Several authors have proposed a similar reaction sequence for the isomerization of olefins by the metal catalysts. The essential steps are reaction of the olefin with the metal hydride to give an alkylmetal intermediate which decomposes to the metal hydride and isomerized olefin.[5] In general, the alkyl–metal bond is attached to the least substituted carbon atom;[5a] however, our results require the rhodium–carbon bond to be attached at C-11, and this is reasonable in terms of the stabilization afforded by the electron-withdrawing lactone group at C-13.[6]

According to this representation, use of RhD$_2$Cl(PPh$_3$)$_2$ in step a would lead to the introduction of one deuterium atom in damsin (**5**) with the formation in step b of RhHDCl(PPh$_3$)$_2$. The hydrogen transferred to rhodium would most reasonably come from the C-7 position of damsin (**5**). The reaction of RhHDCl(PPh$_3$)$_2$ with a second molecule of damsin (**5**) gives isodamsin (**6**) with one or no deuterium atom, and, as the reaction proceeds, RhD$_2$Cl(PPh$_3$)$_2$ is progressively replaced by RhClH$_2$(PPh$_3$)$_2$. These steps explain the fact that the isodamsin (**6**) produced is only 58% labeled.[7] Furthermore, the absence of dideuterated isodamsin (**6**) implies the irreversibility of the initial hydrogen transfer. It has already been shown that the exchange reaction between gaseous hydrogen and RhH$_2$Cl(PPh$_3$)$_2$ is extremely slow.[1a]

The hydrogen requirement of this isomerization implies that the actual catalyst is RhH$_2$Cl(PPh$_3$)$_2$, the hydrogenation catalyst. The behavior with deuterium and with deuterated ethanol is similar to that in the hydrogenation where the reaction occurs under this condition almost without participation of protons from the solvent.[1] To explain our results, one may envision either a different mechanism for this isomerization from that of the hydrogenation of olefins or that a side reaction of the usual hydrogenation mechanism gains importance. A complex between olefin and RhCl(PPh$_3$)$_2$ as intermediate in the isomerization is excluded by the obligatory presence of hydrogen. Furthermore, the formation of a π-allyl complex between damsin (**5**) and RhH$_2$Cl(PPh$_3$)$_2$ would require the unlikely coordination number of eight for the rhodium atom.[8]

We think that the second explanation is more reasonable and we propose the formation of an alkylrhodium hydride as an intermediate in the isomerization of damsin (**5**) as well as in the hydrogenation of olefins with RhH$_2$Cl(PPh$_3$)$_2$. The reverse reaction, alkyl-RhHCl(PPh$_3$)$_2$ $\rightarrow$ olefin + RhH$_2$Cl(PPh$_3$)$_2$, has a much smaller rate than the transfer of the second hydrogen in the usual cases, so that no isomerization can be detected. The stereochemical outcome of the reaction scheme involving an alkylrhodium is expected to be a *cis* process: *cis* addition of rhodium hydride to the double bond, followed by a cleavage of the rhodium–carbon bond with retention. On the basis of this evidence one may not distinguish between the simultaneous transfer of both hydrogens or the reaction scheme involving alkylrhodium hydride as intermediate.

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(5) (a) N. R. Davies, *Rev. Pure Appl. Chem.*, **17**, 83 (1967); (b) R. Cramer, *J. Amer. Chem. Soc.*, **88**, 2272 (1966); (c) P. S. Hallmann, D. Evans, J. A. Osborn, and G. Wilkinson, *Chem. Commun.*, 305 (1967); H. A. Tayim and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, **89**, 3420 (1967).

(6) R. F. Heck and D. S. Breslow, *ibid.*, **83**, 4023 (1961).

(7) According to the low rate of exchange of the two positions of both hydrogen atoms in RhH$_2$Cl(PPh$_3$)$_2$,[1a] the hydrogen introduced during the isomerization of the first molecule of damsin (**5**) by RhD$_2$Cl(PPh$_3$)$_2$ may be used for the reaction of a second molecule of damsin, producing RhDHCl(PPh$_3$)$_2$ and isodamsin (**6**) containing no deuterium atom.

(8) R. V. Parish, *Coordination Chem. Rev.*, **1**, 439 (1966).

The Structure of Sirenin[1]

Sir:

Sirenin is a sperm attractant, active at concentrations of 10^{-10} *M*, produced by the female gametes of the water mold *Allomyces.* The production, isolation, and characterization of sirenin and its 4-(4-nitrophenylazo)-benzoate (NABS) esters have been described.[2] We now present the complete structure of sirenin (I) which becomes the first structurally characterized plant sex hormone.

