S. W. W. wishes to thank the Research Committee at the University of Missouri at St. Louis for their support.

[12] Predoctoral Fellow of the National Institutes of Health.

S. W. Weidman
Department of Chemistry, University of Missouri at St. Louis
St. Louis, Missouri

D. F. Mayers,[12] O. R. Zaborsky,[12] E. T. Kaiser
Department of Chemistry, University of Chicago
Chicago, Illinois

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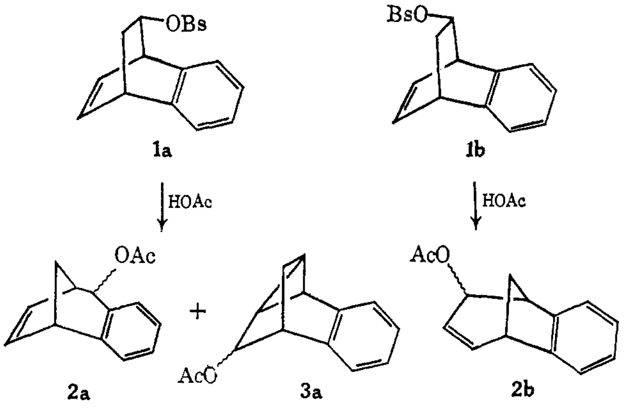
An Unusual Rearrangement of a Benzobicyclo[2.2.2]octadienol

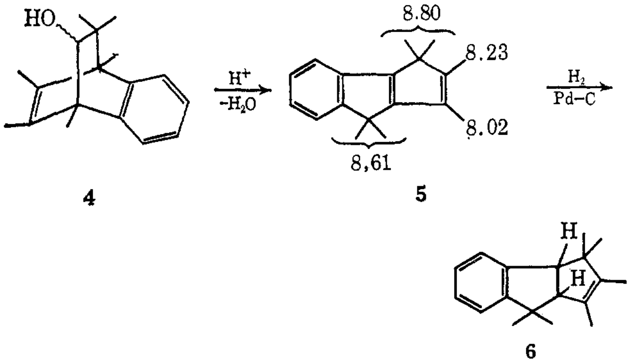
Sir:

Carbonium ion reactions in the bicyclo[2.2.2]-2-octyl series generally lead to products which have either retained the [2.2.2] ring structure or rearranged to the [3.2.1] ring system.[1] In a recent meticulous study, Tanida[2] found that the group which migrates is *anti* to the leaving group. Thus **1a** gave the [3.2.1] vinyl migration product **2a**, whereas **1b** gave the [3.2.1] aryl migration product **2b**. In addition, **1a** gave minor amounts (17%) of cyclopropylcarbinyl product **3a**.[3]



We wish to describe an unexpected, profound, but facile, rearrangement of a highly methyl-substituted derivative of **1**; the product is a benzodihydropentalene.

Addition of benzyne[4] to hexamethyl-2,4-cyclohexadienone[5] gave an adduct, mp 108–108.5°, in 73% yield.[6] Reduction with $LiAlH_4$ in ether at 0° afforded a nearly quantitative yield of the alcohol mixture **4** in which the epimer with OH *anti* to the aryl ring predominated (63:37).[7] The alcohol mixture[8] on treatment with strong acid afforded a crystalline hydrocarbon, mp 101–102°, in 45% yield.[9] It analyzed for $C_{18}H_{22}$; its mass spectrum showed a strong parent peak (*m/e* 238), a base peak at *m/e* 223, and other strong peaks at *m/e* 208, 193, and 178, indicating a fairly stable carbon framework with at least four pendant methyl groups. The nmr spectrum consisted of an aromatic multiplet (τ 2.77–3.02, 4 H), two quartets due to homoallylically coupled methyls (τ 8.02 and 8.23, J = 1 cps, 3 H each), and two very sharp singlets (τ 8.61 and 8.80, 6 H each). The nmr spectrum quickly eliminated all anticipated structures.[10] The ultraviolet spectrum showed an unusually intense long-wavelength band (λ_{max} 321 mμ (log ϵ 4.35)), as well as other bands at λ 246 (log ϵ 3.89), 238 (4.10), and 203 mμ (4.21). On the basis of these data and further conversions, we assign structure **5** to the dehydration product of **4**.[11]



Compound **5** readily absorbed 1 mole of hydrogen (ethanol, 5% Pd–C, room temperature, 1 atm) to give, as the major product, a dihydro derivative (mass spectroscopy) which still had two homoallylically coupled methyl groups (τ 8.28 and 8.45) as well as four separate unsplit aliphatic methyl peaks (τ 8.62, 8.77, 8.92, and 9.41). Thus the hydrogens (AB quartet at τ 6.50 and 6.89) must have added to a tetrasubstituted double bond which did not have any methyl substituents. The ultraviolet spectrum (λ 273 (log ϵ 3.33), 266 (3.33), 260 (3.26), 253 (3.20), and 208 mμ (3.95)) showed that the dihydro compound lacked a styrene chromophore; it is assigned structure **6**.[12]

One of the allylic methyl groups of **5** (τ 8.02) underwent complete exchange when **5** was in contact with excess 80% D_2SO_4–D_2O at room temperature for 3 hr. Since the most stable carbonium ion from protonation

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[1] For a survey of the earlier literature, see J. Berson in "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, pp 213–226.

