Chart I. Energy Level Diagram for 3



could form a dianion relatively readily since a very low energy MO is available. Further, the neutral substrate possesses a different geometry from that of the anionic species. In accord with these speculations, excess 1 does not broaden the hyperfine lines of 3 appreciably. These facts and arguments constitute evidence for the dianion of 3.

The 1,3-dienic MO of 1, which must initially accept the reducing electron, has an HMO energy of $\alpha - 0.62\beta$. As Chart I indicates, the odd electron can occupy a nonbonding MO in 3, thus making the electrocyclic reaction of the anion radical much more facile than that of the neutral molecule. In fact, since the presence of 2 was not observed, it would appear that the rearrangement is exothermic.^{8,9}

The rotatory properties of the reaction $2 \rightarrow 3$ have not yet been ascertained, but are under investigation.

Acknowledgment. The Welch, Sloan, and National Science Foundations supported this work. The National Science Foundation provided funds for the esr spectrometer.

(8) Professor Glen Russell and his group at Iowa State have found an interesting example of an anion radical valence isomerization where the ring-*closed* anion radical is favored over the opened form (personal communication).⁹

(9) G. A. Russell and P. R. Whittle, J. Am. Chem. Soc., 91, 2813 (1969).

(10) Alfred P. Sloan Foundation Fellow, 1966-1968.

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A New Ring-Enlargement Reaction

Sir:

In connection with our efforts in sesquiterpene synthesis, we have been interested in ring-enlargement reactions. Our primary goal has been the transformation of cyclohexenones into cycloheptenones, a reaction which is difficult to perform by literature methods.¹ We now wish to present a preliminary report of a new method we have developed for accomplishing this goal.

It is known that when cyclopentene is treated with cyanogen azide and the product hydrolyzed, cyclopentanone is produced.² The transformation presumably comes about² via 1,3 dipolar addition to the olefin, followed by rearrangement of the cyanotriazoline with hydride migration and loss of nitrogen.

(2) F. D. Marsh and M. E. Hermes, J. Am. Chem. Soc., 86, 4506 (1964).

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We felt that, if a diene such as 2³ were treated with 1 equiv of cyanogen azide, dipolar addition should occur at the more accessible exocyclic double bond in the orientation indicated.⁴ The cyanotriazoline intermediate should then rearrange with migration of the vinyl moiety, and, after hydrolysis, the desired cycloheptenone, 5, would result.



When the reaction was carried out by allowing the diene 2 in acetonitrile to be in contact with 1 equiv of cyanogen azide⁵ for 48 hr in the dark, followed by hydrolysis of the crude product with aqueous methanolic HCl. the sole product isolated (50%) was the starting enone, Presumably, the desired intermediate triazoline did 1. in fact form, but decomposed with cleavage of the allylic bond and resultant loss of diazomethane to give 3-an unexpected but not illogical occurrence. After much experimentation, conditions were found where ring enlargement did occur. Thus when diene 2 was treated with cyanogen axide in the presence of a proton source in a highly ionic medium (2.5 M LiClO₄ in 1:1 CH₃OH-CH₃CN)⁶ for 48 hr at room temperature followed by acid hydrolysis, two ring-expanded products were formed.



Enone 6 [ir (neat) 1650, 1620 cm⁻¹; uv λ_{max}^{EtOH} 240 m μ (ϵ 8000); nmr (CDCl₃) τ 4.26 (s, 1 H), 8.88 (s, 3 H); mass spectrum (80 eV), m/e (relative intensity) 178 (M⁺, 100), 163 (44), 150 (49), 136 (32), 135 (62), 122 (64), 121 (60)], in which C₃-alkyl migration had taken place, was formed in 15% yield. Enone 5 [ir (neat) 1705 cm⁻¹;

(3) Prepared in high yield by Wittig reaction on the corresponding enone according to the general procedure of R. Greenwald, M. Chay-kovsky, and E. J. Corey, J. Org. Chem., 28, 1128 (1963).

(4) For a discussion of orientation in dipolar addition reactions, see R. Huisgen, Angew. Chem. Intern. Ed. Engl., 2, 633 (1963).

(5) Prepared by stirring a solution of cyanogen bromide in dry actonitrile with powdered NaNs for 2 hr. The cyanogen azide containing supernatant is then removed from precipitated NaBr via syringe. A word of caution is in order: although we have conducted well over 100 experiments with cyanogen azide solutions without experiencing the slightest difficulty, the Du Pont workers² warn that "the *pure* azide detonates with great violence when subjected to mild mechanical or thermal shock."

(6) Detailed reasoning for the choice of these conditions will be presented in the full paper.

⁽¹⁾ For a recent review, see C. D. Gutsche and D. Redmore, "Carbocyclic Ring Expansion Reactions," Academic Press, New York, N. Y., 1968. For specific examples, see (a) E. J. Corey, M. Ohno, R. B. Mitra, and P. A. Vatakencherry, J. Am. Chem Soc., **86**, 478 (1964); (b) W. S. Johnson, M. Neeman, S. P. Birkeland, and N. A. Fedoruk, *ibid.*, **84**, 989 (1962); (c) E. Muller, H. Kessler, and B. Zeeh, Fortschr. Chem. Forsch., 7, 128 (1966); (d) G. Stork M. Nussim, and B. August, Tetrahedron Suppl., **8**, Part 1, 105 (1966).

nmr (CDCl₃) 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%vield.

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 ringexpanded 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 C₃-methyl group [ir (neat) 1660, 1620 cm⁻¹; uv $\lambda_{\text{max}}^{\text{EtOH}}$ 243 mµ (ϵ 7500); nmr (CDCl₃) 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 C₁-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 \rightarrow 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 CNN₃ in 1:1 CH₃CN-CH₃OH 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 CNN₃, 2-methylcycloheptanone (2,4-DNP mp 121-122°, lit. 10 121–122) was obtained (80%).

Because of the relative simplicity⁵ 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.

(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 Expan-sion 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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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 cyclopropanols⁴ 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-hexamethylcvclohexane-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 2,2,4,4,6,6hexamethyl-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°; $\nu_{max}^{CHCl_s}$ 1690 and 1720 cm⁻¹; nmr: $\hat{3}$ 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_2O 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 monoace-tate derivative V (mp 78-80°; $\nu_{\text{max}}^{\text{KBr}}$ 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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(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).