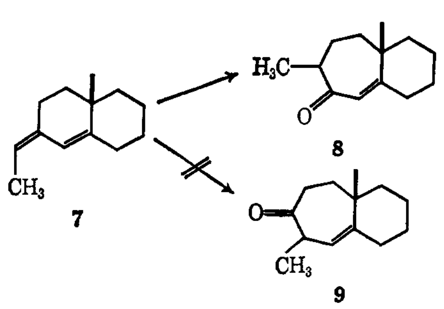
nmr (CDCl$_3$) τ 4.52 (m, 1 H), 9.01 (s, 3 H); mass spectrum (80 eV), *m/e* (relative intensity), 178 (M$^+$, 35), 163 (20), 150 (18), 136 (25), 135 (56), 122 (100), 121 (60)], in which vinyl migration had occurred, was formed in 35% yield.

We next treated the ethylidene compound **7** with cyanogen azide. We again expected attack on the more accessible, exocyclic double bond to yield a methylated cycloheptenone, and, indeed, we isolated (60%) a ring-expanded product. Spectral analysis showed, however, that we had obtained not the expected product **9**, but rather the isomeric enone **8** as a mixture of epimers at the C$_3$-methyl group [ir (neat) 1660, 1620 cm^{-1}; uv $\lambda_{\max}^{\text{EtOH}}$ 243 mμ (ϵ 7500); nmr (CDCl$_3$) τ 4.35 (s, 1 H), 8.79 and 8.81 (two singlets, 3 H total), 8.94 and 8.98 (two doublets, $J = J' = 7$ Hz, 3 H total); mass spectrum (80 eV), *m/e* (relative intensity) 192 (M$^+$, 28), 178 (6), 164 (9), 150 (16), 136 (60), 135 (47), 122 (50), 121 (34)].



8 is evidently formed by migration of the C$_3$-alkyl group in preference to the C$_1$-vinyl group. Since vinyl is usually considered a better migrating group than alkyl,[7] we are unable to explain the observed result. We however point out the synthetic utility of the result since no other method for performing this transformation exists.

Although the cyclohexanone → cycloheptanone transformation is not difficult to accomplish by known methods,[8] it was nevertheless of interest to examine the behavior of simple exocyclic monoolefins with cyanogen azide. Thus when methylenecyclohexane was treated with 1.3 equiv of CNN$_3$ in 1:1 CH$_3$CN-CH$_3$OH for 48 hr and the product hydrolyzed, cycloheptanone (2,4-DNP mp 147–148°, lit.[9] 148) was isolated in 80% yield. Similarly, when ethylidenecyclohexane was treated with CNN$_3$, 2-methylcycloheptanone (2,4-DNP mp 121–122°, lit.[10] 121–122) was obtained (80%).

Because of the relative simplicity[5] of this new ring-expansion method, we feel that it should be of considerable utility, and we are continuing to explore its possibilities.

Acknowledgment. We thank the Petroleum Research Fund and the Division of Natural Sciences, UCSC, for their support of this work.

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(7) H. O. House, E. J. Grubbs, and W. F. Gannon, *J. Am. Chem. Soc.*, **82**, 4099 (1960).

(8) See C. D. Gutsche and D. Redmore, "Carbocyclic Ring Expansion Reactions," Academic Press, New York, N. Y., 1968, for leading references.

(9) Th. J. de Boer and H. J. Backer, *Rec. Trav. Chim.*, **73**, 589 (1954).

(10) D. W. Adamson and J. Kenner, *J. Chem. Soc.*, 181 (1939).

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Received April 9, 1969

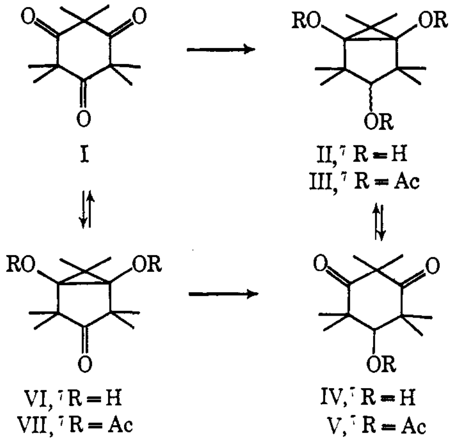
vic-Cyclopropanediols from Lithium in Ammonia Reductions of Cyclic β-Diketones

Sir:

Reductions of unsaturated carbonyl compounds by alkali metal in ammonia solutions generate reactive nucleophilic intermediates which are capable of intra- and intermolecular attack on electrophilic functions.[1–4] In fact, even relatively reactive compounds such as cyclopropanols[4] have been prepared by this kind of transformation. In this communication we report the formation of *vic*-dihydroxycyclopropane derivatives by reduction of suitably oriented 1,3-diketones.