[2] H. Tanida, K. Tori, and K. Kitahonoki, *J. Am. Chem. Soc.*, **89**, 3212 (1967).

[3] We have encountered similar rearrangements with substituted derivatives of **1a** and **1b**; see T. Kakihana, M.S. Thesis, Michigan State University, 1966.

[4] L. Friedman and F. M. Logullo, *J. Am. Chem. Soc.*, **85**, 1549 (1963); M. Stiles, R. G. Miller, and U. Burckhardt, *ibid.*, **85**, 1792 (1963).

[5] H. Hart, P. M. Collins, and A. J. Waring, *ibid.*, **88**, 1005 (1966).

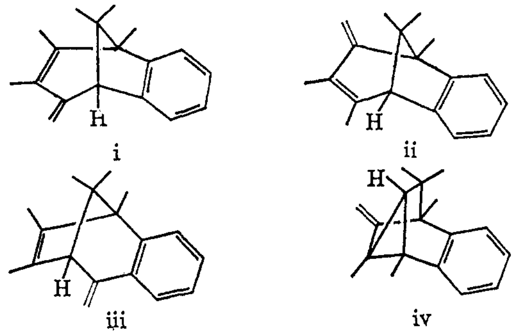
[6] All new compounds gave satisfactory microanalyses and infrared and nmr spectra consistent with the assigned structures.

[7] A complete nmr assignment for each epimer was attained with the aid of syntheses using 3-CD_3 and 5-CD_3 dienone;[5] analysis of the epimeric mixture was based on nmr.

[8] Chromatographic separation of the epimers has thus far failed; attempts using derivatives of **4** are in progress.

[9] The best yield was obtained by adding a $CHCl_3$ solution of the alcohols to a 50:50 sulfuric–trifluoracetic acid mixture at room temperature over 15 min, followed by dilution with ice.

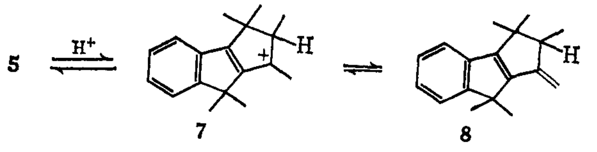
[10] Products of phenyl migration (i or ii), vinyl migration (iii), or double bond participation (iv), followed by proton loss, should have two vinyl protons.

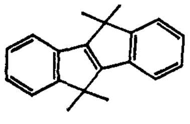


[11] Space limitations preclude presentation of all the supporting evidence for the structural and nmr assignment.

[12] Another dihydro-**5** (from 1,4 addition of hydrogen) and a tetrahydro-**5** have also been identified.

of **5** should be **7** (which can exchange *via* **8**), this experiment supports the illustrated nmr assignment for the allylic methyls in **5**.[11] Comparison of **5** with **9**, in which the *gem*-dimethyls appear at τ 8.53,[13] supports the remainder of the nmr assignment.[11] Finally, **5** gave a crystalline adduct with TCNE, mp 192–193°, assigned structure **10**,[6] and similar adducts with other dienophiles.





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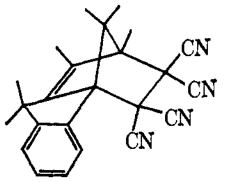

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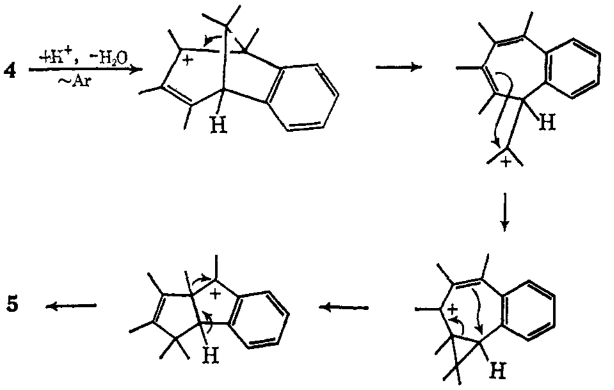
It is believed that **5** arises from the major epimer of **4**, and a plausible (abbreviated) mechanism is shown in Scheme I. This and other possible mechanisms are being tested; the scope of the rearrangement and the chemistry of the products are being investigated.[14]

Scheme I



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(13) J. E. H. Hancock and D. L. Pavia, *J. Org. Chem.*, **26**, 4350 (1961).