Bis-NABS-sirenin (II) had nmr signals[3] at 0.95 (3 H, s, tertiary CH$_3$), 1.78 (3 H, broadened s, C=CCH$_3$), 4.75 (4 H, s, two NABS-OCH$_2$C(C)=C), 5.59 (1 H, t, J = 7 Hz, C=C*H*CH$_2$). Partial ozonolysis at −60° gave three products, purified by tlc on silica gel. One was the NABS ester of hydroxyacetone, identical with an authentic sample.

A second product (III), mol wt 447 (mass spectroscopy), retained nmr signals attributed to the tertiary methyl, one NABS-OCH$_2$C(C)=C, and the vinyl proton at 5.98. New signals appeared at 9.79 (1 H, t, J = 1.45 Hz) and 2.55 (2 H, "t"). The 2.55 "triplet" was composed of two overlapping doublets, J = 6.90 and 7.85 Hz. Each peak of the "triplet" was further split into a doublet with coupling constant corresponding to the 9.79 peak which collapsed to a singlet upon irradiating the signal at 9.79. This product thus results from loss of hydroxyacetone-NABS ester from bis-NABS-sirenin with concomitant formation of an aldehyde, ir[4] peak at 2736 and enhanced absorption at 1722. A propionaldehyde residue attached to an asymmetric center would make the adjacent methylene protons nonequivalent[5] and result in unequal coupling to the methylene group α to the carbonyl. A 5-hydroxy-4-methyl-3-pentenyl moiety in sirenin accounts for these observations.

The third product (IV) retained nmr absorptions characteristic of the pentenyl double bond in II. New signals at 2.53 (2 H, t, J = 6.35 and 6.60 Hz for low- and high-field portions) and 4.95 (2 H, s, identical in chemical shift with NABS-hydroxyacetone) reflected the

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(1) Financial support in part by the National Science Foundation is gratefully acknowledged.

(2) L. Machlis, W. H. Nutting, M. W. Williams, and H. Rapoport, *Biochemistry*, **5**, 2147 (1966).

(3) All nmr data are δ values, recorded at 60 and 100 MHz in CDCl$_3$ with internal TMS (δ 0) unless otherwise stated.

(4) All ir spectra were taken in CHCl$_3$ unless otherwise stated and are given in reciprocal centimeters, cm^{-1}.

(5) See M. L. Martin and G. J. Martin, *Bull. Soc. Chim. France*, 2117 (1966). Dimethyl (+)-*trans*-homocaronate exhibits a multiplet for its methylene group: L. R. Subramanian and G. S. K. Rao, *Tetrahedron*, **23**, 4167 (1967).

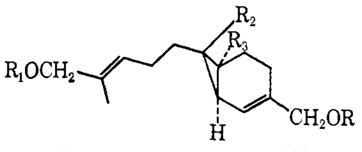
presence of a NABS-hydroxyacetone residue attached to a methylene group. Carbonyl absorptions in IV [ν 1723 (ester), 1736 (ketone)] were superimposable with those of NABS-hydroxyacetone. The other double bond carbon yielded an aldehyde: 9.65 (1 H, d, J = 4.00 Hz) and ν 2740, 1694. The magnitude of the coupling constant suggests a cyclopropylcarboxaldehyde[6] with an α proton, and ir absorption at 1694 also suggests a carbonyl contiguous to a cyclopropane.[7] The large downfield shift to 1.33 in IV from 0.95 in II indicates the tertiary methyl is on the cyclopropane, *cis* to the newly formed aldehyde.[8] These data establish in sirenin a second trisubstituted double bond. It is contained in a ring; one carbon bears an ethylene and a hydroxymethyl group, while the other is attached to a proton and a secondary methylcyclopropane.

Confirmation of the β-cyclopropyl allylic alcohol resulted when sirenin, treated with manganese dioxide,[9] afforded V, mol wt 232 (mass spectroscopy). The presence of two α,β-unsaturated carbonyls was shown by absorption at ν 1686, 1672, and 1630, and $\lambda_{\max}^{\mathrm{EtOH}}$ 232[10] and 260 nm. The latter is typical of β-cyclopropyl-α,β-unsaturated aldehydes or ketones,[11a] and the chromophores had the expected ratio of extinction coefficients.[10,11b] That both carbonyls were aldehydes was shown by absorptions at 9.41 (2 H, two signals separated by ~0.5 Hz) and ν 2710.

