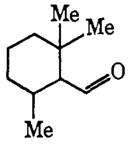
II was condensed with methyl β,β-dimethylacrylate (III) in the presence of potassium amide in liquid ammonia over a period of 48 hr. The product was decomposed with methanol–water and the work-up yielded acid IV: mp 110–111°; uv $\lambda_{\max}^{\mathrm{MeOH}}$ 261 mμ (ε 21,000); ir (KBr): broad absorption at 3200–2600 (carboxyl), 1675 ($\nu_{\mathrm{C=O}}$), 1620, 1590 ($\nu_{\mathrm{C=C}}$), 1445 ($\delta_{as\text{-}\mathrm{CH_3}}$), 1375 ($\delta_{s\text{-}gem\text{-}\mathrm{CH_3}}$), 1255 ($\nu_{\mathrm{C-OH}}$), and 975 cm^{-1} ($\delta_{\mathrm{CH}}$ of *trans* double bond); mass spectrum, molecular ion at *m/e* 236 (calculated for $C_{15}H_{24}O_2$, 236). The configuration about the newly formed double bond is *trans* from spectral data and is also in accord with earlier findings[4,5] on similar condensations.[6] Acid IV was smoothly reduced to alcohol V by means of lithium aluminum hydride in anhydrous ether solution in quantitative yield. V was obtained as an oil and purified by distillation: bp 108° (0.08 mm); uv $\lambda_{\max}^{\mathrm{MeOH}}$ 237 mμ (ε 25,200); ir (neat): 3340 (ν_{OH}), 1630, 1595 ($\nu_{\mathrm{C=C}}$), 1447 ($\delta_{as\text{-}\mathrm{CH_3}}$), 1375 ($\delta_{s\text{-}gem\text{-}\mathrm{CH_3}}$), 1010 ($\nu_{\mathrm{C-OH}}$), and 960 cm^{-1} ($\delta_{\mathrm{CH}}$ of *trans* double bond); mass spectrum, P − 1 peak at 221 (calculated for $C_{15}H_{26}O$, 222); nmr: 1 H, doublet at τ 3.75 (J = 16 cps), 2 H, complex multiplet at 5.42, 2 H, doublet at 5.80 (J = 7 cps), 1 H, broad singlet at 6.74, 3 H, sharp singlet at 8.20, 6 H, singlet at 9.21, and a complex region, 7.80–9.30. V was oxidized with "active" manganese dioxide[7] in carbon tetrachloride solution to give the aldehyde VI, purified in 62% yield by distillation: bp 96–98° (0.07 mm); uv $\lambda_{\max}^{\mathrm{EtOH}}$ 285 mμ (ε 28,900); ir (neat): 2740 (ν_{CHO}), 1665 ($\nu_{\mathrm{C=O}}$), 1627, 1580 ($\nu_{\mathrm{C=C}}$), 1448 ($\delta_{as\text{-}\mathrm{CH_3}}$), 1357 ($\delta_{s\text{-}gem\text{-}\mathrm{CH_3}}$), and 960 cm^{-1} ($\delta_{\mathrm{CH}}$ of *trans* double bond); mass spectrum, molecular ion at *m/e* 220 (calculated for $C_{15}H_{24}O$, 220). The 2,4-dinitrophenylhydrazone derivative of VI was prepared as red crystals: mp 182–185°; uv $\lambda_{\max}^{\mathrm{MeOH}}$ 392 mμ. Attempted purification of the aldehyde by column chromatography on neutral alumina was frustrating since the compound extensively decomposed on the column.