(14) We are indebted to the National Science Foundation for financial support of this work.

(15) To whom inquiries should be directed.

A. C. Gripper Gray, Tsuyoshi Kakihana
Peter M. Collins, Harold Hart[15]
Department of Chemistry, Michigan State University
East Lansing, Michigan 48823

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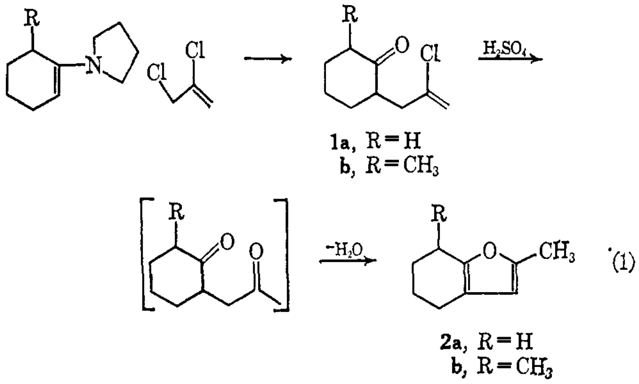
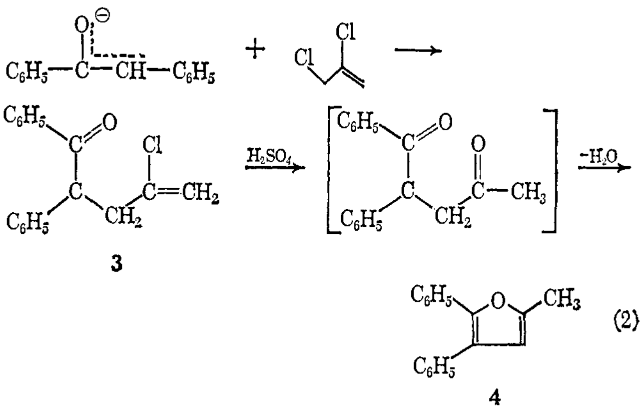
A Convenient Synthesis of Substituted Furans

Sir:

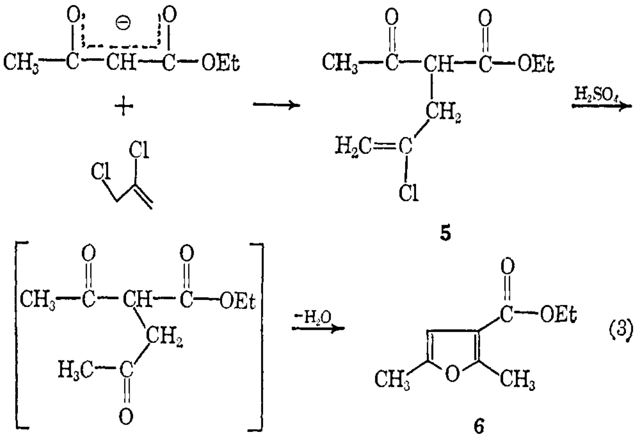
In a previous communication[1] we reported initial examples of a simple synthetic sequence leading to cyclic ketones of varying ring size. The reported synthesis utilized the β-chloroallyl group which acted both as a nucleophile and as a "masked" ketone. We have further investigated the chemistry of the β-chloroallyl group when placed in a position α to a carbonyl group and now wish to report initial examples of a convenient synthesis of substituted furans. The synthesis is illustrated below in several examples[2] wherein enolate ions are alkylated and the resulting β-chloroallyl ketone is subjected to sulfuric acid hydrolysis. The resulting 1,4-dicarbonyl compound (not isolated) undergoes subsequent sulfuric acid dehydration analogous to the Paal–Knoor[3] synthesis of oxygen, nitrogen, and sulfur heterocycles.



(1)



(2)



(3)

The "one-pot" hydrolysis–dehydration of **1a** proceeded in *ca.* 80% yield to the known[4] 2-methyltetrahydro-4,5,6,7-benzofuran (**2a**), identified as its maleic anhydride adduct. In like manner, **1b** proceeded in excellent yield to 2,7-dimethyltetrahydro-4,5,6,7-benzofuran (**2b**). Sequence 1 thus suggests a potential route to elusive substituted benzofurans by aromatization of the tetrahydro-4,5,6,7-benzofuran system. In addition,

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(1) P. T. Lansbury and E. J. Nienhouse, *J. Am. Chem. Soc.*, **88**, 4290 (1966).

(2) All new compounds gave satisfactory elemental analysis and were further characterized by spectroscopic methods. The furans, in particular, were further characterized by their ability to form crystalline maleic anhydride adducts.

(3) (a) L. Knoor, *Ber.*, **18**, 299 (1885); (b) C. Paal, *ibid.*, **18**, 367 (1885).

(4) T. Monel and P. E. Verkade, *Rec. Trav. Chim.*, 70, 3549 (1951).