that only 0.2% of the product was ethane after 5 hr. This suggests that the complexing of acetylene is so strong that it is bound exclusively and that as soon as reduction to ethylene occurs (a relatively slow process), this ethylene molecule is immediately replaced by acetylene. These reductions are accompanied by the evolution of much hydrogen gas produced by the decomposition of $NaBH_4$.[12] This decomposition is *not* to be considered as a model for the ATP-dependent hydrogen evolution catalyzed by nitrogenase,[8] as previously suggested.[9]

Experiments involving molecular nitrogen have been carried out at ambient temperature and pressure in systems similar to those described above. Small yields of ammonia of the order of 5% based on catalyst concentration have been obtained in both static and flow systems over 5-hr periods, and we are presently involved in attempts to optimize the catalytic activity of these systems.

The reactions of other types of iron complexes were also studied. For example, the ability of the compounds[13] dihydridotris(ethyldiphenylphosphine)-iron(II) (FeH_2L_3) and its dinitrogen adduct ($FeH_2(N_2)L_3$) to take part in reduction reactions similar to those described above was examined. Both of these compounds, without added reductant in benzene or ethanol, reduced *ca.* 0.4 mol of acetylene/mol of complex in 20 hr at 25° producing ethylene (0.35 mol), ethane (0.04 mol), and some unidentified polymeric material. With azide ion in ethanol FeH_2L_3, in the presence of sodium borohydride, produced *ca.* 2 mol of ammonia/mol of iron complex in 5 hr at 25°. Ammonia was also formed in 1 *M* HCl-ethanol (1:1) solutions containing iron(II) chloride, ethyldiphenylphosphine, and azide only, *i.e.*, without borohydride, the yield leveling off after 3-4 days at 25° at an ammonia to phosphine ratio of one.

At this time, it seems appropriate to include some words of caution about the indiscriminate application of the results from model chemistry to enzyme systems. In agreement with recent work,[9] we have also found that the unidentified complexes produced by iron(II) and simple thiol compounds have very little activity in these reductions. However, the environment at the active site of the enzyme has not been shown to consist exclusively of thiol ligands. Thus, taking into account the recent report[9] on Mo chemistry and the work on Fe detailed above, conclusions excluding either Mo or Fe from a catalytic role at the active site of the enzyme cannot be drawn at this time. It must be pointed out that model experiments carried out under one particular set of conditions can easily lead to erroneous conclusions when applied to the enzyme, even though the model chemistry itself is valid. Finally, the very sensitive acetylene reduction assay for nitrogenase activity is well known and extensively used, but its use as the *sole* criterion for N_2-reducing ability is invalid. The crucial test of a nitrogenase model is its ability to catalyze the reduction of molecular nitrogen at ambient temperature and pressure. The ability to satisfy the requirements with respect to the reduction of the other substrates of nitrogenase may be used, in a supportive role, as a measure of the closeness of the chemistry of the model system to that of the enzyme and indeed may help to elucidate the mechanism(s) of the enzymatic reactions.

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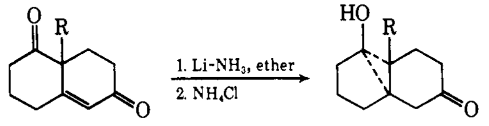
Transformations of Cyclopropanol Intermediates. I. Synthesis of Angularly Substituted Perhydroindan Systems *via* a Stereospecific Cyclopropanol Rearrangement

Sir:

We recently described a novel reductive cyclization of angularly substituted bicyclo[4.4.0]dec-1-ene-3,7-diones (I and II) to 1-substituted 2-hydroxytricyclo-[4.4.0.0^{2,6}]decan-8-ones (III and IV, respectively).[1] Subsequent study has demonstrated that these cyclopropanols can be transformed into several isomeric bicyclic ring systems, and in this and the following communication the synthetic versatility of these remarkable intermediates will be illustrated using the cyclopropanol III derived from the Wieland-Miescher ketone I.[2,3]



I, R = CH_3
II, R = $CH_2CH{=}CH_2$

III, R = CH_3
IV, R = $CH_2CH{=}CH_2$

Reduction of I by a solution of lithium in ammonia and ether yielded up to 80% of the cyclopropanol III:[4] mp 98-100°; ν_{max} 3590 and 1705 cm^{-1}; nmr signals at δ 0.9 (3 H, singlet), 1.4-2.5 (12 H, m), and 4.55 (1 H, singlet, rapidly exchanged with D_2O); molecular ion at *m/e* 180 in the mass spectrum. Although III is unstable, it can be stored for several days in a refrigerator and has been converted to a stable methyl ether semicarbazone derivative, mp 212-213°. Treatment of III with aqueous ferric chloride regenerated I in 70% yield.

