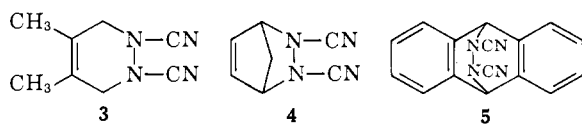
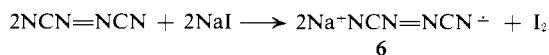


is formed in 3 days at room temperature (*Anal.* Calcd. for **5**: C, 74.4; H, 3.9; N, 21.7. Found: C, 75.2;



H, 4.1; N, 20.9). On heating at 120°, **5** reverts to **1** and anthracene.⁴

Azodicarbonitrile is reduced chemically or electrolytically to a stable anion radical. Sodium azodicarbonitrilide (**6**), prepared in 94% yield from **1** and sodium iodide in acetonitrile, is a bronze, explosive powder,



soluble and stable in water, methanol, and dilute base. *Anal.* Calcd. for **6**: C, 23.3; N, 54.4. Found: C, 23.2; N, 52.5; $\lambda_{\text{max}}^{\text{CH}_3\text{CN}}$ 222 (ϵ 5270), 372 (ϵ 4560), 525 $\text{m}\mu$ (ϵ 120); $\lambda_{\text{max}}^{\text{KBr}}$ 4.62 μ . Polarographic reduction of **1** to **6** is a reversible, one-electron process at $E_{1/2} + 0.40$ v. vs. s.c.e., *i.e.*, more facile than the reduction of tetracyanoethylene (+0.152 v.) or of tetracyanoquinodimethane (+0.127 v.).⁵ Molecular orbital calculations on **1** indicate an unfilled bonding orbital is present at +0.42 β . Electron spin resonance of **6** in acetonitrile shows 5 lines, each split to 5 lines, thus indicating two equivalent pairs of nitrogen atoms.

(4) J. Harley-Mason and J. C. W. Tims, *Proc. Chem. Soc.*, 345 (1963), report an analogous reaction, the formation of ethyl cyanoazofornate from its anthracene adduct.

(5) L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson, and W. E. Mochel, *J. Am. Chem. Soc.*, **84**, 3374 (1962).

F. D. Marsh, M. E. Hermes

Contribution No. 1062, Central Research Department
Experimental Station, E. I. du Pont de Nemours and Company
Wilmington, Delaware

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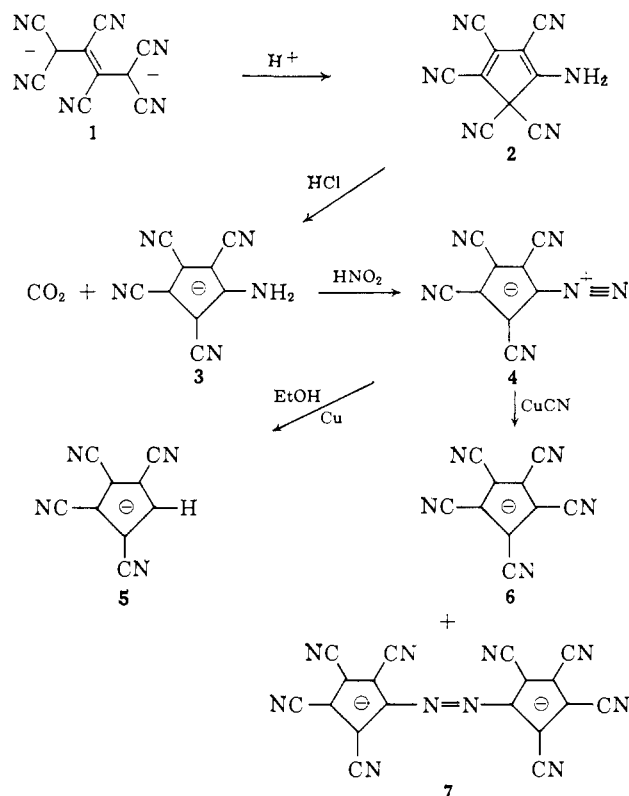
Diazotetracyanocyclopentadiene and Its Conversion to Tetracyanocyclopentadienide and Pentacyanocyclopentadienide

Sir:

We have synthesized diazotetracyanocyclopentadiene (**4**) from hexacyanobutenediide¹ (**1**) and used this "diazonium" compound to make the very stable tetra- and pentacyanocyclopentadienide anions **5** and **6**. Because of the marked stabilizing effect of the four cyano groups, the chemical properties of the "diazonium" group in diazotetracyanocyclopentadiene and the carbon-hydrogen bond in tetracyanocyclopentadienide parallel those of a benzene diazonium group and benzene carbon-hydrogen bonds. Thus, the aromaticity of the cyclopentadienide system can now be examined by classical chemical means.

