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THE ACID CATALYZED TRANSFORMATION OF METHYL CYCLODODECADIENE CARBOXYLATE TO THE HEXAHYDROBENZ[e]INDENE SYSTEM

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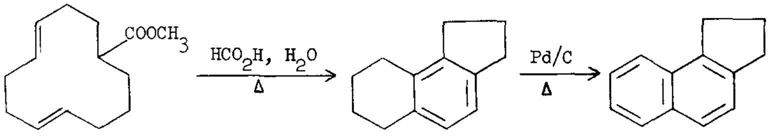
Research augmented by the sudden availability of the 1,5,9-cyclododecatrienes by trimerization of butadiene (1) has revealed many fascinating aspects of the chemistry of twelve-membered ring olefins (2-4). We wish to report here a most remarkable acid-catalyzed transformation of methyl 4,8-*trans*,*trans*-cyclododecadiene-1-carboxylate (I) to 2,3,6,7,8,9-hexahydro-1H-benz[e]indene (II). The ease of preparation of the starting ester and the inaccessibility of the hexahydrobenz[e]indene by other means accords this reaction synthetic utility.



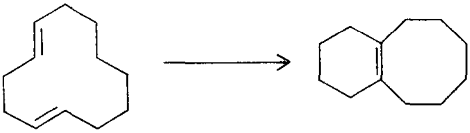
I II III

Treatment of 50.0 g. of the ester I [b.p. 105° (0.9 mm.); infrared: λ^{film} 5.78 μ (ester), 10.35 μ (*trans*-olefin); n.m.r.: multiplet centered at τ 4.9 (4 olefinic protons), τ 7.50-8.20 (8 allyl protons, 1 proton *α*- to ester), τ 8.20-8.90 (6 methylene protons)], prepared from

1,5,9-*trans*,*trans*,*trans*-cyclododecatriene by monohydrobromination, Grignard formation and carboxylation (5), with 610.0 g. of 90% formic acid at 100° and rapid stirring for 72 hr. afforded the hexahydrobenzindene II (6) in 31% yield. Although a mixture of inseparable formate esters (18%) and polymeric material (49%) was formed, only trace quantities of other aromatic hydrocarbons were detected in the reaction mixture. Other carboxylic acids of $pK_a < 4$, e.g. 90% chloroacetic, 100% trifluoroacetic, 50% trifluoroacetic in acetic, effected the conversion of I → II in 9-18% yields.

The structure II was established from the infrared spectrum which showed λ^{film} 6.28 and 6.75 μ (aromatic); 12.05 and 12.5 μ (1,2,3,4-tetrasubstitution); the n.m.r. spectrum which showed the aromatic protons as an AB quartet with signals centered at τ 3.12 (doublet, J = 9.0 c.p.s.) and τ 3.30 (doublet, J = 9.0 c.p.s.), the benzyl protons in the region of τ 7.00-7.65 and the methylene protons in the region of τ 7.70-8.40 in the ratio 2.1:8.1:5.9; the ultraviolet spectrum which showed λ_{max} 269 mμ (ε 556), 273 mμ (ε 468), 278 mμ (ε 556); and the mass spectrum which showed a parent ion and mass peak of m/e 172 and principal fragments at m/e 28 and 144. The structure III was further confirmed by dehydrogenation (10% Pd-C, 225-235°, 24 hr.) to the known 2,3-dihydrobenz[e]indene (III, 68%), the physical properties and spectral data of which were identical with an authentic sample. A mixture melting point of the picrate derivative of III, m.p. 108-108.5°, and an authentic specimen of III picrate was undepressed.

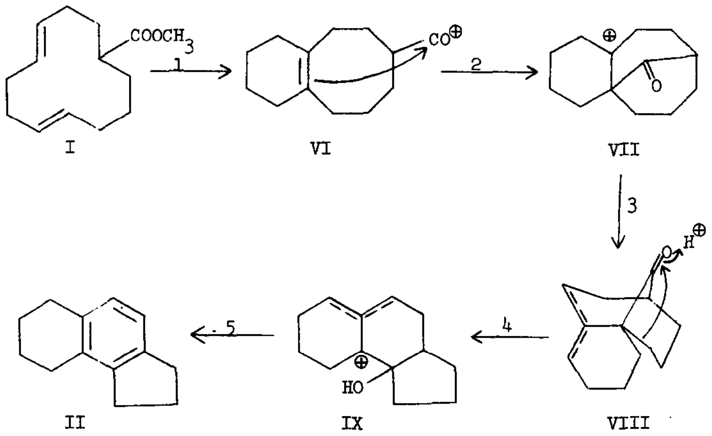
When 1,5-*trans*,*trans*-cyclododecadiene (IV) (7) [b.p. 83° (3.8 mm.), n_D^{25} 1.4940, infrared: λ 10.3 μ (*trans* double bond), iodine value 311.5] was treated with 90% formic acid for 24 hr. at 100°, $\Delta^{1,8}$-bicyclo[6.4.0]-dodecene (V) (8) [b.p. 91° (4.2 mm.), yellow color with tetranitromethane, n.m.r.: τ 7.5-8.2 (broad multiplet, 8 allyl protons); τ 8.3-8.5 (broad multiplet, 12 methylene protons)] was isolated in 48% yield. In view of this latter observation it is tempting to treat the conversion of



IV

V, 48%

I → II as proceeding through the bicyclic olefin VI as outlined below. Interaction of the acylonium ion and the double bond in VI (step 2), olefin formation (step 3), rearrangement of the bicyclic ketone VIII to the highly stabilized tertiary allyl carbonium ion IX (step 4), and dehydration (step 5) complete the process. Cyclizations involving interactions of an incipient acylonium ion and a double bond (9) (step 2) and Wagner-Meerwein rearrangements entailing α,β-sigma bond migration of ketones (10) (step 4) are classical organic processes. That bicyclo[3.3.1]nonan-2-ol derivatives are the principal products from the solvolysis of 4-cyclooctenyl methyl toluene sulfonate (11) and hydrindyl derivatives are the principal products from the solvolysis of bicyclo[3.3.1]nonyl-9-tosylate (12) lends further plausibility to the proposed reaction sequence. Investigation of the mechanism of this reaction is in progress and will be reported later.



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3. E. T. Niles and H. R. Snyder, J. Org. Chem., 26, 330 (1961).

4. D. L. Crain, R. F. Kleinschmidt and H. A. Hartzfeld, Abstracts, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964, p. 86S.

5. Preparation of the starting esters will be described in detail in the complete paper. Satisfactory combustion analyses and molecular weight determinations (mass spectroscopy) have been obtained for each new compound described here.

6. The hexahydrobenzindene II was isolated by petroleum ether extraction and elution with the same solvent from activity I alumina as a colorless liquid, b.p. 65° (0.6 mm.), which was purified for analysis

by preparative gas chromatography; 4,5-dinitro derivative, yellow prisms from ethanol, m.p. 137-138.8°.

7. Prepared by reduction of 1-bromo-4,8-*trans*,*trans*-cyclododecadiene with two molar equivalents of sodium in liquid ammonia. Detailed description of the preparation and structure determination of this diene will be described in the complete paper.
8. Identified by ozonolysis to the known cyclododeca-1,6-dione, m.p. 93.4-93.8°; diphenylhydrazone, m.p. 210-211°, according to the method of Niles and Snyder (3). We are indebted to Prof. Snyder for an authentic specimen of the dione for comparison purposes.
9. The conversion of geranic acid to piperitenone is illustrative, C. Balant, C. A. Vodoz, H. Kappeler and H. Schinz, *Helv. Chim. Acta*, **34**, 722 (1951).
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