relative intensities), (2) a 5% density difference between the amorphous and crystalline polymers (0.99 as against 1.04), (3) a 35° difference in softening points between the amorphous and crystalline polymers (37 as against 72°), (4) the observation of definite birefringent spherulites, and (5) a splitting of infrared bands which disappears above 72° and reappears on cooling. The change in the appearance of the infrared absorption spectrum on melting is shown in Fig. 1 for the frequency range between 1500 and 1050 cm.$^{-1}$.

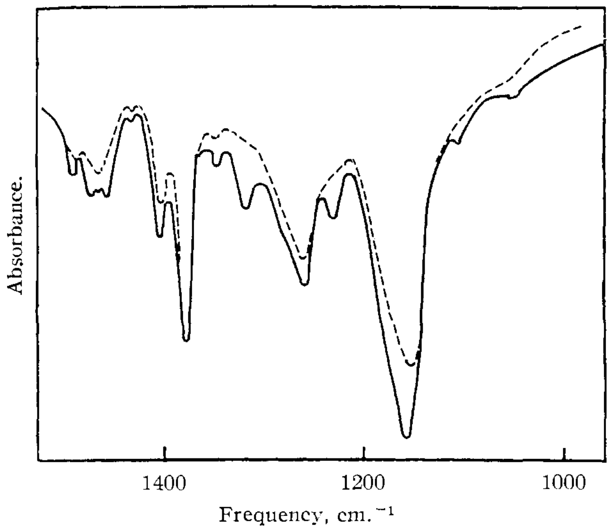


Fig. 1.—Infrared absorbance of poly-(*t*-butyl acrylate): --------, melted; ———, crystalline.

The same polymerization technique gave crystalline polymer from *t*-butyl methacrylate but not from methyl acrylate, *n*-butyl, *sec*-butyl or *iso*-butyl acrylates (or the corresponding methacrylates[1]). This suggests that steric factors are helpful in obtaining stereospecific polymerization. We were not able to prepare crystalline polymers from cyclohexyl acrylate.

---

[1] Fox and associates, THIS JOURNAL, **80**, 1768 (1958), have prepared crystalline poly-(methyl methacrylate) using different techniques from ours and lower temperatures.

POLYMER RESEARCH DEPARTMENT
STAMFORD LABS. RES. DIV.
AMERICAN CYANAMID COMPANY
STAMFORD, CONN.

M. L. MILLER
C. E. RAUHUT

RECEIVED JUNE 3, 1958

STRUCTURE OF SUPRASTEROL-II[1]

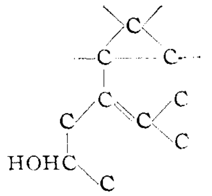
Sir:

Suprasterol-II, an ultraviolet irradiation transformation product of Vitamin D$_2$, has been shown to possess the normal ergosterol side-chain[2] and an acylatable hydroxyl group.[3,4] The nature of the ring system[5] and the degree of unsaturation remained in doubt.[5,6] Present findings permit the assignment of a novel structure to this material.

Suprasterol-II possesses 4 C-methyl groups (Kuhn–Roth) and upon quantitative microhydrogenation in acetic acid is found to have three reactive groupings, one of which is the *trans*-symmetrically disubstituted double bond (970 cm.$^{-1}$) in the side-chain. The nuclear magnetic resonance spectrum indicates only *two* vinyl protons. Hydrogenation over Pd–CaCO$_3$ yields the 22-dihydro derivative (no 970 cm.$^{-1}$ band; m.p. 120–121°; C, 84.12; H, 11.64) which shows no vinyl proton absorption in the n.m.r. Suprasterol-II with osmium tetroxide gives a triol (m.p. 248–256°; C, 77.95; H, 10.06; 970 cm.$^{-1}$) which upon hydrogenation yields a 22-dihydro derivative (m.p. 232–233°; C, 77.71; H, 11.45) possessing no absorption in the ultraviolet (ϵ_{205} 140). Thus, suprasterol-II possesses a *trans*-disubstituted and a tetrasubstituted double bond and five rings, one of which is reactive toward hydrogenolysis.

Tetrahydrosuprasterol-II (m.p. 99–100°, lit.[6] 99–102°) shows high end absorption in the ultraviolet (ϵ_{205} 5200) and no vinyl proton absorption in the n.m.r. and possesses 4 C-methyl groups. The triol (m.p. 180–182°; C, 77.19; H, 11.36) obtained by OsO$_4$ reaction shows no ultraviolet absorption and upon cleavage with lead tetraacetate yields an oily product possessing no aldehyde groupings. Thus, tetrahydrogenation saturates the side-chain double bond and cleaves a ring (indicating a cyclopropane structure) and leaves the tetrasubstituted olefinic linkage. The generation of no additional C-methyl groups suggests the absence of a methylenic grouping in the cyclopropane ring.

