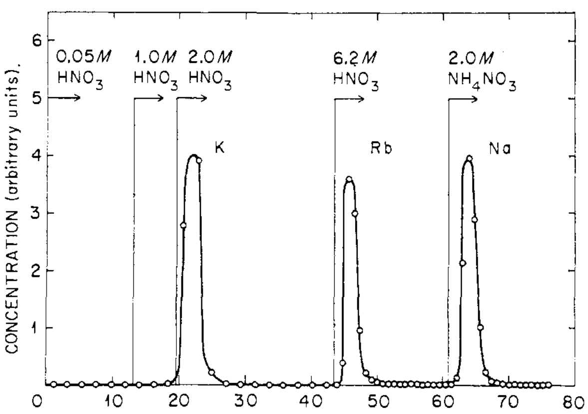

Fig. 1.—Separation of alkali metals with hydrous zirconium antimonate: (80–170 mesh, drying temp. 25°, 2.6 cm. × 0.19 cm.² column.

However, it is believed that neither the Sb(V)/Zr(IV) ratio nor the water content are particularly critical. The material is reasonably stable in concentrated and dilute HNO_3 and NH_3, and it is not appreciably attacked by H_2SO_4, HCl, and NaOH up to concentrations of about 2 M. Cs^+ uptake by the solid was approximately 0.5 mole/kg. from 0.05 M $CsNO_3$ at pH 3; total Na^+ uptake by the exchanger originally in the H^+-form was about 5 moles/kg. from 0.9 M NaOH.

Some preliminary rate studies with alkali metals indicate that the material behaves comparably to other inorganic ion exchangers of this type prepared at this laboratory. The ideality of the exchange reaction was checked for the Rb^+ (tracer)–H^+ system in the range 0.2 to 2.0 M HNO_3; log D for Rb^+ was a linear function of log M HNO_3 with a slope of approximately −1 as expected.

The zirconium antimonate showed unusual selectivities for the alkali metals, alkaline earths and the rare earths compared with zirconium phosphate, zirconium tungstate, and zirconium molybdate. Distribution coefficients in 1 M HNO_3 were >100 for some alkaline earths (Ca, Sr) and rare earths. Ba(II) has a D of approximately 12 in the same medium. In contrast, the distribution coefficients for the same elements in the same medium are <1 for the zirconium phosphate. The alkali metals showed a unique order of selectivity; instead of following the order of atomic numbers, as is commonly observed, Na^+ was more strongly adsorbed than either K^+ or Rb^+, while Rb^+ is more strongly adsorbed than K^+. Differences in selectivity are large and separations can be made with small columns as indicated in Fig. 1. In this experiment, K^+ was removed by 1 M HNO_3, ahead of Rb^+ which was removed by 6.2 M HNO_3. Both ions were removed ahead of Na^+, which cannot be removed even by concentrated HNO_3, but was eluted readily by 2 M NH_4NO_3. Li^+ and Cs^+, if they had been present in the mixture, would have been eluted by <0.1 M and 6 M HNO_3, respectively.

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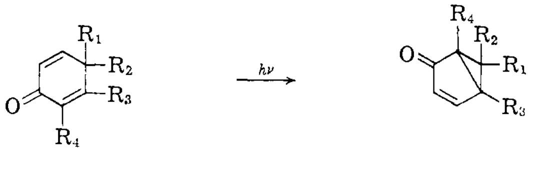
PHOTOISOMERIZATION OF Δ^4-CHOLESTEN-3-ONE[1]

Sir:

The number of dienones observed to undergo light-induced rearrangement of the santonin → lumisantonin type is sufficient to permit classification of the reaction as general.[2–4] It is stereospecific and therefore almost certainly concerted.



The obvious similarity of this reaction (excited state) to the Wagner–Meerwein rearrangement (ground state) prompted the study of unsaturated carbonyl compounds possessing less extensive pi-electron systems.

