mol. wt. (Rast), 221.

The infrared spectrum exhibited peaks at 6.2, 6.3 and 6.7 μ. The ultraviolet spectrum (in ethanol) showed three main areas of absorption, with peaks at 254.5 mμ (ε 65,000), 322.5 mμ (ε 4575) and 402μ (ε 40,000).[6] The dipole moment, measured in benzene, was approximately zero.

An alternative structure which could accommodate many of the physical properties of this molecule as well as its mode of formation is dibenzo-1,2,5,6-tetraazacycloöctatetraene (IV). Derivatives of the simple tetraazacycloöctatetraene ring system have been described[7] as high-melting, fluorescent solids of high thermal stability. However, the complexity of the proton n.m.r. spectrum of the present dibenzo compound compared to naphthalene (A_2B_2 system), would appear to favor the dibenzotetraazapentalene I.[8]



IV

Chemical evidence supporting this conclusion was obtained by the synthesis of an analogous molecule in which one of the benzene rings is replaced by a naphthalene nucleus with fusion at the α,β-positions.

Two *nonsuperimposable* isomers (Va and Vb) would be expected on thermal decomposition of 2-(*o*-azidophenyl)-2,1,3-α,β-naphthotriazole (VI) by formation of a bond between the azido nitrogen and

---

[1] This compound may be named 5,11-dehydrobenzotriazolo[2,1-a-]benzotriazole. The trivial name dibenzo-1,3a,4,6a-tetraazapentalene is henceforth used in this article.

[2] T. J. Katz and M. Rosenberger, *J. Am. Chem. Soc.*, **84**, 865 (1962).

[3] C. T. Blood and R. P. Linstead, *J. Chem. Soc.*, 2263 (1952).

[4] R. A. Carboni, U. S. Patent 2,904,544 (1959).

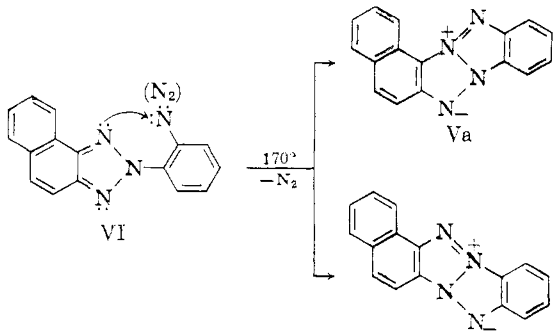
[5] R. Willstätter and A. Pfannenstiel, *Ber.*, 2349 (1905).

[6] Only the most intense bands are given for the two longer wavelength regions, each of which displays prominent fine structure.

[7] R. Metze, *Angew. Chem.*, **68**, 581 (1956); R. Pfleger and H. G. Hahn, *Ber.*, **90**, 2411 (1957).

[8] The authors express their thanks to Professor J. D. Roberts for this interpretation.

the 1- or 3-nitrogen of the triazole. Only one isolable form is possible for the tetraazacycloöctatetraene.



VI

Va

The evolution of one mole of nitrogen from VI proceeded smoothly at 170° in decalin to yield a yellow crystalline solid, m.p. 190–230°. The solid gave a good analysis for $C_{16}H_{10}N_4$ despite its wide melting-point range. Chromatography on Woelm non-alkaline alumina yielded two sharp-melting products, m.p. 212–213° and 243–245°. The infrared spectra of the two products showed some differences, despite their general similarity. A spectrum of a composite of the two pure isomers contained all of the peaks of the unseparated mixture.

The properties and reactions of this new system as well as some theoretical calculations will be reported in a later paper.