The partial structures deduced from the ozonolysis data account for the carbon, oxygen, and 23 of 24 hydrogens in sirenin ($C_{15}H_{24}O_2$[2]) and the four unsaturations (two rings and two double bonds). Structure I embodies all these features and accommodates the stereochemistry relevant to the cyclopropyl substituents.

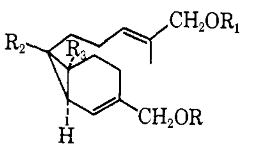
Periodate–permanganate[12] oxidation of sirenin yielded acid VI, converted to trimethyl ester VII ($[\alpha]^{22}\mathrm{D}$ $-20°$ (c 1.0, $CHCl_3$)) with diazomethane. Ester VII shows three methyl ester signals at 3.61, 3.60, and 3.58 (CCl_4) and, in accord with formula $C_{14}H_{22}O_6$, mass spectral peaks at m/e 271 ($M^+ - 15$) and at 254, 222, and 190 for the formal loss[13] of one, two, and three molecules of methanol.

Ester VII and its methoxycarbonyl epimer were synthesized *via cis* diacid VIII.[14] Esterification[15] gave IX[16] which was isomerized[17] to a 1 : 2 *cis–trans* mixture; *trans*-IX[18] was isolated by glpc (30% QF-1). Reaction with methyl diazoacetate[19] converted *trans*-IX into a mixture of triesters X and XI, the latter predominating. The stereospecificity[20] of the reaction places the propionate residues *trans*. Separation by silica gel chromatography ($CHCl_3$) and glpc (10% QF-1) afforded pure triester X.



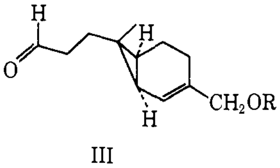
I, R = R₁ = R₃ = H; R₂ = CH₃

Ia, R = R₁ = R₂ = H; R₃ = CH₃

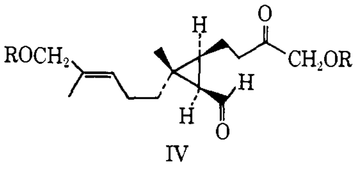


Ib, R = R₁ = R₃ = H; R₂ = CH₃

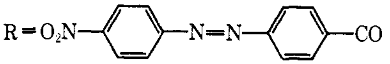
Ic, R = R₁ = R₂ = H; R₃ = CH₃

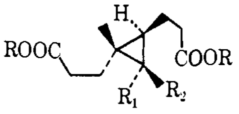


III



IV

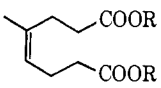




VI, R = R₁ = H; R₂ = COOH

VII, X, R = CH₃; R₁ = H; R₂ = COOCH₃

XI, R = CH₃; R₁ = COOCH₃; R₂ = H



VIII, R = H

IX, R = CH₃

The tertiary methyl absorption in X exhibited an upfield shift from 1.15 to 1.07 in changing from CCl_4 to benzene, while in XI a correspondingly larger shift from 1.11 to 0.80 occurred. This behavior is well documented for methylcyclopropanes bearing a carbonyl function[21] and establishes the methyl and methoxycarbonyl as *cis* in X and *trans* in XI. Triester X was identical with triester VII, derived from sirenin, by comparison of their nmr, ir, and mass spectra, tlc, and glpc. Therefore X is *dl*-VII.

Consideration of the possible structures for sirenin[22] eliminates Ia, Ib, and Ic which would yield isomers of VII with tertiary methyl *trans* to methoxycarbonyl. Since periodate–permanganate oxidation of sirenin in deuterated medium afforded VII with no deuterium incorporated (mass and nmr spectra), no epimerization occurred in producing VII; therefore its stereochemistry is the same as sirenin's.

Evidence for assignment of *trans* stereochemistry to sirenin's acyclic double bond followed from comparison

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[6] G. J. Karabatsos and N. Hsi, *J. Am. Chem. Soc.*, **87**, 2864 (1965).

[7] K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962, p 42.

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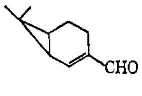
[10] K. L. Stevens, R. E. Lundin, and R. Teranishi, *J. Org. Chem.*, **30**, 1690 (1965), report $\lambda_{\max}^{\mathrm{EtOH}}$ 230 mμ (ϵ 13,000) for tetrahydrosinensal.

