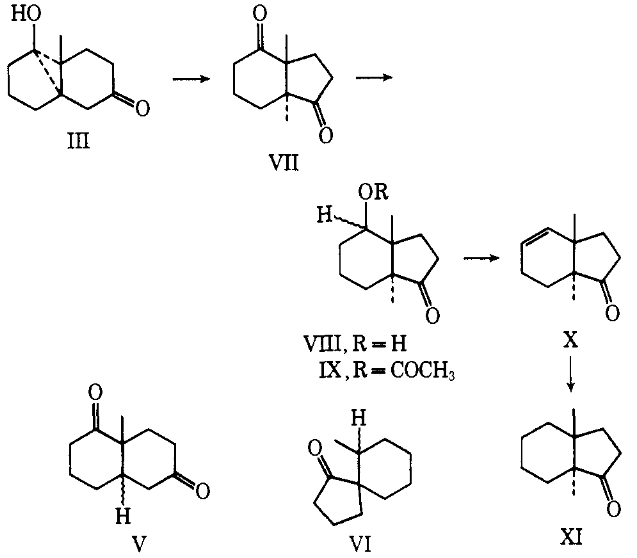
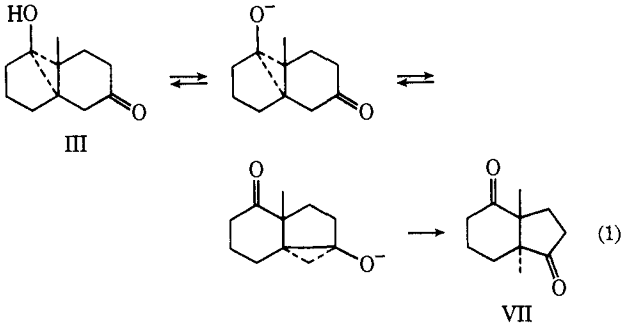
as *trans*-1,6-dimethylbicyclo[4.3.0]nona-2,7-dione (VII) on the strength of spectroscopic measurements and chemical transformations. Infrared absorptions at 1735 and 1705 cm^{-1}, nmr signals at δ 0.9 (3 H, singlet), 1.2 (3 H, singlet), and 1.5–2.4 (10 H), and a parent ion at *m/e* 180 in the mass spectrum 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

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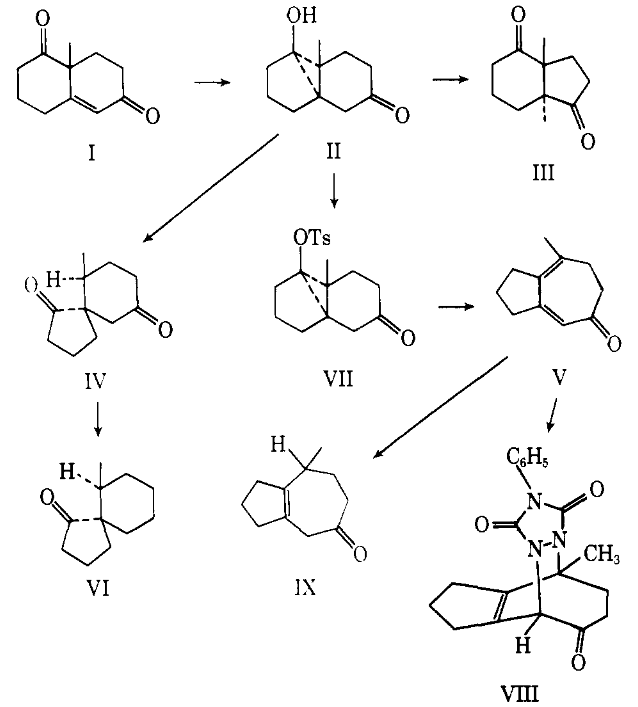
[1] P. S. Venkataramani, J. E. Karoglan, and W. Reusch, *J. Amer. Chem. Soc.*, **93**, 269 (1971).

[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).



broad 13-proton multiplet from δ 2.2 to 2.7, and a strong parent ion at *m/e* 180 in the mass spectrum.