Irradiation of a 0.5% solution of Δ^4-cholesten-3-one (I) in *tert*-butyl alcohol with ultraviolet light[5] to 75% disappearance of the 240 mμ band afforded 25% of a photoisomer, *lumicholestenone* (II), m.p. 165–166°, $[\alpha]^{25}\text{D}$ +70°.[6] A small amount of the reported photodimer[7] also was obtained; it was removed by filtration before the isolation of II. The diminished rate of formation of this dimer is presumed to result from the use of more dilute solutions. No crystalline material other than I, II and dimer could be isolated. It is assigned formulation II on the basis of the following evidence. Its infrared spectrum possesses a sharp, weak spike at 3021 cm.$^{-1}$ (cyclopropane C–H stretching[8]) and a stronger peak at 1714 cm.$^{-1}$ (bicyclo[3.1.0]-hexan-2-one carbonyl stretching[9]). The ultraviolet spectrum has maxima at 212 mμ (ε 7,900), characteristic of a ketone carbonyl adjacent to a cyclopropane ring,[10] and at 285 mμ (ε 69). The lone proton on the cyclopropane ring gives rise to an unsplit peak at 8.5τ in the n.m.r. spectrum. This spectrum also shows the 19-Me peak at 0.16τ lower field than its position in the spectrum of cholestan-3-one. The rotatory dispersion curve[11] of II exhibits a strong positive Cotton effect with

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(1) Supported by the National Institutes of Health (Grant RG-7861).

(2) K. Weinberg, E. C. Utzinger, D. Arigoni and O. Jeger, *Helv. Chim. Acta*, **43**, 236 (1960), and references cited therein.

(3) D. H. R. Barton, J. McGhie and M. Rosenberger, *J. Chem. Soc.*, 1215 (1961), and references cited therein.

(4) H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **83**, 4486 (1961).

(5) All experiments were conducted with a filter of Pyrex glass at least 2 mm. in thickness. A yield of *ca.* 25% was obtained using sunlight (30 days), a 200-w. Hanovia mercury vapor lamp (170 hours) or a 1000-w. General Electric vapor lamp (24 hours). The product was isolated by chromatography on alumina.

(6) Satisfactory analytical data were obtained for all substances described. Solutions for rotation and infrared measurements were prepared in chloroform. Ultraviolet spectra were obtained using 95% ethanol.

(7) A. Butenandt, L. Poschmann, G. Failer, U. Schiedt and E. Biekert, *Ann.*, **575**, 123 (1951).

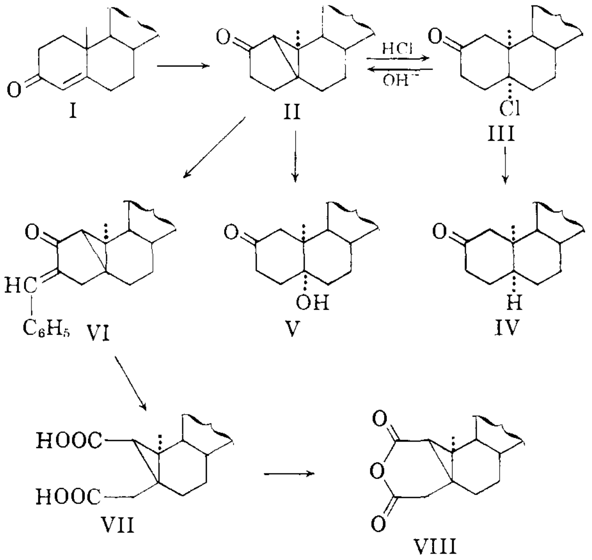
(8) H. T. Hoffman, Jr., G. E. Evans and G. Glockler, *J. Am. Chem. Soc.*, **73**, 3028 (1951).

(9) D. H. R. Barton, P. de Mayo and M. Shafiq, *J. Chem. Soc.*, 140 (1958).

(10) R. H. Eastman, *J. Am. Chem. Soc.*, **76**, 4115 (1954).

(11) We are indebted to Professor W. Klyne, The University of London, for obtaining and interpreting all of the rotatory dispersion data described. Methanol was the solvent.

a peak at 307.5 mμ ([M] +11,700°), a +29,000°! This spectrum bears a strong resemblance to those of dihydrolumisantonin (peak +8,000° at 310 mμ and trough at 275 mμ, a +22,000°) and dihydrolumi-1-dehydro-4-methyltestosterone acetate (peak +8,400° at 315 mμ and trough at 280° mμ, a +22,600°).[12]



Brief treatment of II with hydrochloric acid in acetic acid afforded (95%) a chloro ketone (III), m.p. 155–156°, $[\alpha]^{25}\text{D}$ +53°. This substance was reconverted to lumicholestenone in nearly quantitative yield by refluxing (10 min.) ethanolic potassium hydroxide. The infrared spectrum of III has a carbonyl band at 1711 cm.$^{-1}$ (cyclohexanone). The n.m.r. spectrum shows the 19-Me at only 0.08τ lower field than that of cholestan-3-one and thus indicates that the chlorine atom is positioned at least one atom removed from C-10.[13] The assignment of configuration at C-5 is supported by the weak negative Cotton effect (a, −3000°) in the rotatory dispersion curve as well as by the facile interconversion of II and III which suggests a near linear disposition of the chlorine atom and two carbon atoms involved.

