

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

J. Herbert Hall

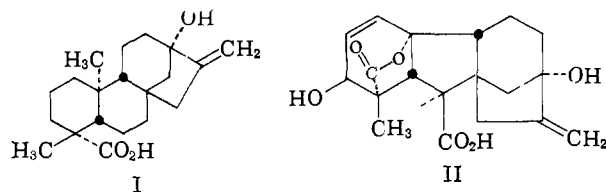
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A New Cyclization. 2-Methylenecyclopentanols by the Chemical Reduction of γ -Ethinyl Ketones

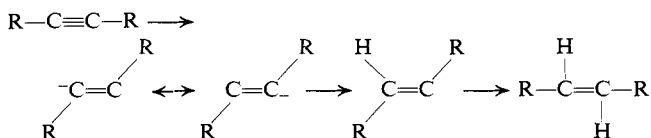
Sir:

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

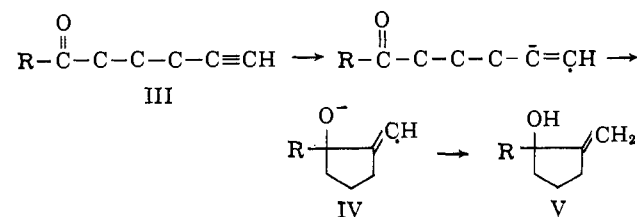


methylene group adjacent to a bridgehead tertiary hydroxyl provided the stimulus for the development of the new synthetic method which we are now reporting.

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).

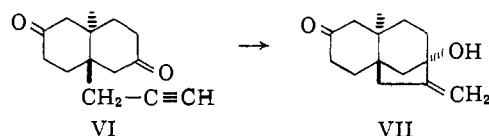
(4) G. Stork, P. Rosen, N. Goldman, R. V. Coombs, and J. Tsuji, *J. Am. Chem. Soc.*, **87**, 275 (1965).

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.

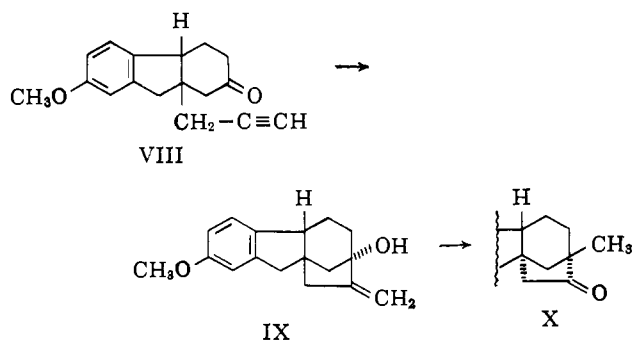
The situation would be expected to be more favorable if the propargyl group were in a 1,3-axial position to the carbonyl group. We have examined such a case, 10-propargyl-*trans*-decalin-2,7-dione (VI), m.p. 149–150°. *Anal.* Found: C, 76.53; H, 7.89. Addition of lithium to a mixture of VI with liquid 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,



which showed absorption at τ 4.9 and 5.1 (1 H each) characteristic of the terminal methylene group. Final chemical confirmation of the structure of IX follows from its rearrangement,⁵ on heating with methanolic hydrochloric acid, into the tetracyclic ketone X, m.p. 132–134° (*Anal.* Found: C, 79.53; H, 7.75), which had the typical cyclopentanone absorption at ~ 1750 cm^{-1} , while the n.m.r. spectrum showed the disappearance of vinylic absorption and the appearance of a characteristic methyl absorption at τ 9.0 (singlet, 3 H).⁶

(5) *Cf.* ref. 1a and J. F. Grove, T. P. C. Mulholland, J. MacMillan, and W. B. Turner, *J. Chem. Soc.*, 3049 (1960).

(6) This work was supported, in part, by the National Science Foundation.

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The Direct Observation of a Norcaradiene–Cycloheptatriene Equilibrium

Sir:

Although the existence of simple norcaradiene derivatives has recently been demonstrated,¹ the question of the relationship between cycloheptatrienes and norcaradienes remained to be answered.^{2,3} The presence of small equilibrium concentrations of norcaradienes has been invoked frequently to account for certain reactions of cycloheptatrienes, notably Diels–Alder additions, in which products derived from the norcaradiene structures usually are obtained.⁴ Recent low-temperature n.m.r. studies of cycloheptatriene⁵ and certain of its derivatives⁶ uncovered no evidence for the presence of the corresponding norcaradienes.

We now wish to present evidence showing that the adduct of cyanotrifluoromethylcarbene to benzene is, at room temperature, a rapidly equilibrating mixture of

(1) E. Ciganek, *J. Am. Chem. Soc.*, **87**, 652 (1965).

