gives even higher log Q_1 values than reported in Table II. This suggests that this peptide probably shows some increased complex stability arising from electron release by the methyl group, enhanced in this instance by the positive character of the adjacent peptide nitrogen. The small size of the methyl group does not produce any steric interference in the complex formation.

A similar electronic effect might be expected with the benzyl group particularly under the influence of the positive peptide nitrogen, but the glycylphenylalanines show about the same stability as glycylglycine. A study of Fisher–Hirschfelder scale models shows that the phenyl ring does not directly interfere with chelation at the peptide bond, but when chelation occurs, the bulky phenyl ring is forced into close proximity to other atoms in the molecule. Such steric interaction may offset any electronic influence present.

The over-all stability constants (log Q_1Q_2) given in Table II and summarized in Fig. 2 show the same general trends revealed by the constants involving the uptake of the first peptide molecule, although the calculated differences are greater. This is to be expected if steric factors are important, for the presence of two phenyl groups in these complex structures should increase the steric interferences compared to structures containing only one ligand molecule. Calculations using $pK'_2 = 8.16$ for both glycylphenylalanines give stability constants for the D-isomer of 5.30 with cobalt and 8.58 with copper. The differences recorded in Table II for these peptides thus appear to be the result of reasonable experimental error in the determination of pK'_2 rather than a real variation in complex stabilities.

It is apparent that variations in stability constants of dipeptide–metal ion complexes can be correlated with peptide structures. The variations can to some extent be ascribed to the electron-releasing or withdrawing character of the group attached to the α-carbon, but steric interferences may be more significant when large side chains are present, particularly adjacent to the peptide bond. The results show that the largest changes occur when structural changes significantly alter the basic strength of the terminal amino group. Structural changes adjacent to the peptide bond are much less effective in altering complex stability.

It has been observed that small differences in the amino dissociation constants employed can lead to relatively large and apparently significant variations in computed stability constants. Direct comparison of stability constants must, therefore, be made with extreme caution and with a knowledge of the correctness of the dissociation constants used in the calculations.

SYRACUSE 10, N. Y.

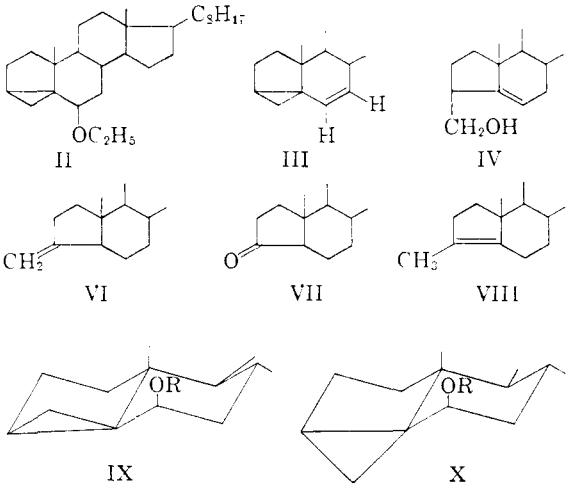
COMMUNICATIONS TO THE EDITOR

PHOTOCHEMICAL TRANSFORMATIONS. V. THE REACTION OF 3,5-CHOLESTADIENE[1,2]

Sir:

The photochemical sensitivity of homoannular dienes is well established,[3-5] and we now wish to report a photochemical induced transformation of a heteroannular diene.

The tetracyclic 3,5-cholestadiene, I ($C_{27}H_{44}$), in ethanol, upon irradiation with a mercury arc yielded 50% of an ethyl ether of a pentacyclic sterol,[6] II, ($C_{29}H_{50}O$, m.p. 104–105°, $[\alpha]^{25}D$ + 18.3°, ϵ_{200} 100, ν_{max} 3030 cm.$^{-1}$). II upon treatment with alumina at room temperature[7] lost one mole of ethanol and gave rise to an olefin, III ($C_{27}H_{44}$, m.p. 109.5–110.2°, $[\alpha]^{25}D$ + 41°, λ_{max} 207 mμ (ϵ 12,000), n.m.r., two vinyl hydrogens) which, in turn, upon reaction with osmium tetroxide yielded a saturated diol (m.p. 132–134°, $[\alpha]^{25}D$ + 52°, ϵ_{200} 100). These data establish in II a cyclopropylcarbinyl ethyl ether grouping such as is found in a 3,5-cyclo-6-ol steroid.