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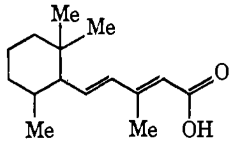

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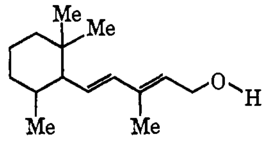

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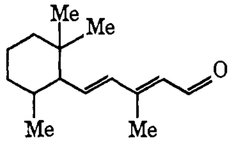

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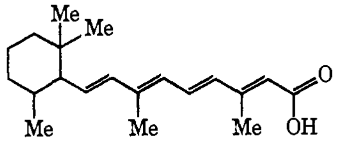
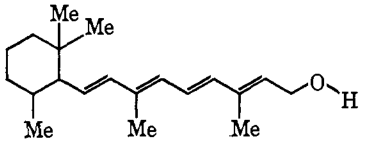


VII



VIII

Repetition of the base-catalyzed condensation of III with VI in the presence of potassium amide furnished acid VII[8] in 63% yield: mp 157–158°, pale yellow needles from ethanol; uv $\lambda_{\max}^{\mathrm{MeOH}}$ 325 mμ (ε 40,000); ir (KBr): broad absorption at 3200–2700 (carboxyl), 1678 ($\nu_{\mathrm{C=O}}$), 1588 ($\nu_{\mathrm{C=C}}$), 1450 ($\delta_{as\text{-}\mathrm{CH_3}}$), 1375 ($\delta_{s\text{-}gem\text{-}\mathrm{CH_3}}$), 1250 ($\nu_{\mathrm{C-OH}}$), and 965 cm^{-1} ($\delta_{\mathrm{CH}}$ of *trans* double bond); mass spectrum, no molecular ion was observed but a P − 44 peak (at *m/e* 258) was prominent, presumably caused by loss of carbon dioxide (calculated for $C_{20}H_{30}O_2$, 302). Reduction of VII with $LiAlH_4$ in ether yielded alcohol VIII as a viscous yellow oil in near-quantitative yield. It was analyzed by thin layer chromatography on silica gel G and found to be homogeneous. It was further characterized by the following: uv $\lambda_{\max}^{\mathrm{MeOH}}$ 323.0 (ε 28,100), 308.0 (35,300), and 295.0 mμ (26,800); ir (neat): 3320 (ν_{OH}), 1610 ($\nu_{\mathrm{C=C}}$), 1450 ($\delta_{as\text{-}\mathrm{CH_3}}$), 1380 ($\delta_{s\text{-}gem\text{-}\mathrm{CH_3}}$), 1000 ($\nu_{\mathrm{C-OH}}$), and 960 cm^{-1} ($\delta_{\mathrm{CH}}$ of *trans* double bond); mass spectrum, molecular ion at *m/e* 288 (calculated for $C_{20}H_{32}O$, 288).

We have oxidized the above alcohol to *all-trans*-5,6-dihydroretinal (IX), with "active" manganese dioxide.[7] However, *all-trans*-IX will not interact with opsin. Preliminary experiments[9] indicate that an irradiated (at 425 mμ) sample of IX couples with cattle opsin to form a synthetic visual pigment which exhibits $\lambda_{\max}$ 463 mμ. We believe that during the process of irradiation either the 9-*cis* or the 11-*cis* or both of these isomers of IX are formed. Just as in the case of visual pigments formed from retinal and 3-dehydroretinal, the visual pigment formed from irradiated IX also undergoes bleaching when exposed to white light. Further characterization of the pigment is in progress and will be reported separately.

Acknowledgment. This investigation was supported by Public Health Service Research Grant No. NB 06712-02.

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[4] M. Matsui, K. Yamashita, M. Miyano, S. Kitamura, S. Okano, A. Kobayashi, T. Sato, and R. Mikami, *J. Vitaminology* (Tokyo), **4**, 190 (1958).

[5] U. Schwieter, C. von Planta, R. Rüegg, and O. Isler, *Helv. Chim. Acta*, **45**, 528 (1962).

[6] A detailed study of the nmr spectra of IV and several other related compounds are in progress and will be reported later.

[7] Supplied by General Metallic Oxides Co., Jersey City, N. J.