Reduction of III with sodium–ammonia afforded a mixture of 10-epicholestan-2-one (IV), m.p. 99–100°, $[\alpha]^{25}\text{D}$ +50° and an alcohol which was converted readily to IV by mild oxidation. Support for formulation IV came from the infrared spectrum (carbonyl absorption at 1712 cm.$^{-1}$) and the rotatory dispersion curve which was nearly superimposable on that of the chloro ketone (III).

When II was heated under reflux in aqueous acetic acid it furnished 5α-hydroxy-10-epicholestan-2-one (V), m.p. 166–167°, $[\alpha]^{25}\text{D}$ +61°. Infrared absorption at 3530 and 1709 cm.$^{-1}$ suggested that ring-opening had followed the same course as in the II → III conversion. Proton resonance of the 19-Me group was observed at 0.02τ lower than in cholestan-3-one.

Treatment of either II or III with benzaldehyde and potassium hydroxide (methanol) afforded the same benzylidene derivative (VI), m.p. 196–197°. Ozonation of VI and then treatment with hydrogen peroxide gave dicarboxylic acid VII, m.p. 198–201°, $[\alpha]^{25}\text{D}$ +68°. The anhydride (VIII) was prepared from VII by reaction with acetic anhydride, m.p. 144–146°, $[\alpha]^{26}\text{D}$ +106°. The positions in the infrared of the anhydride bands at 1787 and 1738 cm.$^{-1}$ are as might be expected for a glutaric anhydride (1802 and 1761 cm.$^{-1}$) fused to a cyclopropane ring.

Several interesting transformation products of the diacid (VII), including members of the 10-epi-A-norcholestane series, were prepared. These will be described later in the complete paper.

Experiments designed to give information regarding the nature of the excited state involved in the photoisomerization of Δ^{4}-cholesten-3-one are not yet complete. It is important to note, however, that the process differs from the isomerization of homoannular dienones in that it must begin with the breaking (concerted to some extent with other changes) of a *sigma* bond. This formalism is characteristic of ground state reactions having an ionic origin and thereby suggests that the excited state giving rise to II is polar.

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RECEIVED MARCH 7, 1962

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(12) D. Arigoni, H. Bosshard, H. Bruderer, G. Büchi, O. Jeger and L. J. Krebaum, *Helv. Chim. Acta*, **40**, 1732 (1957). Values given here were estimated from the published curve.

(13) L. M. Jackman, "Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, New York, N. Y., 1959, pp. 53–54.

KINETICS OF DISSOCIATION OF ORGANIC DIMERIC DI-ANIONS INTO MONOMERIC RADICAL-IONS[1]

Sir:

In electron transfer initiation of anionic polymerization[2] the monomer M is converted into radical-ions, M$^-$. Dimerization of M$^-$ yields di-anions, *e.g.*, $2CXY{=}CH_2^- \rightarrow {}^-CXYCH_2CH_2CXY^-$, whereas their reaction with the monomer yields dimeric radical-ions, *i.e.*, $CXY{=}CH_2^- + CH_2CXY \rightarrow {}^-CXYCH_2CH_2CXY\cdot$. Studies of the kinetics of these reversible processes are currently being pursued in our Laboratory, and some methods for determining the rate constants of dissociation of $^-M{\cdot}M^-$ into 2M$^-$ are reported in this note.

Di-anions of 1,1-diphenylethylene do not undergo any polymerization on monomer addition as the bulkiness of phenyl groups introduces too large a steric strain. Hence, the rate constant of the dissociation

$$^{-}C(Ph)_2CH_2CH_2C(Ph)_2^{-} \xrightarrow{k_d} 2CH_2{=}C(Ph)_2^{-}$$

was determined[3] by studying the exchange between the di-anions and the radioactive monomer in tetrahydrofuran solution. Thus, k_d was found[3] to be 8×10^{-7} sec.$^{-1}$ at 30°, the respective E_d being about 10 kcal./mole.

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(1) This investigation was supported by the National Science Foundation through Grant No. G14393.

(2) (a) M. Szwarc, M. Levy and R. Milkovitch, *J. Am. Chem. Soc.*, **78**, 2656 (1956). (b) M. Szwarc, *Nature*, **178**, 1168 (1956); *Makromol. Chemie*, **35**, 132 (1960).

(3) G. Spach, H. Monteiro, M. Levy and M. Szwarc, *Trans. Faraday Soc.*, in press.