II upon reaction with aqueous acid in acetone yielded a β,γ-unsaturated primary alcohol, IV (m.p. 102–103°, $[\alpha]^{25}D$ −45°, no reaction with MnO_2 in acetone), and Oppenauer oxidation of IV gave rise to an oily α,β-unsaturated aldehyde (ν_{max} 2700, 1668, 1630 cm.$^{-1}$; 2,4-dinitrophenyl-

(1) For paper IV, see W. G. Dauben, K. Koch and W. E. Thiessen, THIS JOURNAL, in press.

(2) This work was supported in part by Grant No. A-709(C6)-B-10, U. S. Public Health Service.

(3) L. Velluz, G. Amiard and B. Goffinet, *Bull. soc. chim. France*, 882 (1957); M. P. Rappoldt, J. A. Keverling-Busiman and E. Havinga, *Rec. trav. chim.*, **77**, 327 (1958); R. J. DeKoch, Doctoral Dissertation, University of Leiden.

(4) D. H. R. Barton and A. S. Kende, *J. Chem. Soc.*, 688 (1958); R. L. Autrey, D. H. R. Barton and W. H. Rausch, *Proc. Chem. Soc.*, 55 (1959).

(5) W. G. Dauben and G. J. Fonken, THIS JOURNAL, **81**, 4060 (1959).

(6) All analyses are in agreement with the theoretical valuef.

(7) A. Romeo and R. Villotti, *Ann. Chim. (Rome)*, **47**, 684 (1957); *C. A.*, **52**, 1194 (1958).

hydrazone, m.p. 226–229°, λ_{max} 390 mμ (ε 20,000)). Dihydrogenation of IV yielded a saturated alcohol, V (m.p. 89.6–90.2°, $[\alpha]^{25}D$ − 3.6°), which was converted into a crystalline tosylate (m.p. 89.0–90.5°, $[\alpha]^{25}D$ + 3.6°). The tosylate upon reaction with activity III alumina yielded olefin VI (m.p. 90.6–91.8°, $[\alpha]^{25}D$ + 88.2°) which possessed an exocyclic methylene group (ν_{max} 880 cm.$^{-1}$). Ozonolysis of VI gave rise to formaldehyde and the known A-norcoprostane-3-one[8] (m.p. 75.8–76.8°, $[\alpha]^{25}D$ + 126°; semicarbazone, m.p. 265–268°). The tosylate upon reaction with activity I alumina yielded the known olefin, 3-methyl-$\Delta^{3(5)}$-A-norcholestene, VIII[9] (m.p. 63–64°, $[\alpha]^{25}D$ + 59.6°; identical with authentic sample). These data establish the structure of IV and show that no asymmetric centers present in the original diene have been affected in the irradiation reaction.

When the structure of IV is coupled with the fact that II can be transformed to a conjugated cyclopropane-ene possessing two vinyl hydrogens, only the 6-ethoxy-3,5-*cyclo*steroid structure II is possible. Since either the 6α- or 6β-oxy derivatives of 3α,5α-*cyclo*cholestane are known to yield cholesterol under the conditions in which II yielded IV,[10] the difference must lie in the stereochemistry of the cyclopropane ring, and II must possess the 3β,5β-*cyclo* structure shown in X. The mechanistic implications of the diaxial elimination leading from II to IV will be discussed in the completed manuscript.

(8) A. Windaus, *Ber.*, **52**, 170 (1919); B. B. Smith and H. R. Nace, THIS JOURNAL, **76**, 6119 (1952).

(9) H. Schmid and K. Kägi, *Helv. Chim. Acta*, **33**, 1582 (1950).

(10) S. Winstein and E. M. Kosower, THIS JOURNAL, **81**, 4399 (1959).

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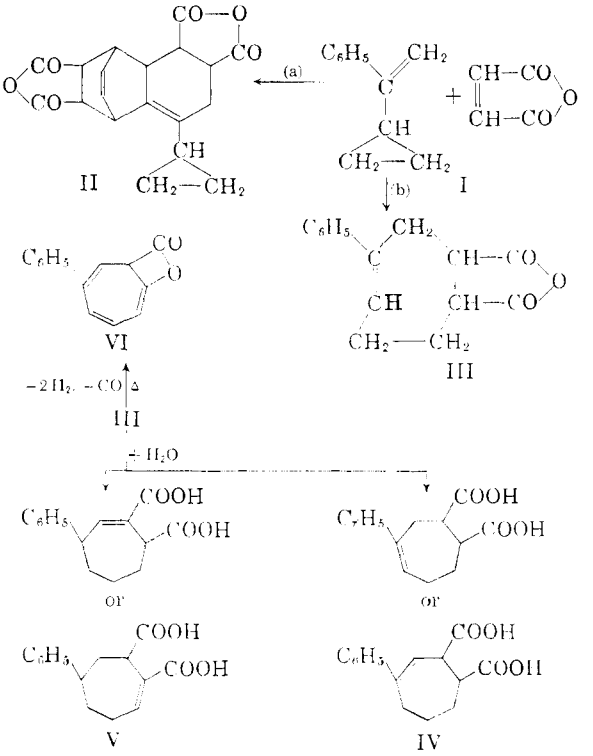
A NOVEL CONJUGATIVE 1,5-ADDITION REACTION INVOLVING THE VINYLCYCLOPROPANE SYSTEM