Reduction of a dilute THF–ammonia solution of 2,2,4,4,6,6-hexamethylcyclohexane-1,3,5-trione (I)[5] with an excess of lithium gave a 65–95% recovery of a relatively insoluble white powder, melting with decomposition above 160°. Crystallization of this material from acetic acid or pyridine followed by sublimation did not improve the melting point or completely remove an impurity absorbing at 1710 cm^{-1} in the infrared, but achieved sufficient purification to permit a tentative identification of the major component as 2,2,4,4,6,6-hexamethyl-1,3,5-trihydroxybicyclo[3.1.0]hexane (II). Oxidation of crude II with aqueous ferric chloride,[6] chromic oxide–pyridine complex, or oxygen yielded 2,2,4,4,6,6-hexamethyl-5-hydroxycyclohexane-1,3-dione (IV) (mp 66–67°; $\nu_{\max}^{\text{CHCl}_3}$ 1690 and 1720 cm^{-1}; nmr: 3 H singlet at δ 1.27, 9 H singlet at 1.21, 6 H singlet at 1.19, 1 H doublet at 3.69 (J = 5 cps), 1 H doublet at 3.51 (J = 5 cps); in D$_2$O the δ 3.69 doublet becomes a singlet and the 3.51 doublet vanishes). Treatment of IV with acetyl chloride (50° in acetic acid solution) gave the monoacetate derivative V (mp 78–80°; $\nu_{\max}^{\text{KBr}}$ 1730, 1720, 1690 cm^{-1}; nmr: 6 H singlet δ 1.10, 9 H singlet at 1.23, 3 H singlet at 1.28, 3 H singlet at 2.04, 1 H singlet at 5.02).

Reduction of IV with lithium in THF–ammonia solution produced pure II, free from the carbonyl-con-



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(1) M. Smith in "Reduction," R. L. Augustine, Ed., Marcel Dekker, New York, N. Y., 1968.

(2) G. Stork and S. D. Darling, *J. Am. Chem. Soc.*, **86**, 1761 (1964).

(3) G. Stork, P. Rosen, N. Goldman, R. Coombs, and J. Tsuji, *ibid.*, **87**, 275 (1965).

(4) P. S. Venkataramani and W. Reusch, *Tetrahedron Letters*, 5283 (1968).

(5) J. L. E. Erickson and G. Kitchens, *J. Org. Chem.*, **27**, 460 (1962).

(6) S. E. Schaafsma, H. Steinberg, and Th. J. DeBoer, *Rec. Trav. Chim.*, **85**, 73 (1966).

(7) The structures of these compounds are supported by combustion analyses (Spang Microanalytical Laboratory) which are in excellent agreement with the calculated compositions (*i.e.*, within 0.25% for C and 0.1% for H).

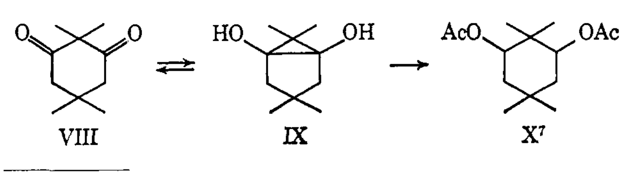
taining impurity mentioned earlier. The nmr spectrum of II in DMSO-d_6 exhibited singlets at δ 0.90 (6 H), 0.94 (6 H), 1.00 (3 H), 1.18 (3 H), and 4.48 (2 H) and doublets ($J \sim 5$ cps) at δ 3.38 (1 H) and 4.33 (1 H). The signals at δ 4.33 and 4.48 vanish on exchange with D_2O, while that at δ 3.38 becomes a singlet. A triacetate derivative, III, mp 159–160.5°, was prepared by treatment of II with acetyl chloride. The infrared and nmr spectra of III are in complete accord with the structure assigned here.

Reduction of I with 2 equiv of lithium gave 2,2,4,4,6,6-hexamethyl-1,5-dihydroxybicyclo[3.1.0]hexan-3-one (VI) in 55% yield (70% based on recovered I). This crystalline substance melted with decomposition above 150° and exhibited infrared absorption at 1730 cm^{-1} and nmr absorption (in pyridine) characterized by singlets at δ 1.15 (3 H), 1.32 (6 H), 1.50 (6 H), and 1.56 (3 H). The corresponding diacetate derivative VII, prepared in 80% yield by treatment of VI with acetyl chloride, was crystallized from methanol (mp 128–130°) and displayed infrared absorption at 1750 and 1735 cm^{-1} and nmr singlets at δ 1.17 (3 H), 1.27 (9 H), 1.43 (6 H), and 2.14 (6 H).

We find that solutions of VI are readily oxidized by the oxygen in air. An ethyl acetate solution of VI was stable under a blanket of nitrogen for a 24-hr period at 25°. When air was admitted under the same conditions, only the triketone I was recovered. The crystalline state of VI is apparently unaffected by exposure to air for longer periods longer than a month.