We were surprised to find that reaction of III with a solution of *p*-toluenesulfonic acid in refluxing benzene (1 hr) or a methanolic potassium hydroxide solution at room temperature (3 hr) did not produce either of the bicyclic isomers (V or VI) expected from simple ring cleavage of the cyclopropanol moiety.[5] The major product (up to 60% from both of these reactions) was a colorless solid, mp 166-167°, which was identified

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[12] "Sodium Borohydride; Handling, Properties and Uses," Metal Chemical Division, Ventron Corp., Beverly, Mass., p 25, and references therein.

[13] A. Sacco and M. Aresta, *Chem. Commun.*, 1223 (1968).

[1] P. S. Venkataramani and W. Reusch, *Tetrahedron Lett.*, 5283 (1968).

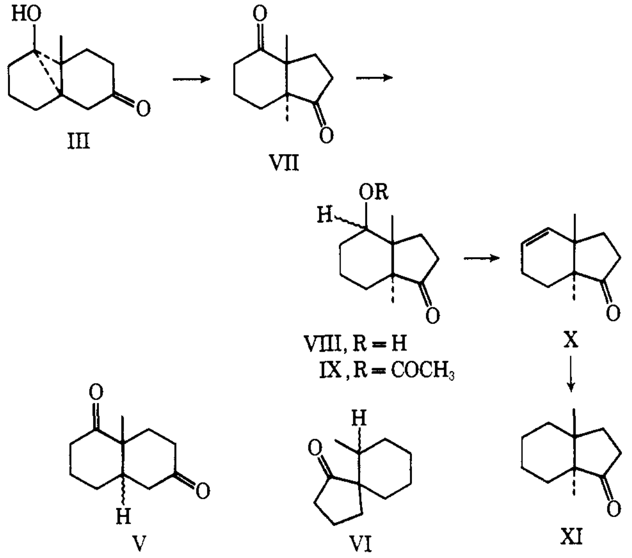
[2] S. Ramachandran and M. S. Newman, *Org. Syn.*, **41**, 38 (1961).

[3] Part of this work was reported at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969.

[4] With the exception of X, all new compounds described in this communication have elemental compositions confirmed by combustion analysis (Spang Microanalytical Laboratory, Ann Arbor, Mich.) to within 0.3% in carbon, 0.1% in hydrogen, and 0.15% in nitrogen.

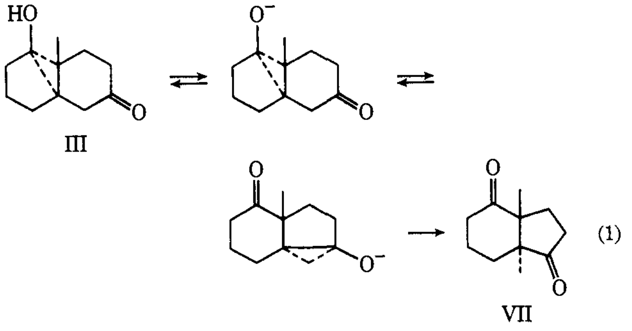
[5] C. H. DePuy, *Accounts Chem. Res.*, **1**, 33 (1968).

as *trans*-1,6-dimethylbicyclo[4.3.0]nona-2,7-dione (VII) on the strength of spectroscopic measurements and chemical transformations. Infrared absorptions at 1735 and 1705 cm^{-1}, nmr signals at δ 0.9 (3 H, singlet), 1.2 (3 H, singlet), and 1.5–2.4 (10 H), and a parent ion at *m/e* 180 in the mass spectrum all support the assigned structure VII, which is further corroborated by the exchange of four methylene protons in hot alkaline deuterium oxide.