In dilute aqueous acid, disodium hexacyanobutenediide cyclizes to 1-amino-2,3,4,5,5-pentacyanocyclopentadiene² (**2**), a bright yellow unstable solid, $\lambda_{\text{max}}^{\text{CH}_3\text{CN}}$ 413 $\text{m}\mu$ (ϵ 7000). One of the cyano groups at the 5-position

in **2** is hydrolyzed by concentrated hydrochloric acid at 15°, and the resulting carboxylic acid group spontaneously loses carbon dioxide to generate aminotetracyanocyclopentadienide (**3**), m.p. (tetraethylammonium salt) 126–127°. Its aqueous solutions are neutral, which indicates the tetracyanocyclopentadienidyl portion of the ion is withdrawing electrons from the amino group.



Diazotetracyanocyclopentadiene (**4**) results when aminotetracyanocyclopentadienide is diazotized under conditions ordinarily used to prepare aromatic diazonium compounds. Diazotetracyanocyclopentadiene, recrystallized from acetonitrile, is a light-yellow, water-insoluble solid which decomposes at ~200°. It does not appear to be shock sensitive. In view of its high dipole moment, 11.44 D., and chemical properties, which parallel aromatic diazonium compounds, a zwitterion structure is preferred.

Diazotetracyanocyclopentadiene reacts with cuprous cyanide to give pentacyanocyclopentadienide (**6**) and azotetracyanocyclopentadienide (**7**). Pentacyanocyclopentadienide salts are remarkably stable. For instance, the potassium salt can be heated at 400° in air without decomposition. Spectrophotometrically, we could not detect any protonation of the anion by perchloric acid in acetonitrile. The $\text{p}K_a$ of pentacyanocyclopentadiene in this solvent is therefore less than -2.³ For comparison, the $\text{p}K_a$ of sulfuric acid in acetonitrile is +7.25.⁴

Diazotetracyanocyclopentadiene is reduced by ethanol in the presence of copper powder to tetracyanocyclopentadienide (**5**), isolated as the tetraethylammonium salt, m.p. 130–132°. Its $\text{p}K_a$ in acetonitrile

(1) O. W. Webster, *J. Am. Chem. Soc.*, **86**, 2898 (1964).

(2) Satisfactory analytical results were obtained on all compounds.

(3) The $\text{p}K_a$ measurements were made by Dr. J. Fok.

(4) I. M. Kolthoff, S. Bruckenstein, and M. K. Chantooni, Jr., *J. Am. Chem. Soc.*, **83**, 3927 (1961).

is 0. The nuclear magnetic resonance for the aromatic hydrogen is at τ 3.23.

O. W. Webster

Contribution No. 1051, Central Research Department
Experimental Station

E. I. du Pont de Nemours and Company
Wilmington, Delaware 19898

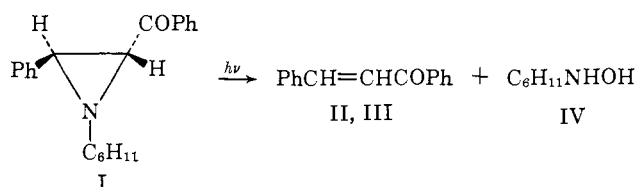
Received December 25, 1964

The Photochemical Deamination of a 2-Benzoylaziridine

Sir:

In view of the structural relationship between the ethylenimine ketones and the epoxy ketones¹ and as a logical extension of our photochemical studies of small-ring carbonyl compounds² it was of interest to determine if the photochemical properties of 2-benzoylaziridines would parallel those of benzoyl epoxides. We now wish to describe the photochemistry of the 2-benzoylaziridine system, in which the relative position of the substituents on the three-membered ring influences the mode of reaction.

trans-1-Cyclohexyl-2-phenyl-3-benzoyl ethylenimine (I) was prepared by treating a mixture of *trans*-benzalacetophenone (II) and cyclohexylamine with iodine in methanol.³ This isomer was initially prepared by Cromwell and co-workers from α,β -dibromobenzylacetophenone and cyclohexylamine.⁴ Irradiation of I in aqueous ethanol at 25° with ultraviolet light of wave length above 305 m μ ⁵ afforded a mixture of *trans*- and *cis*-benzalacetophenone (II and III) and N-cyclohexylhydroxylamine (IV) in high yield. N-Cyclohexylhydroxylamine was identified by its reaction with



benzaldehyde to give the known N-cyclohexyl nitron of benzaldehyde, m.p. 80–82°, in high yield.⁶

A striking feature of this photochemical reaction is the deamination to a mixture of *cis*- and *trans*-benzalacetophenone.⁷ Particular interest is attached to the mechanism of formation of the olefinic mixture.⁸ A conceivable pathway could involve rapid *cis*-*trans* photoisomerization of the 2-benzoylaziridine followed

(1) N. H. Cromwell, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **19**, 214 (1958).