22-Dihydrosuprasterol-II (λ_{max} 210 mμ, ϵ 7100) upon oxidation with CrO$_3$–H$_2$SO$_4$ in acetone yields an oily ketone (no maximum above 220 mμ) which upon chromatography over alumina gives 22-dihydroisosuprasterone-II (λ_{max} 268 mμ, ϵ 19,200; m.p. 125–126°; C, 84.39; H, 11.06; semicarbazone m.p. 234–235° (dec.); C, 77.39; H, 10.26). These data show that the tetrasubstituted double bond in suprasterol-II is β,γ to the hydroxyl and that the cyclopropane ring is attached to the β-carbon of the olefinic linkage, *i.e.*, conjugated before and after bond migration.



Tetrahydrosuprasterol-II upon similar oxidation also gives rise to an oily non-conjugated ketone which upon chromatography yields a crystalline, conjugated, unsaturated ketone, tetrahydroisosuprasterone-II (λ_{max} 242 mμ, ϵ 14,600; m.p. 66–68°; semicarbazone, m.p. 233–234° (dec.); C, 76.24; H, 10.75). Ozonization of the ketone, and then methylation of the resulting keto-ester, yields a liquid ester (C, 77.21; H, 11.09) with infrared absorption at 1736 cm.$^{-1}$ (ester) and 1704 cm.$^{-1}$ (six or larger ring ketone). Thus, the ketone possesses a trisubstituted double bond which

---

[1] This work was supported, in part, by grant No. G-3589(C)-Bio(5), U. S. Public Health Service.

[2] A. Guiteras, Z. Nakamiya and H. H. Inhoffen, *Ann.*, **494**, 116 (1932).

[3] A. Windaus, J. Gaede, J. Köser and G. Stein, *ibid.*, **483**, 17 (1930).

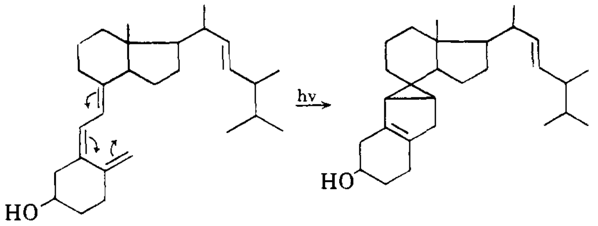
[4] P. Setz, *Z. physiol. Chem.*, **215**, 183 (1933).

[5] M. Müller, *ibid.*, **233**, 223 (1935).

[6] G. Ahrens, E. Fernholz and W. Stoll, *Ann.*, **500**, 109 (1933).

is both exocyclic to a six or larger membered ring originally containing the cyclopropane-ene system and conjugated to a ketone in a six or larger membered ring.

The most likely structure which could arise from vitamin D_2 and contain the structural requirements is shown below.



WILLIAM G. DAUBEN
IAN BELL
THOMAS W. HUTTON
GEORGE F. LAWS
ALFRED RHEINER, JR.
HANS URSCHELER

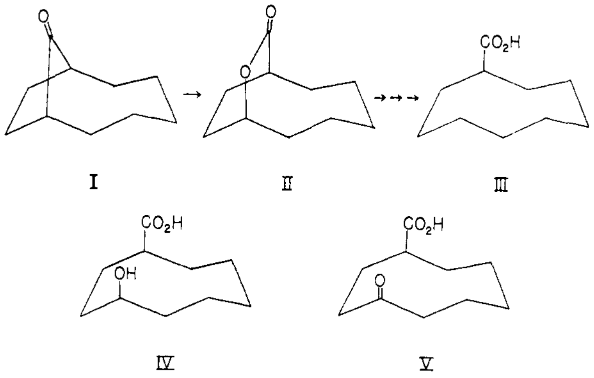
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA
BERKELEY 4, CALIFORNIA

RECEIVED MAY 26, 1958

A NEW METHOD FOR THE SYNTHESIS OF BRIDGED RING KETONES AND MEDIUM SIZE RING COMPOUNDS

Sir:

Seventeen years ago a brief report from the Leverkusen laboratories appeared[1] in which the reaction between cyclohexanone and 1,4-bisdiazobutane was described as yielding a C_{10} product with a terpene-like odor. The structure of this material now has been established as 10-ketobicyclo[5,2,1]decane (I) by this series of reactions: Compound I, prepared in *ca.* 25% yield by the *in situ* ring enlargement procedure[2] from N,N′-dinitroso - N,N′ - dicarbethoxy - 1,4 - diaminobutane[3] and cyclohexanone, m.p. 113–115° (clear at 120°), $\bar{\nu}_{\max}^{\text{liquid}}$ 1735 cm.$^{-1}$ (C=O in 5-membered ring), (*anal.* found for $C_{10}H_{16}O$: C, 78.63; H, 10.37) was converted to the lactone II with peroxytrifluoroacetic acid,[4] m.p. 96–98° (*anal.* found for $C_{10}H_{16}O_2$: C, 70.89; H, 9.38; saponif. equiv. 167.9). The lactone (II) was heated with thionyl chloride in benzene solution,[5] treated with ethanol, and subjected to catalytic hydrogenation (one mole equivalent absorbed). The resulting product was saponified, converted to the acid chloride, and treated with aniline to yield the anilide of the known cyclononanecarboxylic acid,[6] m.p. 140–141° (*anal.* found for $C_{16}H_{23}NO$: C, 78.36; H, 9.39). Thus, the presence of a 5-membered ring (infrared) and a 9-membered ring taken in conjunction with a simple interpretation of the course of the reaction[2] leaves structure I as the most reasonable one. Further support for I is provided by the facile formation of a dibromide, m.p. 134–135° (*anal.* found for $C_{10}H_{14}Br_2O$: C, 39.05; H, 4.77) and by the base-catalyzed exchange of two hydrogen atoms for deuterium atoms. These latter reactions indicate the compound to be readily, a fact not unexpected from a consideration of the molecular model of I, although this structure resides at the edge of Bredt rule territory.[7] The ring enlargement of cycloalkanones with bis-diazoalkanes provides a method for the synthesis of certain bicyclic systems (carbobicyclo[5,2,1] systems apparently have not been prepared previously) as well as a method for the synthesis of medium size carbocyclic ring compounds. The potentiality of the latter is suggested by the conversion of II to 4-hydroxycyclononanecarboxylic acid (IV), m.p. 86–87.5° (*anal.* found for $C_{10}H_{18}O_3$: C, 64.68; H, 9.58) and to 4-ketocyclononanecarboxylic acids (V), m.p. 33–35° (*anal.* found for $C_{10}H_{16}O_3$: C, 64.81; H, 8.55). Accompanying I are other materials, the structures of which have yet to be elucidated.


I II III IV V

Acknowledgment.—This research was supported, in part, by grants-in-aid from the National Science Foundation and the Office of Ordnance Research.

---

(1) Petersen, U. S. Dept. of Commerce, Office of Technical Service Report PB 694 (1941).

(2) C. D. Gutsche, "Organic Reactions," Vol. VIII, John Wiley and Sons, Inc., New York, N. Y., 1954, p. 364.

(3) C. M. Samour and J. P. Mason, THIS JOURNAL, **76**, 441 (1954).

(4) W. D. Emmons and G. B. Lucas, *ibid.*, **77**, 2287 (1955).

(5) J. Cason, C. E. Adams, L. L. Bennett, Jr., and U. D. Register, *ibid.*, **66**, 1764 (1944).

(6) K. Schenker and V. Prelog, *Helv. Chim. Acta.*, **36**, 896 (1953). We are indebted to Professor Prelog for carrying out the melting point and infrared comparisons with our sample.

(7) F. S. Fawcett, *Chem. Rev.*, **47**, 219 (1950).

C. DAVID GUTSCHE
TERRILL D. SMITH
MARTIN F. SLOAN
JOHN J. QUARLES VAN UFFORD
DONALD E. JORDAN

DEPARTMENT OF CHEMISTRY
WASHINGTON UNIVERSITY
ST. LOUIS 5, MISSOURI

RECEIVED JUNE 12, 1958

DEPENDENCE OF THE OPTICAL ROTATORY POWER OF PROTEINS ON DISULFIDE BONDS

Sir:

It has been known for a long time that most of the native proteins are levorotatory and that their rotation on denaturation increases considerably in the levo direction. An increase in levorotation also has been observed when the helical form of polyamino acids in non-polar solvents was converted into a random coil form by adding increasing amounts of a polar solvent.[1,2] It has been suggested,[3,4] therefore, that the decrease in levorotation

---

(1) P. Doty, J. H. Bradbury and A. M. Holtzer, THIS JOURNAL, **78**, 947 (1956); P. Doty, A. M. Holtzer, J. H. Bradbury and E. R. Blout, *ibid.*, **76**, 4493 (1954).

(2) E. R. Blout and M. Idelson, *ibid.*, **78**, 497 (1956).

(3) J. T. Yang and P. Doty, *ibid.*, **79**, 761 (1957).

(4) G. Markus and F. Karush, *ibid.*, **79**, 134 (1957).