(2) For a recent review of the cycloheptatriene–norcaradiene problem, see S. J. Rhoads in "Molecular Rearrangements," P. De Mayo Ed., Part I, Interscience Publishers, Inc., New York, N. Y., 1963, pp. 700–703.

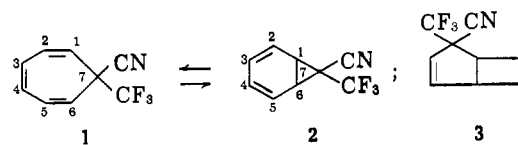
(3) In the special case of benzonorcaradiene, the inversion of the cyclopropane ring observed at elevated temperatures is believed to involve the corresponding *o*-quinonoid cycloheptatriene as an intermediate [E. Vogel, D. Wendsch, and W. R. Roth, *Angew. Chem.*, **76**, 432 (1964)].

(4) Other possible explanations are discussed by R. Huisgen and G. Juppe, *Chem. Ber.*, **94**, 2332 (1961), and in ref. 6.

(5) F. A. L. Anet, *J. Am. Chem. Soc.*, **86**, 458 (1964); F. R. Jensen and L. A. Smith, *ibid.*, **86**, 956 (1964).

(6) K. Conrow, M. E. H. Howden, and D. Davis, *J. Am. Chem. Soc.*, **85**, 1929 (1963).

7-cyano-7-trifluoromethylcycloheptatriene (1) and 7-cyano-7-trifluoromethylnorcaradiene (2). Thermolysis of cyanotrifluoromethyldiazomethane⁷ in benzene gave



as the main product (77% yield) a colorless liquid,⁸ b.p. 76° (7.5 mm.), $\lambda_{\text{max}}^{\text{cyclohexane}}$ 258 $\text{m}\mu$ (ϵ 3740) (unchanged between room temperature and -100°). The room temperature F^{19} n.m.r. spectrum in fluorotrichloromethane shows only one singlet at $+4125$ c.p.s. (relative to the solvent signal; 56.4 Mc.) with a width at half-height of 1.9 c.p.s.; the room temperature proton n.m.r. spectrum (same solvent) displays a complex multiplet at τ 3.2 to 3.8 (4 protons) and a doublet (separation 7 c.p.s.), split further, centered at τ 5.30 (2 protons). On lowering the temperature to *ca.* -85° , the singlet in the F^{19} n.m.r. spectrum broadens gradually; on further cooling, new signals of unequal intensities appear at $+4187$ and $+3760$ c.p.s. Similarly, the high-field doublet in the proton n.m.r. spectrum, on cooling, first broadens and then gives rise to two new signals, a doublet ($J = 7$ c.p.s.) centered at τ 4.60 and a fairly broad singlet (half-band width 12 c.p.s. at -112°), with no discernible fine structure, at τ 7.05. The areas of the τ 4.6 and 7.0 signals were in the ratio of *ca.* 80:20. The n.m.r. spectra thus show the presence of two species which are in rapid equilibrium at room temperature.⁹ The major component is undoubtedly the cycloheptatriene 1 (only olefinic protons in the H^1 n.m.r. spectrum).¹⁰ The low energy of activation for the equilibration excludes any structure but that of a valence tautomer for the minor component. The position of the τ 7.05 signal (assigned to protons 1 and 6 in structure 2) is that expected for a norcaradiene,¹ but it is also compatible with the other valence tautomer, 4-cyano-4-trifluoromethylbicyclo[3.2.0]hepta-2,6-diene (3). However, the known¹¹ high activation energy required for the conversion of the parent bicyclo[3.2.0]hepta-2,6-diene to cycloheptatriene and the absence of any bicyclo[3.2.0]heptane derivatives in the hydrogenation products of the mixture of 1 and 2 (see below) strongly indicate that the second species is actually the norcaradiene 2. The absence of a third signal in the low-temperature F^{19} n.m.r. spectrum shows that only one of the two possible isomers of 2 is present in detectable amounts.

Catalytic hydrogenation of the equilibrium mixture gave 7-cyano-7-trifluoromethylnorcarane (4; one isomer), 1-cyano-1-trifluoromethylcycloheptane (5), and α -cyclohexyl- β,β,β -trifluoropropionitrile (6) in different ratios depending on the catalyst used. With rhodium,

(7) S. Proskow, to be published.

(8) All new compounds gave satisfactory elemental and molecular weight analyses.

(9) J. A. Pople, W. O. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp. 218–225.

(10) The major component 1 itself may be a rapidly equilibrating mixture of the two nonplanar 7-cyano-7-trifluoromethylcycloheptatrienes, as indicated by the observed broadening of the 4187 c.p.s. signal in the F^{19} n.m.r. spectrum on cooling to below -112° ; the half-band width of the 3760 c.p.s. signal, assigned to 2 on the basis of its relative area, remained constant.

(11) W. G. Dauben and R. L. Cargill, *Tetrahedron*, **12**, 186 (1961).