[11] (a) S. Julia, M. Julia, S.-Y. Tchen, and P. Graffin, *Bull. Soc. Chim. France*, 3207 (1964); (b) G. Büchi, W. Hofheinz, and J. V. Paukstelis, *J. Am. Chem. Soc.*, **88**, 4113 (1966), report $\lambda_{\max}^{\mathrm{EtOH}}$ 263 mμ (ϵ 11,700) for



[12] E. von Rudloff, *Can. J. Chem.*, **43**, 2660 (1965), and references therein.

[13] R. Ryhage and E. Stenhagen, "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press Inc., New York, N. Y., 1963, p 446.

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[15] F. H. Stodola, *J. Org. Chem.*, **29**, 2490 (1964).

[16] Intermediates leading to ester IX were prepared by Kent E. Opheim.

[17] C. Moussebois and J. Dale, *J. Chem. Soc., Sect. C*, 260 (1966).

[18] Distinguished from the *cis* isomer by glpc and 100-MHz nmr (CCl_4) which shows its vinyl methyl 3 Hz upfield from that in the *cis* isomer; *cf.* R. B. Bates and D. M. Gale, *J. Am. Chem. Soc.*, **82**, 5749 (1960).

[19] F. B. LaForge, W. A. Gersdorff, N. Green, and M. S. Schechter, *J. Org. Chem.*, **17**, 381 (1952); E. B. Womack and A. B. Nelson, *Org. Syn.*, **24**, 56 (1944).

[20] E. W. Warnhoff and V. Dave, *Can. J. Chem.*, **44**, 621 (1966), and references therein.

[21] J. Seyden-Penne, T. Strzalko, and M. Plat, *Tetrahedron Letters*, 3611 (1966); P. S. Wharton and T. I. Bair, *J. Org. Chem.*, **30**, 1681 (1965).

[22] Fusion of the cyclopropane and cyclohexene rings is assumed possible only with *cis* geometry.

with the nmr spectra of *cis*- and *trans*-2-methyl-2-penten-1-ol.[23] Vinyl proton absorption occurred at 5.25 and 5.40, respectively; sirenin exhibited a signal at 5.38.

These data establish I uniquely as the structure of sirenin.

[23] Prepared by Robert A. Jewell by lithium aluminum hydride reduction of *cis*- and *trans*-2-methyl-2-pentenoic acids (H. J. Lucas and A. N. Prater, *J. Am. Chem. Soc.*, **59**, 1682 (1937)).

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Some Novel Reactions of a "Tetravalent Sulfur" Species

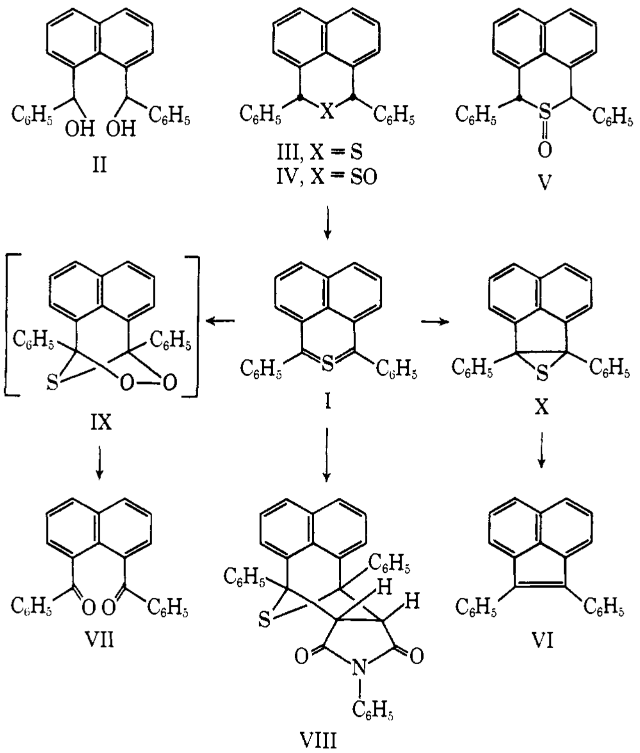
Sir:

Recently, a new class of highly reactive heterocycles containing a tetravalent sulfur atom has been described.[1] Chemical studies on these compounds have been confined thus far to their behavior in the Diels–Alder reaction. We wish to report some novel reactions arising from 1,3-diphenyl-2-thiaphenalene (I), a transient tetravalent sulfur species obtained by dehydration of its corresponding sulfoxide.

