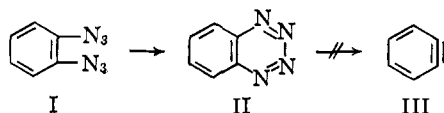


Dinitrenes from *o*-Diazides.
Synthesis of 1,4-Dicyano-1,3-butadienes

Sir:

o-Diazidobenzene has been synthesized in quantitative yield from *o*-azidoaniline¹ by diazotization with sodium nitrite in dilute hydrochloric acid, followed by treatment of the diazonium solution with sodium azide. *o*-Diazidobenzene is a light yellow liquid, which freezes at 22–23°. It undergoes rapid decomposition at 160–170° and explosive decomposition when heated rapidly to 250°. Due to its explosive character, it was not distilled. *Anal.* Calcd. for C₆H₄N₆: C, 45.0; H, 2.52; N, 52.4. Found: C, 44.9; H, 2.45; N, 52.6. The major peaks in the infrared (neat) are (in cm.⁻¹) at: 2120 (s), 1590 (m), 1493 (m), 1452 (m), 1300 (s), 1160 (w), 1088 (m), 747 (s), and 698 (m).

The thermal decomposition of *o*-diazidobenzene (I) was investigated as a possible source of benzyne. It was postulated that when I decomposed it might be expected to do so with the intermediate formation of the heterocycle II, which in turn might be expected to undergo further decomposition to give benzyne. To



check this possibility, *o*-diazidobenzene was allowed to decompose in hexadecane solution containing anthracene. If benzyne is formed in the decomposition, it should be trapped by its Diels–Alder reaction with anthracene to give tryptycene.² However, when the reaction was worked up no tryptycene could be isolated. Instead the reaction yielded recovered anthracene and two colorless solids with melting points of 187° (A) and 129° (B).

Compound B was easily obtained in high yield (79%) by the dropwise addition of *o*-diazidobenzene to refluxing decalin. The analyses and molecular weight determination of B indicated a molecular formula of C₆H₄N₂. *Anal.* Calcd. for C₆H₄N₂: C, 69.2; H, 3.87; N, 26.9; mol. wt., 104. Found: C, 69.3; H, 3.80; N, 27.0; mol. wt., 110. The infrared spectrum of B (Nujol mull) contained peaks (in cm.⁻¹) at: 2220 (w), 1348 (w), 1204 (m), 983 (w), and 753 (s). The infrared absorption at 2220 cm.⁻¹ suggested the presence of cyano groups. Hydrolysis of B in refluxing concentrated hydrochloric acid gave a dicarboxylic acid which was subsequently identified by mixture melting point and comparison of infrared spectra as *trans,trans*-muconic acid. These results clearly indicate that B is 1,4-dicyano-1,3-butadiene (IV).

Compound A analyzed correctly for the Diels–Alder adduct of IV with anthracene. *Anal.* Calcd. for C₂₆H₁₄N₂: C, 85.1; H, 5.00. Found: C, 85.0; H, 4.94. The infrared spectrum of A (Nujol mull) exhibited a weak absorption at 2220 cm.⁻¹, indicating the presence of cyano groups. Compound A was also obtained by direct reaction of IV and anthracene in refluxing *m*-xylene.

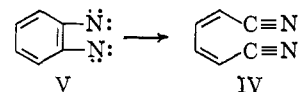
The fact that IV hydrolyzes to *trans,trans*-muconic acid does not mean that IV has the *trans,trans* configura-

(1) P. A. S. Smith, J. H. Hall, and R. O. Kan, *J. Am. Chem. Soc.*, **84**, 485 (1962).

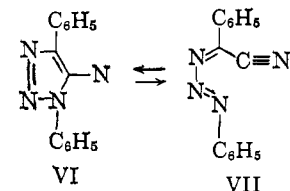
(2) L. Friedman and F. M. Logullo, *ibid.*, **85**, 1549 (1963).

tion, since it is quite likely that isomerization would occur in the strongly acidic media. Indeed, IV might be expected to have the *cis,cis* configuration due to the method of synthesis. Two 1,4-dicyano-1,3-butadienes with melting points of 160–162° and 124–125° have been reported in the literature.^{3–5} The isomer melting at 124–125° is reported to have an infrared absorption peak at 1555 cm.⁻¹. Since this peak is absent in the spectrum of IV, it seems likely that these are not the same compound. The infrared spectrum of IV does not contain a peak in the carbon–carbon double bond stretching region. Olefins with a high degree of symmetry normally do not show an absorption in this region.⁶ Further experiments are being designed to establish the configuration of each of these isomers.