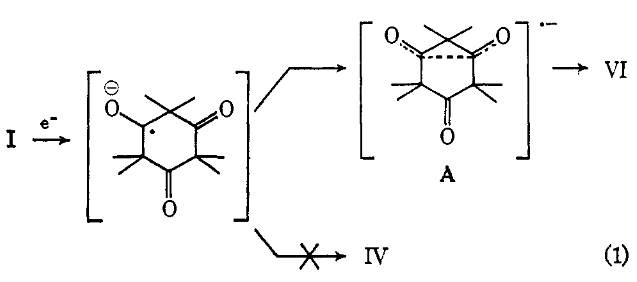
Since the three-membered ring of cyclopropanols is known to be cleaved by the action of acids or bases,[8] a corresponding reaction of the cyclopropanediols reported here would help to confirm our structural assignments. Treatment of VI (under nitrogen) with refluxing methanolic potassium hydroxide for 8 hr gave IV in 62% yield. No reaction of VI was apparent after 24 hr in methanolic hydrogen chloride, but more vigorous acid treatment (*e.g.*, concentrated H_2SO_4) gave rearrangement products that are currently being studied. A similar treatment of II with refluxing methanolic potassium hydroxide in the absence of oxygen gave a complex mixture of diastereoisomeric keto diols apparently contaminated with IV.

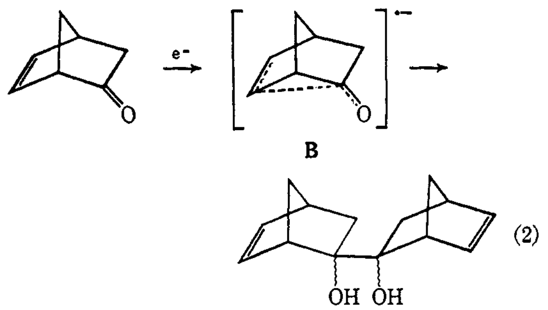
When 2,2,5,5-tetramethyl-1,3-cyclohexanedione (VIII) was reduced by lithium in ammonia solutions, an unstable colorless solid was obtained. This material was essentially transparent in the carbonyl stretching region of the infrared, but reverted to diketone VIII on standing overnight at room temperature. Acting on the assumption that this reduction product was the cyclopropanediol IX, we prepared a diacetate derivative (X), mp 87–89°, in the usual manner. The structure of X was confirmed by a strong carbonyl absorption at 1745 cm^{-1} in the infrared and an nmr spectrum (in $CDCl_3$) displaying singlets at δ 0.92 (3 H), 0.96 (3 H), 1.16 (6 H), and 2.10 (6 H) and an AB quartet (4 H) at δ 1.65 and 2.00 ($J \sim 14$ cps).



Some of the cyclopropanediol derivatives reported here have been examined by mass spectrometry, but the spectra have not been very informative. Since the molecular ions could not be detected and since complex fragmentation patterns were observed, we decided to confirm the molecular weights of III and VII by vapor pressure osmometry (the rapid oxidation of dilute solutions of VI prevented us from including this compound as well). The observed molecular weights agreed well with the expected values: III, 347 ± 10 (calcd 340); VII, 297 ± 6 (calcd 296).

The timing of the three-membered ring formation in these reactions is defined in the following manner. The ground-state conformation of I is a twist boat,[9] and the electronic spectrum of this compound shows no evidence of interaction between the carbonyl functions ($\lambda_{\max}^{C_6H_{12}}$ 300 mμ (ϵ 80)). However, since reduction of I with a limited amount of lithium gave VI as the only reduction product, the radical anion A is apparently formed more rapidly than conventional reduction to IV (eq 1). A similar radical anion (B) was proposed in the Li-NH_3 reduction of norbornenone to diastereoisomeric pinacols (eq 2).[10]





Cyclopropanediols have been proposed as intermediates in the Clemmensen reduction of β diketones.[11,12]

Acknowledgment. We thank the National Institutes of Health for their support of this work (AM 10849).

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[8] C. H. DePuy, *Accounts Chem. Res.*, 1, 33 (1968).

[9] J. Dale, *J. Chem. Soc.*, 1028 (1965).

[10] B. Ortiz de Montellano, B. Loving, T. Shields, and P. D. Gardner, *J. Am. Chem. Soc.*, 89, 3365 (1967).

[11] N. Cusack and B. R. Davis, *J. Org. Chem.*, 30, 2062 (1965).

[12] E. Kariv and E. Wenkert, *Israel J. Chem.*, 5, 68 (1967).

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Received April 9, 1969

Benzocyclobutadiene Radical Anion

Sir:

We wish to report the preparation of a new radical anion which from all indications is the benzocyclobutadiene radical anion. Neutral benzocyclobutadiene