[8] All new compounds (IV, V, VI, VII, and 2,4-dinitrophenylhydrazone of VI) gave satisfactory elemental analyses.

[9] Performed by Dr. Peter B. Dewhurst in our laboratories.

Paul E. Blatz, Padma Balasubramaniyan, V. Balasubramaniyan
Department of Chemistry, University of Wyoming
Laramie, Wyoming 82070

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A Thiocarbonyl Complex of Iron

Sir:

The thiocarbonyl complexes, *trans*-$RhX(CS)[P(C_6H_5)_3]_2$, where X = Cl or Br, have been recently prepared[1] by the reaction of $RhX[P(C_6H_5)_3]_3$ with CS_2 in the presence of excess $P(C_6H_5)_3$ and CH_3OH. These complexes were also oxidized with halogen, X_2, to the octahedral $RhX_3(CS)[P(C_6H_5)_3]_2$. In this communication we report the synthesis of $[C_5H_5Fe(CO)_2(CS)]PF_6$

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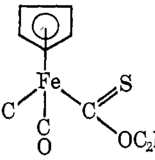
[1] M. C. Baird, G. Hartwell, Jr., and G. Wilkinson, *J. Chem. Soc., A*, 2037 (1967).

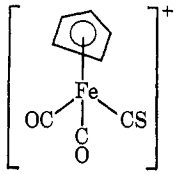
by a method which appears to be applicable to the preparation of other thiocarbonyl complexes.

It has been shown[2] that $Mn(CO)_5^-$ reacts with ethyl chloroformate, $ClC(O)OC_2H_5$, to give $Mn(CO)_5C(O)OC_2H_5$ which on treatment with HCl yields the cation, $Mn(CO)_6^+$. The complex, $C_5H_5Fe(CO)_2C(O)OCH_3$, prepared by a different method, also is converted to the cation, $C_5H_5Fe(CO)_3^+$, on reaction with HCl.[3] We have used similar reactions in the preparation of $[C_5H_5Fe(CO)_2(CS)]^+$. Thus treatment of $NaFe(CO)_2C_5H_5$ (readily accessible from $[C_5H_5Fe(CO)_2]_2$ and excess 1% sodium amalgam[4]) with ethyl chlorothioformate, $ClC(S)OC_2H_5$, gives $C_5H_5Fe(CO)_2C(S)OC_2H_5$ (I) that was obtained as an impure orange-brown product. Its infrared spectrum in pentane solution shows two carbonyl stretching frequencies at 2031 (s) and 1989 cm^{-1} (s) and a C–S stretching absorption at 1250 cm^{-1}. The reaction of a benzene solution of I with gaseous HCl produces a brown oil. Dissolution of the oil in acetone followed by treatment with an acetone solution of NH_4PF_6, filtration, and precipitation with ether gives the pale yellow, air-stable $[C_5H_5Fe(CO)_2(CS)]PF_6$ (II) in approximately 10% yield. It may be recrystallized from acetone–ether.

Anal. Calcd for $[C_5H_5Fe(CO)_2(CS)]PF_6$: C, 26.25; H, 1.38; S, 8.76. Found: C, 26.42; H, 1.53; S, 9.27.



I



II

The infrared spectrum of II taken in a hexachlorobutadiene mull exhibits a strong C–S stretching absorption at 1348 cm^{-1}. This compares with[1] 1299 cm^{-1} for *trans*-$RhCl(CS)[P(C_6H_5)_3]_2$ and 1362 cm^{-1} for $RhCl_3(CS)[P(C_6H_5)_3]_2$. The C–O stretching frequencies of II occur at 2093 (s) and 2064 cm^{-1} (s). Table I compares these values with those of other complexes of the type $[C_5H_5Fe(CO)_2L]^+$. If it is assumed that C–O stretching frequencies indicate the π-bonding ability of L (and there is considerable doubt about the validity of this assumption),[5–7] the data in Table I indicate that the CS group is one of the best π-bonding ligands.