The 1,4-dicyano-1,3-butadiene, produced by decomposition of *o*-diazidobenzene, is a bond isomer of the dinitrene V. The infrared peak at 2220 cm.⁻¹, the

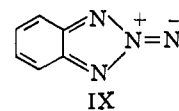


Diels–Alder adduct with anthracene, and the hydrolysis to muconic acid all indicate the dinitrile structure of IV. It is interesting to compare this result with that of Smith, Krbecek, and Resemann.⁷ Decomposition of the corresponding heterocyclic azide gave the nitrene VI which they considered to be in equilibrium with the nitrile VII. On the basis of chemical reactions, they



concluded that their compound had the nitrene structure VI. However, since their compound also absorbed weakly in the infrared at 2200 cm.⁻¹, it was necessary to postulate that VI was in equilibrium with the nitrile VII.

The dinitrene V could arise in several ways. It could arise directly by decomposition of both azido groups, by decomposition of the intermediate II, or by further decomposition of an intermediate such as IX.



The decomposition of aromatic *o*-diazides to butadienedinitriles seems to be a general reaction. Both 2,3-diazidotoluene and 3,4-diazidotoluene have been synthesized and decomposed to the corresponding di-

(3) F. S. Fawcett and C. M. Langkammer, U. S. Patent 2,564,102 (Aug. 14, 1951).

(4) H. F. Piepenbrink, *Ann.*, **572**, 83 (1961).

(5) P. Kurtz, H. Gold, and H. Disselnkötter, *ibid.*, **624**, 1 (1959).

(6) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 38.

(7) P. A. S. Smith, L. O. Krbecek, and W. Resemann, *J. Am. Chem. Soc.*, **86**, 2025 (1964).

nitriles. Several other *o*-diazides are currently under investigation.

J. Herbert Hall

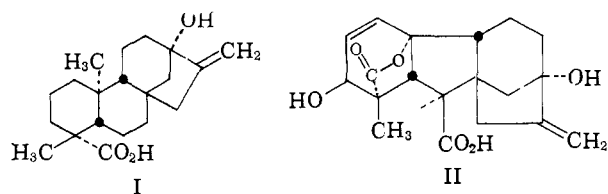
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A New Cyclization. 2-Methylenecyclopentanols by the Chemical Reduction of γ -Ethinyl Ketones

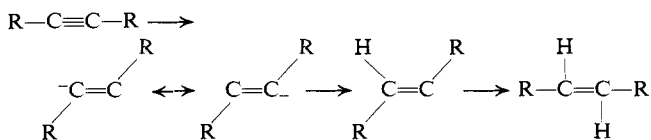
Sir:

The existence in some natural products such as steviol (I)^{1a,b} and gibberellic acid (II)² of a bicyclo[3.2.1]-octane system with the unusual features of an exocyclic

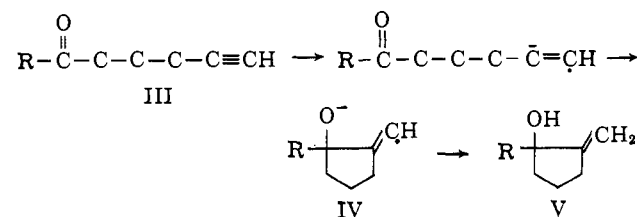


methylene group adjacent to a bridgehead tertiary hydroxyl provided the stimulus for the development of the new synthetic method which we are now reporting.

The chemical reduction of a triple bond is well-known to lead to an ethylenic link.³ It is not unreasonable to assume that the reaction involves formation of an ion-radical which acquires a proton from the solution; addition of another electron and another proton then gives the final ethylene.



It appeared possible that a suitably placed electrophilic center could trap the carbanion intermediate in competition with an external proton source. In fact, we have shown previously that the related anionic species from electron addition to α,β -unsaturated ketones can be trapped in favorable cases.⁴ With a γ -ethynyl ketone the desired process would be as shown below.