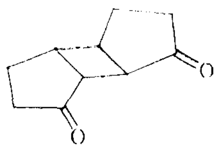
CONTRIBUTION NO. 791 FROM THE
CENTRAL RESEARCH DEPARTMENT
EXPERIMENTAL STATION
E. I. DU PONT DE NEMOURS AND COMPANY
WILMINGTON, DELAWARE
R. A. CARBONI
J. E. CASTLE

RECEIVED APRIL 27, 1962

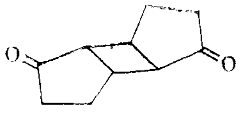
ON THE MECHANISM OF THE PHOTODIMERIZATION OF CYCLOPENTENONE

Sir:

We have shown recently that, on exposure to ultraviolet radiation, 2-cyclopentenone is converted rapidly and in high yield to the dimers I and II.[1] These are formed in approximately equal amounts; although both are sensitive to prolonged irradiation, we have found no evidence of interconversion.

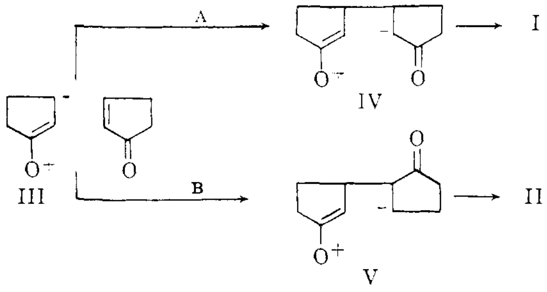


I



II

In its least sophisticated form, the mechanism of light-induced dimerization of α,β-unsaturated ketones can be represented as the attack of a photoexcited molecule on non-excited substrate. At the present time, it is not possible to describe completely the excited state of cyclopentenone. Although the initial excitation is presumably to the singlet state (N → π^* at 308 mμ), crossover to the triplet state is highly probable.[2] In either case, the charge distribution within the excited molecule at the time of reaction is not known. For the moment, the polarized form III may be taken as an adequate representation.[3] *If* the two carbon–carbon bonds to be made in the dimerization are not formed concertedly, two pathways for reaction, A and B, can be envisioned.[4]



Interaction of the negative charge with the adjacent carbonyl group should result in some stabilization of IV relative to V. Route A then appears more attractive than route B; dimer I should be the preferred product. The same conclusion can be reached by taking an uncharged diradical as the favored form of the excited state.

The non-concerted mechanism cannot be reconciled with the observation that dimers I and II are formed in similar yields unless the stabilization of the anion (or radical) in IV by the adjacent carbonyl group is inconsequential in comparison to the energies associated with IV and V. Alternatively, a one-step mechanism in which the new carbon–carbon bonds are formed concertedly may apply.

An obvious implication of either reasoning is that the carbonyl group of the non-excited partner in the photo-reaction plays an unimportant role. Indeed, we have now shown this to be true.

Irradiation of a solution of 2-cyclopentenone (0.064 mole) in cyclopentene (0.64 mole) led to rapid consumption of the unsaturated ketone. A Hanovia, 450-watt mercury arc lamp equipped with a Pyrex filter was employed as the light source. The reaction was complete within three hours. The excess olefin was removed, and the residue was fractionated through a 61-cm. spinning band column. The main fraction, b.p. 78–80° (0.7 mm.), 67% based on cyclopentenone, was shown to be homogeneous by vapor phase chromatography. The material was reduced readily under Wolff–Kishner conditions to the known hydrocarbon *cis,trans,cis*-tricyclo[5.3.0.0^{2,6}] decane[1] and was therefore assigned structure VI. The small forerun from the distillation contained VI contaminated only by unreacted cyclopentenone and by an unsaturated aldehyde which arises from

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(1) P. E. Eaton, *J. Am. Chem. Soc.*, **84**, 2344 (1962).

(2) We have shown that cyclopentenone sensitizes several reactions in the same fashion as does acetophenone, presumably *via* the triplet state; *cf.* G. S. Hammond, N. J. Turro and A. Fischer, *J. Am. Chem. Soc.*, **83**, 4674 (1961).

(3) See, for example, H. E. Zimmerman and D. I. Schuster, *ibid.*, **83**, 4486 (1961).

(4) Product decay to the ground state is assumed. If triplet states are involved, electron re-pairing can occur after the formation of the cyclobutane ring.