Confirmation of structure IV and elucidation of its stereochemistry was achieved by reduction of the spirodiketone (*via* an ethylenethioketal derivative) to VI, which proved to be identical (infrared, nmr, and mass spectra) with the 6-methylspiro[4.5]decan-1-one stereoisomer obtained by catalytic reduction of the Diels–Alder adduct from *trans*-2-ethylidenecyclopentanone[4] and 1,3-butadiene. Thus, in the conversion of II to IV, stereospecific protonation with retention of configuration has occurred at C-1 (nomenclature for II).

The conversion of II to 6-methylbicyclo[5.3.0]deca-1,6-dien-3-one (V) requires two steps. Reaction of II with *p*-toluenesulfonyl chloride in pyridine solution gave the unstable tosylate VII, mp 73.5–74.5°, in greater than 75% yield. This intermediate was characterized by infrared absorption at 1712, 1590, 1365, 1188, and 1175 cm^{-1}, and nmr absorption at δ 1.15 (3 H, singlet), 1.5–2.4 (12 H, multiplet), 2.43 (3 H, singlet), 7.25, and 7.73 (4 H, AB quartet, $J = 8$ Hz). Acetolysis of VII produced an unstable liquid, the major component of which was V; the yield of crude dienone exceeded 85%. The ultraviolet absorption spectrum of V (λ_{max} 316 (ϵ 6170) and 242 nm (ϵ 2970)) is similar to that of eucarvone (λ_{max} 303 (ϵ 6800), with a shoulder at *ca.* 230 nm), and this together with carbonyl absorptions at 1710, 1650 (very strong), and 1510 cm^{-1} in the infrared spectrum, characteristic nmr absorptions for a vinyl hydrogen (δ 5.90) and vinyl methyl (δ 1.95), and a strong parent ion at *m/e* 162 in the mass spectrum establishes the proposed structure V. Reduction of dienone V by a solution of lithium in ammonia gave in over 80% yield a nonconjugated enone believed to be IX[5] on the strength of infrared carbonyl absorption at 1710 cm^{-1}, an nmr methyl doublet at δ 1.05 ($J = 6$ Hz), and a parent ion at *m/e* 164 in the mass spectrum.

Because V proved to be rather unstable, a standard microanalysis was not attempted;[6] instead, the dienone was converted by reaction with 4-phenyl-1,2,4-triazolin-3,5-dione to a crystalline adduct VIII, mp 167.5–169°, in 57% yield. The structure assigned to this adduct, VIII, agrees with its nmr spectrum, which shows clearly defined signals for the bridgehead methyl group (δ 1.93), the bridgehead proton (δ 5.16), and the phenyl group (δ 7.44); the remaining protons give rise to a complex absorption in the δ 2.00–3.12 region. Furthermore, infrared absorptions at 1700 (very strong) and 1760 cm^{-1} confirm the presence of ketone and imide carbonyl functions.

We anticipate that cyclopropanol intermediates related to II will provide advantageous new routes for the synthesis of sesquiterpenes of the vetivane and guaiane classes.

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[6] With the exception of V and IX, 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, 0.15% in nitrogen, and 0.02% in sulfur.

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Deaminations with Nitrogen Oxides. A New Synthesis of Alkyl Nitrates

Sir:

We reported briefly on the deamination of trimethylsilylamines with dinitrogen tetroxide.[1] Also, we postulated that the trimethylsilyl group may be necessary for the success of the reaction because previous attempts to deaminate amines with nitrogen oxides were unsuccessful;[2] however, deaminations with NOCl are known to be relatively efficient.[2a,3]

Deaminations (replacement of a C–N bond by a C–heteroatom bond) of primary carbinamines may be accomplished *via* thermolysis of *N*-nitrosourethanes, *N*-nitrosoamides, nitroamides, and nitrososulfonamides,[3] solvolysis of diazotate salts,[4] decomposition of triazenes,[5] and displacement of sulfonimides.[6] Nitrous acid deaminations and their nonaqueous counterparts (amyl nitrite nitrosation)[3] have been investigated extensively but the yields of substitution are, in most cases, not competitive with the above-mentioned methods.

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[6] P. J. De Christopher, J. P. Adamek, G. D. Lyon, J. J. Galante, H. E. Haffner, R. J. Boggio, and R. J. Baumgarten, *J. Amer. Chem. Soc.*, **91**, 2384 (1969).