Table I. C–O Stretching Frequencies of $[C_5H_5Fe(CO)_2L]^+$

Complex	ν_{C-O}	Ref
$[C_5H_5Fe(CO)_2(CS)]PF_6$	2093, 2064[a]	
$[C_5H_5Fe(CO)_2(C_2H_4)]PF_6$	2083, 2049	*c*
$[C_5H_5Fe(CO)_2(P(C_6H_5)_3)]Cl$	2066, 2030[a]	*d*
$[C_5H_5Fe(CO)_2(CH_3CN)]PF_6$	2080, 2035[b]	*e*
$[C_5H_5Fe(CO)_2(py)]PF_6$	2070, 2025[b]	*e*

[a] Hexachlorobutadiene mull. [b] CH_2Cl_2 solution. [c] E. O. Fischer and K. Fichtel, *Chem. Ber.*, **94**, 1200 (1961). [d] A. Davison, M. L. H. Green, and G. Wilkinson, *J. Chem. Soc.*, 3172 (1961). [e] P. M. Treichel, R. L. Shubkin, K. W. Barnett, and D. Reichard, *Inorg. Chem.*, **5**, 1177 (1966).

The preparation of other thiocarbonyl complexes of the transition metals is in progress, and the results of these investigations will be reported at a later date.

Acknowledgment. We are grateful for support of this research by the National Science Foundation.

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Luigi Busetto, Robert J. Angelici
Department of Chemistry, Iowa State University
Ames, Iowa 50010

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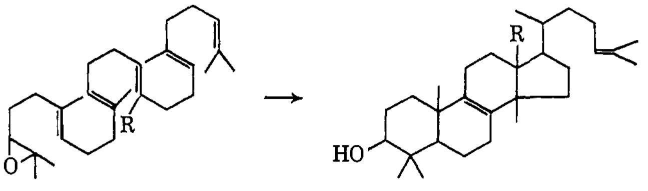
Enzymic Cyclization of 15-Norsqualene 2,3-Oxide

Sir:

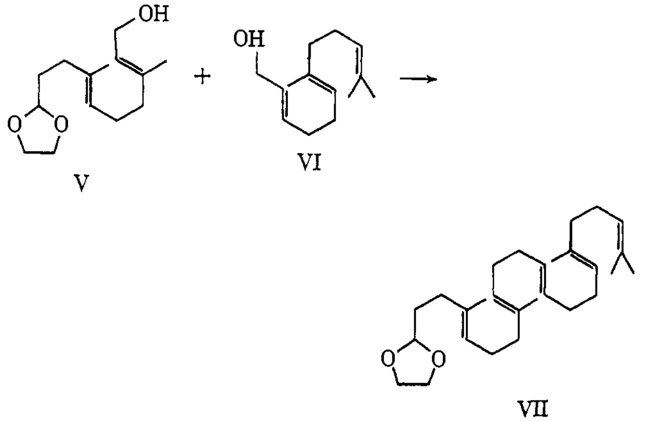
In mechanistic studies of lanosterol (II) biosynthesis we have selectively modified the normal precursor, squalene 2,3-oxide (I), in the central and terminal zones in order to gauge the effect on cyclization and thereby become informed as to the initiation,[1] sequential,[2] and side-chain[3] aspects of the normal annulation. In experiments designed to increase understanding of the factors controlling the later stages of lanosterol formation, especially the methyl–hydrogen migrations, we now find that 15-norsqualene 2,3-oxide (III) is enzymically transformed without incorporation of a proton from the medium to a lanosterol analog of the gross structure IV.



I, R = CH_3
III, R = H

II, R = CH_3
IV, R = H

Synthesis of the radiolabeled substrate III was achieved by employing in the critical stage cross-coupling of the *trans,trans*-acetal dienol V[5] and *trans,trans*-3-norfarnesol



V

VI

VII

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