Reaction of α,α'-dihydroxy-1,8-dibenzylnaphthalene (II)[2] with phosphorus pentasulfide in pyridine[3] gave in 95% yield a single highly crystalline sulfide, III, mp 168°.[4] Oxidation of III with *m*-chloroperbenzoic acid in ether afforded the corresponding sulfoxide IV, mp 247° dec, in 90% yield. Treatment of this sulfoxide with sodium methoxide in methanol gave in quantitative yield a new sulfoxide, V, mp 250°.

Sharp singlets for the two protons α to the sulfur atom in V appeared at δ 5.18 and 5.45, indicating *trans* geometry for this sulfoxide.[5] The corresponding protons of sulfide III and sulfoxide IV appeared as singlets at δ 5.67 and 5.55, respectively. This resonance is compatible with the *cis* stereochemistry assigned to these compounds.

Upon heating the *cis* sulfoxide IV with acetic anhydride in the presence of excess N-phenylmaleimide at 120° three products were obtained. These materials were identified as 1,2-diphenylacenaphthylene (VI),[6] 1,8-dibenzoylnaphthalene (VII),[7] and the Diels–Alder adduct VIII[8] formed in yields of 15, 7, and 11%, respectively. The following series of experiments indicate heterocycle I to be involved in the formation of all of these products.



When the previous reaction was carried out in rigorously degassed acetic anhydride the only products formed were adduct VIII, 70% yield, and hydrocarbon VI, 15% yield. The same reaction run in the presence of oxygen gave the diketone VII as the major product, along with VI and VIII. Hydrocarbon VI, adduct VIII, and N-phenylmaleimide were found to be stable under these conditions.

These results suggest that I undergoes an addition reaction with oxygen giving rise to an intermediate peroxide adduct IX. Collapse of IX with loss of sulfur would yield diketone VII. Heterocyclic systems similar to I have not been observed to react with oxygen.[1]

Upon treatment with acetic anhydride at 120° in the absence of oxygen and added dienophile sulfoxide IV afforded VI in quantitative yield. Decomposition of IV at 100° gave a second component in addition to the orange hydrocarbon VI. Careful thick layer chromatography of the reaction mixture resulted in the isolation of colorless crystals, mp 110–120° dec, in 40% yield. This material has been identified as the episulfide X.

Compound X showed an ultraviolet spectrum intermediate between that of 1,2-diphenylacenaphthene[9]

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[1] (a) R. H. Schlessinger and I. S. Ponticello, *J. Am. Chem. Soc.*, **89**, 3641 (1967); (b) R. H. Schlessinger and I. S. Ponticello, *Tetrahedron Letters*, 4057 (1967); (c) M. P. Cava and N. M. Pollack, *J. Am. Chem. Soc.*, **89**, 3639 (1967); (d) M. P. Cava, N. M. Pollack, and D. A. Repella, *ibid.*, **89**, 3640 (1967).

[2] R. L. Letsinger and P. T. Lansbury, *ibid.*, **81**, 935 (1959).

[3] We are deeply indebted to Dr. P. M. Weintraub for the discovery of this reaction.

[4] All melting points are uncorrected. Satisfactory analyses were obtained for all new compounds reported.

[5] Nmr spectra were determined in $CDCl_3$.

[6] G. Wittig, M. Leo, and W. Wiemer, *Ber.*, **64**, 2405 (1931).

[7] W. Schlenk and J. Holtz, *ibid.*, **50**, 268 (1917).

[8] The structure of VIII was confirmed by the following observations. The mass spectrum of VIII showed a retro-Diels–Alder-type fragmentation pattern with peaks at m/e 336 (heterocycle I) and 173 (N-phenylmaleimide) as well as the parent ion at 509. That the peak at m/e 336 represents I is substantiated by the occurrence of a strong peak at 304 (hydrocarbon VI; sulfur extrusion from I). The peaks at 509 and 336 showed correct ${}^{34}S$ isotopic abundance. The nmr spectrum of VIII showed resonance for the two protons α to the imide carbonyls at δ 4.88, a position similar to the corresponding proton of the adduct of 9-phenylanthracene and N-phenylmaleimide. Molecular models indicate deshielding of these protons by the adjacent phenyl substituent for both compounds.

[9] H. J. Richter and W. C. Feist, *J. Org. Chem.*, **25**, 356 (1960).