Sir:

Although there is considerable evidence that cyclopropane can enter into conjugation similarly to a double-bond,[1] no evidence exists of a successful cyclic addition reaction involving either a vinylcyclopropane[2] or a dicyclopropyl[3] system, analogous to the Diels–Alder reaction. This communication presents evidence that vinylcyclopropane is an active conjugated system when properly activated, for example, by a phenyl substituent.

A mixture of equimolar quantities of α-cyclopropylstyrene (I) λ_{max}^{EtOH} 242 mμ (ε 9700) and maleic anhydride in dry benzene was refluxed for 48 hours. After removal of solvent and starting materials the residue was extracted with methanol leaving behind an insoluble white bis-adduct (II) (12% yield), m.p. 255–257°, showing no bands for phenyl in the infrared (*Anal.* Found for $C_{19}H_{16}O_6$:



C, 67.18; H, 4.78). The residue from the methanolic extract was distilled at reduced pressure giving 4-phenylcyclohept-4-ene-1,2-dicarboxylic anhydride (III) (40% yield) as light-yellow oil (b.p. 170–180° (2 mm.), λ_{max} 240 mμ, ε 8500, λ_{max}^{liquid} 5.60μ, 5.80μ; *anal.* found for $C_{15}H_{14}O_3$: ε, 73.8; H, 6.1; mol. wt., 228 (benzene); sapn. equiv., 115). In platinum-catalyzed hydrogenation III absorbed one mole of hydrogen, providing an oily dihydro derivative having no maximum at 240 mμ. Oxidation of III by means of CrO_3–H_2SO_4 provided benzoic acid. Hydrolysis of III and chromatography over Florisil provided two isomeric diacids: (1) (IV) m.p. 103–105°, λ_{max}^{EtOH} 211 mμ (ε 11800), 243 mμ (ε 11400); λ_{max}^{KBr} 5.82μ, (*anal.* found for $C_{15}H_{16}O_4 \cdot H_2O$: C, 64.5; H, 6.2), and (2) (V) m.p. 190–192°, λ_{max}^{EtOH} 233–236 mμ (ε 8000), λ_{max}^{KBr} 5.82μ, 5.88μ (*anal.* found for $C_{15}H_{16}O_4$: C, 69.29; H, 6.15). Compounds IV and V show no bands for C-methyl in the infrared. The distillation of III was accompanied with white crystals of a new β-lactone (VI) (8% yield) (m.p. 161–162°, λ_{max}^{EtOH} 230 mμ (ε 6300), 277 mμ (ε 6600), λ_{max}^{KBr} 5.5μ; *anal.* found for $C_{14}H_{10}O_2$: C, 80,2; H, 5.1; mol. wt., 202 (ethylene dibromide)). The thermal oxidative-decarbonylation reaction of III and the physical and chemical properties of VI will be discussed in the full paper.

We observed that I does not isomerize on being heated in benzene for 48 hours with 10% mole of maleic anhydride. The palladium-catalyzed addition of one mole of hydrogen to I provided 2-phenylpent-2-ene (VII) (λ_{max}^{EtOH} 244 mμ, $E_{1cm}^{1\%}$ 44.5) in quantitative yield. The osmium tetroxide-catalyzed periodate oxidation of VII afforded acetophenone as the only identifiable ketone.

The data clearly indicate that I adds maleic anhydride by two different routes under the same

(1) For more fully documented accounts of certain aspects of the problem see E. N. Trachtenberg and G. Odian, THIS JOURNAL, **80**, 4018 (1958).

(2) R. van Volkenburgh, K. W. Greenlee, J. M. Derfer and C. E. Boord, *ibid.*, **71**, 172, 3595 (1949).

(3) L. I. Smith and E. R. Rogier, *ibid.*, **73**, 3840 (1951).