Although both cis and trans ring fusions are possible in this perhydroindan system, compound VII appears to be stereochemically homogeneous (tlc, vpc, and nmr criteria) and is assigned a trans configuration, primarily as a consequence of its conversion to XI.[6]

Reduction of VII with sodium borohydride gave the ketol VIII, mp 110–112°, in 85% yield. The acetate IX, mp 35–38°, derived from VIII in quantitative yield, gave on pyrolysis at 480–515° a pale yellow unpleasant smelling liquid. This, on glc analysis, proved to be mainly the olefin X, characterized by infrared absorptions at 3000, 1740, and 1605 cm^{-1}, nmr absorptions at δ 0.85 (3 H, singlet), 0.9 (3 H, singlet), 1.4–3.1 (8 H), and 5.2–5.85 (2 H), and a parent ion at *m/e* 164 in the mass spectrum. Catalytic reduction of X using a palladium catalyst consumed 1.05 equiv of hydrogen and yielded the saturated perhydroindanone XI, mp 110–111°, which formed a 2,4-DNP derivative, mp 137–138°.[6]



The formation of VII can be rationalized by the cyclopropoxide isomerization shown in eq 1 (presumably a similar acid-catalyzed isomerization can also take place). In agreement with this mechanism, we find that the reaction of III with sodium methoxide in methanol-d_1 containing a little heavy water gives VII, having the following deuterium distribution (mass spectrum): d_4, *ca.* 10%; d_5, 25.0%; d_6, 38.0%; d_7, 27.0% (clearly the rate of α-proton exchange is equal to or greater than the rate of cyclopropanol ring opening). The curious inversion of configuration at C-6 (numbering system used previously for III) requires further study, inasmuch as molecular models indicate that bond shifting with retention of configuration should also be possible.

The rearrangement described here should be general for angularly substituted enediones related to I (II has also been transformed to a corresponding perhydroindandione *via* cyclopropanol IV), and we believe that this synthetic method will provide an attractive approach to sesquiterpenes such as pinquisone.[7]

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[6] We are indebted to Professor E. Wenkert for information regarding XI and its cis isomer and for samples of the corresponding 2,4-DNP derivatives: E. Wenkert, J. Zylber, E. Kariv, and K. Kavkova, unpublished work; E. Kariv, Ph.D. Dissertation, Weizmann Institute of Science, Rehovoth, Israel, 1967; and J. Yoder, Ph.D. Dissertation, Indiana University, Indianapolis, Ind., 1969, have shown that Clemmensen reduction of I leads to compounds V, VI, and VII as well as related cyclopropanol methyl ethers. For a discussion of such reductions see J. G. Buchanan and P. D. Woodgate, *Quart. Rev., Chem. Soc.*, 23, 522 (1969).

[7] V. Benesova, Z. Samek, V. Herout, and F. Sorm, *Collect. Czech. Chem. Commun.*, 34, 582 (1969).

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Transformations of Cyclopropanol Intermediates. II. Selective Ring Opening Reactions of 1-Methyl-2-hydroxytricyclo[4.4.0.0^{2,6}]decan-8-one

Sir:

The unexpected course of acid- and base-catalyzed isomerizations of cyclopropanol II[1] has provided a simple two-step conversion of the Wieland–Miescher ketone[2] I to the perhydroindandione III. We now report that II can also be selectively transformed into the isomeric spirodiketone IV or the dienone V, making it a remarkably versatile intermediate.

Transformation of II into 10-methylspiro[4.5]deca-1,7-dione (IV) was accomplished in greater than 75% yield by adding methanol dropwise to a *rapidly stirred* suspension of the cyclopropanol sodium salt in benzene (prepared by the reaction of II with sodium hydride). The success of this novel preparation apparently depends on the heterogeneity of the reaction mixture,[3] since similar treatment of a homogeneous benzene–DMF solution of the sodium salt gave III. The spirodiketone IV, mp 60–62°, exhibited infrared absorption at 1735 and 1705 cm^{-1}, nmr absorption in the form of a three-proton doublet at δ 0.85 (J = 6.5 Hz) and a

[1] P. S. Venkataramani, J. E. Karoglan, and W. Reusch, *J. Amer. Chem. Soc.*, **93**, 269 (1971).

[2] S. Ramachandran and M. S. Newman, *Org. Syn.*, **41**, 38 (1961).

[3] See, for example: N. Kornblum and A. Lurie, *J. Amer. Chem. Soc.*, **81**, 2705 (1959).