We have examined three cases of γ -ethynyl ketones of varying complexity. The structurally simplest case, 6-heptene-2-one (III, R = CH₃), b.p. 82–85° (41 mm.),

(1) (a) F. Dolder, H. Lichti, E. Mosettig, and P. Quitt, *J. Am. Chem. Soc.*, **82**, 246 (1960); (b) C. Djerassi, P. Quitt, E. Mosettig, R. C. Campbell, P. S. Rutledge, and L. H. Briggs, *ibid.*, **83**, 3720 (1961).

(2) F. McCapra, A. I. Scott, G. A. Sim, and D. W. Young, *Proc. Chem. Soc.*, 1851 (1962); J. A. Hartruck and W. N. Lipscomb, *J. Am. Chem. Soc.*, **85**, 3414 (1963).

(3) For a review of chemical reductions of acetylene, see K. N. Campbell and B. K. Campbell, *Chem. Rev.*, **31**, 77 (1942).

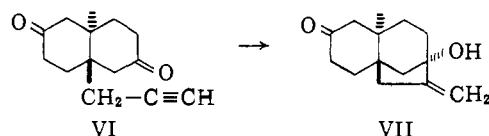
(4) G. Stork, P. Rosen, N. Goldman, R. V. Coombs, and J. Tsuji, *J. Am. Chem. Soc.*, **87**, 275 (1965).

was prepared from the dioxolane of 3-bromopropyl methyl ketone and sodium acetylide in liquid ammonia, followed by deketalization (1.5 hr. heating with 1 drop of hydrochloric acid in 50% methanol). It was characterized as its 2,4-dinitrophenylhydrazone, m.p. 118–119°. *Anal.* Found: C, 53.49; H, 4.72.

Addition of lithium to a liquid ammonia-tetrahydrofuran solution of III (R = CH₃), containing ammonium sulfate, led in moderate yield to a mixture of products which obviously contained the desired 1-methyl-2-methylenecyclopentanol (V, R = CH₃), in addition to uncyclized reduction products.

Although we were not able to obtain a pure sample of V, its presence in the reduction products to the extent of ca. 50% was established by the n.m.r. spectrum, which showed a singlet methyl at τ 8.6 and the expected absorption due to the methylene hydrogens around τ 5.4.

The situation would be expected to be more favorable if the propargyl group were in a 1,3-axial position to the carbonyl group. We have examined such a case, 10-propargyl-*trans*-decalin-2,7-dione (VI), m.p. 149–150°. *Anal.* Found: C, 76.53; H, 7.89. Addition of lithium to a mixture of VI with liquid ammonia-ether containing ammonium sulfate led to ~50% of the tricyclic alcohol VII, m.p. 152–153°. *Anal.* Found: C, 76.12; H, 9.20. The structure follows from the presence of hydroxyl (2.9 μ) and exocyclic methylene groups (11.15 μ), as well as from the n.m.r. spectrum. The latter showed two multiplets (1 H each), centered at τ ~4.9 and 5.1, arising from the terminal methylene group.



Although these results were encouraging they were not completely convincing because of the small amounts of substance available or of difficulties in separation. We have therefore made a careful examination of a further series of obvious interest in connection with gibberellic acid.

The tricyclic ketoacetylene VIII, m.p. 71–72°, was not expected to cyclize as readily as VI because the most stable conformer is almost certainly that in which the propargyl group is equatorial to the ketonic ring. In fact, cyclization attempts with various alkali metals in liquid ammonia gave mixtures containing considerable quantities of the product of simple reduction of the acetylene without cyclization, as shown by the strong absorption at 10.9 μ due to the terminal vinyl group. Absorption at 11.1 μ due to the terminal methylene of the cyclized compound was, however, also observed, and the best conditions (addition of 600 mg. of potassium to 400 mg. of VIII in a mixture of 15 ml. of tetrahydrofuran and 20 ml. of anhydrous ammonia containing 400 mg. of ammonium sulfate) led to a mixture from which the crystalline tetracyclic alcohol IX, m.p. 73–74.5°, could be separated.

The structure of IX follows unambiguously from its analysis (Found: C, 79.80; H, 7.97), from its infrared spectrum (hydroxyl at 3600 and 3460 cm.⁻¹, exocyclic methylene at 900 cm.⁻¹), and from its n.m.r. spectrum,