(2) A. Padwa, *Tetrahedron Letters*, No. 15, 813 (1964).

(3) P. L. Southwick and D. R. Christman, *J. Am. Chem. Soc.*, **74**, 1886 (1952).

(4) N. H. Cromwell, N. G. Barker, R. A. Wankel, P. G. Vanderhorst, F. W. Olson, and J. H. Anglin, *ibid.*, **73**, 1044 (1951).

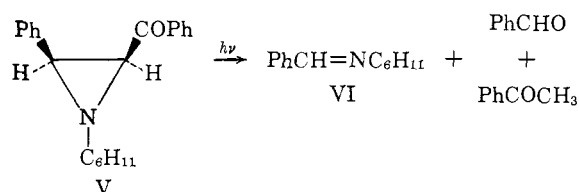
(5) The photolysis was conducted using an internal water-cooled mercury arc lamp (Hanovia, Type L-450 watts) with a soft glass filter to eliminate wave lengths below 305 m μ .

(6) J. Thesing and W. Sirrenberg, *Chem. Ber.*, **91**, 1978 (1958).

(7) The deamination of saturated aziridines with nitrosyl chloride has been reported to give nitrous oxide and the corresponding olefin with greater than 99% stereoselectivity [R. D. Clark and G. K. Helm-kamp, *J. Org. Chem.*, **29**, 1316 (1964)].

(8) Stereospecific deamination of I to II followed by rapid photoisomerization of the olefin is an alternate possibility. A detailed study of the stereospecificity of the photodeamination is in progress.

by deamination of the mixture to give equal amounts of the isomeric olefins. The *cis*-*trans* photoconversion of the three-ring nitrogen compound was considered a likely possibility since similar isomerizations have been reported for related small ring carbonyl compounds.^{9,10} This sequence however is eliminated by the finding that irradiation of *cis*-1-cyclohexyl-2-phenyl-3-benzoyl-ethylenimine (V) does not afford I. Further, the course of the over-all photoreaction is altered drastically for the *cis* isomer. Irradiation of V in aqueous ethanol gave the Schiff's base of benzaldehyde (VI) as the major product (25%), together with a number of minor components. Careful examination of the photolysis mixture revealed the presence of benzaldehyde (6%) and acetophenone (8%), but showed that no detectable amounts of II, III, phenacyl alcohol, or phenacyl ethyl ether were present.¹¹



The low-energy $n-\pi^*$ bands in the spectra of I and V are undoubtedly the significant absorption bands, since light above 310 m μ was employed. The light absorbed by I and V possesses sufficient energy to effect a bond cleavage. The energy corresponding to 316 m μ radiation (90.8 kcal./mole) is substantially greater than the maximum energy required for bond dissociation in aziridine itself, which in turn is higher than that required for bond rupture in I and V. Despite the fact that $n-\pi^*$ excitation would be expected to develop appreciable charge density on nitrogen as a result of a heterolytic cleavage of the aziridine carbon-nitrogen bond, the products obtained from the irradiation of I seem to be those characteristic of an electron deficient nitrogen.¹² A related situation has been noted for the $n-\pi^*$ photochemical transformations of cyclohexadienones.¹³ An electron demotion process was suggested for these cases in order to resolve the enigma of carbonium ion type reactions occurring from an $n-\pi^*$ state.¹³ It is tempting to hypothesize that the aziridine system is behaving analogously and that a related electron demotion from the already weakened C-N bond occurs. This mechanism allows for free rotation of the zwitterion about the central carbon-carbon single bond and consequently is in accord with the formation of a mixture of *cis*- and *trans*-benzalacetophenone.

The molecular changes involved in the photochemistry of the 2-benzoylaziridine system are markedly dependent on the initial stereochemistry. From the results we conclude that the relative positions of the substituents influence the mode of ring opening. To account for

(9) G. W. Griffin, W. J. O'Connell, and H. A. Hammond, *J. Am. Chem. Soc.*, **85**, 1001 (1963).

(10) H. E. Zimmerman, Abstracts, Seventeenth National Organic Chemistry Symposium, Bloomington, Ind., June 1961, p. 31.

(11) The low yields found can be attributed to a competing dark reaction. The thermal and solvolytic reactions of 2-benzoylaziridines will be the subject of a future publication.

(12) It remains to be established whether the cleavage reaction involves an electronically excited species or is a thermal reaction of the molecule in the ground state formed by isoenergetic crossing from an electronically excited state.

(13) H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **84**, 4527 (1962).