Therefore the indications are that the transitory phosphorylation product is either unstable or remains enzyme-bound. The results presented support the concerted mechanism shown below.

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[7] Holder of a Stipend from the Netherlands Organization for the Advancement of Pure Research (Z.W.O.).

[8] Holder of a Postdoctoral Fellowship from the United States Public Health Service.

CONVERSE CHEMICAL LABORATORY
HARVARD UNIVERSITY
CAMBRIDGE, MASSACHUSETTS
A. DE WAARD[7]
A. H. PHILLIPS[8]
KONRAD BLOCH

RECEIVED APRIL 11, 1959

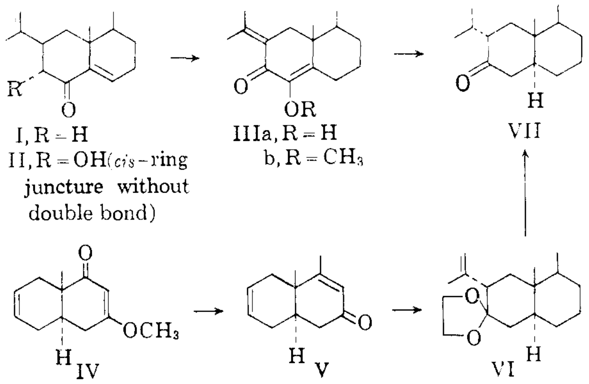
TERPENOIDS. XL.[1] ABSOLUTE CONFIGURATION OF EREMOPHILONE[2]

Sir:

The *relative* configuration of eremophilone (I)[3] has been established recently[4] by relating it, as well as naturally occurring[3] hydroxyeremophilone (IIIa), to hydroxydihydroeremophilone (II),[3] which already has been submitted to X-ray analysis.[5] In order to gain insight into the biogenetic precursor of these three sesquiterpenes (I,II,IIIa) which do not follow the isoprene rule, it was necessary to determine their absolute configuration and this now has been accomplished.

The (+)-antipode of IV of known absolute configuration[6] upon treatment with methyl lithium and acid cleavage afforded (+)-*trans*-2-keto-4,10-dimethyl-$\Delta^{3,6}$-hexahydronaphthalene (V) (m.p. 42–44°, $\lambda_{\max}^{\text{MeOH}}$ 236 mμ, log ε 4.02, rotatory dispersion curve very similar to that[7] of analog lacking C-4 methyl group; *anal.* found for $C_{12}H_{16}O$: C, 81.68; H, 9.18). Palladium-catalyzed hydrogenation of V in the presence of alkali provided (+)-*trans*-4,10-dimethyl-Δ^{6}-octalone-2[8] (b.p. 110–111° (1.5 mm.), negative R.D. Cotton effect; *anal.* found for $C_{12}H_{18}O$: C, 81.16; H, 10.18). Wolff-Kishner reduction led to (+)-*trans*-1,9-dimethyl-Δ^{6}-octalin,[9] which was transformed with perbenzoic acid to the 6α,7α-epoxide,[9] reduced with lithium aluminum hydride to the alcohol[9] and oxidized to (+)-*trans*-5,10-dimethyldecalone-2 (m.p. 29–30°, positive R.D. Cotton effect (amplitude reduced 68% upon addition of HCl—see ref. 8); *anal.* found for $C_{12}H_{20}O$: C, 79.72; H, 10.95). Condensation with ethyl oxalate and sodium hydride gave the glyoxalate,[9] which was decarbonylated thermally in the presence of powdered glass to (+)-*trans*-3-ethoxycarbonyl-5,10-dimethyldecalone-2 (b.p. 65° (0.01 mm.)), purple ferric chloride test; *anal.* found for $C_{15}H_{24}O_3$: C, 70.89; H, 9.14). Conversion to the cycloethylene ketal,[9] treatment with methylmagnesium iodide and dehydration of the crystalline (m.p. 55–60°) carbinol with phosphorus oxychloride in pyridine yielded (+)-*trans*-2-ethylenedioxy-3-isopropenyl-5,10-dimethyldecalin (VI) (b.p. 90–105° (0.1 mm.), $\lambda_{\max}^{\text{CHCl}_3}$ 6.08, 11.15 μ; *anal.* found for $C_{17}H_{28}O_2$: C, 76.94; H, 10.89). Hydrogenation of VI provided (+)-*trans*-2-ethylenedioxy-3-isopropyl-5,10-dimethyldecalin,[9] which was cleaved with hydrochloric acid–methanol to *trans*-3-isopropyl-5,10-dimethyldecalone-2 (VII) (b.p. 75–85° (0.04 mm.), infrared spectrum unchanged after equilibration with alkali, *positive* R.D. Cotton effect with peak at $[\alpha]_{312\,m\mu}^{\text{MeOH}}$ +530° (*c*, 0.21); *anal.* found for $C_{15}H_{26}O$: C, 80.79; H, 11.69; yellow 2,4-dinitrophenylhydrazone, m.p. 169–172°).

In order to provide an experimental connection with VII, hydroxyeremophilone (IIIa)—which has already been related[3,4] to eremophilone (I)—in the form of its methyl ether IIIb[3] was hydrogenated with palladium-charcoal in ethanol solution to its tetrahydro derivative.[9] Equilibration of the latter with alkali followed by demethoxylation with calcium in liquid ammonia led to *trans*-3-isopropyl-5,10-dimethyldecalone-2 (VII), identical in all respects (including rotatory dispersion curve with *positive* Cotton effect) with the above-described synthetic specimen.



I, R = H
II, R = OH (*cis*-ring juncture without double bond)
IIIa, R = H
b, R = CH_3
VII
IV
V
VI

These interconversions demonstrate that eremophilone and its relatives possess the absolute configurations[10] implicit in stereoformulas I, II and IIIa and that the eudalenoid biogenetic precursor[11] has the same absolute configuration as eudesmol.[12]

We are deeply indebted to Dr. Maurice D. Sutherland of the University of Queensland for a generous gift of hydroxyeremophilone and to Monsanto

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[1] Paper XXXIX. C. Djerassi and S. Burstein, *Tetrahedron*, in press.

[2] Supported by the Division of Research grants (No. RG-3863) of the National Institutes of Health, U. S. Public Health Service.

[3] J. Simonsen and D. H. R. Barton, "The Terpenes," Cambridge University Press, New York, N. Y., 1952, Vol. III, pp. 212–224.

[4] C. Djerassi, R. Mauli and L. H. Zalkow, THIS JOURNAL, **81**, July (1959).

[5] D. F. Grant and D. Rogers, *Chemistry and Industry*, 278 (1956); D. F. Grant, *Acta Crystal.*, **10**, 498 (1957).

[6] A. J. Speziale, J. A. Stephens and Q. E. Thompson, THIS JOURNAL, **76**, 5011 (1954).

[7] C. Djerassi, R. Riniker and B. Riniker, *ibid.*, **78**, 6377 (1956).

[8] The equatorial orientation of the C-4 methyl group was demonstrated by the ease of hemiketal formation using rotatory dispersion (C. Djerassi, L. A. Mitscher and B. J. Mitscher, *ibid.*, **81**, 947 (1959)).

[9] All compounds were characterized by analysis, infrared spectrum and rotatory dispersion.

[10] The earlier (opposite) assignment of absolute configuration involving rotatory dispersion comparisons (C. Djerassi, R. Riniker and B. Riniker, THIS JOURNAL, **78**, 6362 (1956)) was predicated on an α-oriented isopropenyl substituent in I. See also footnote 8 in ref. 4.

[11] R. Robinson, "The Structural Relations of Natural Products," Oxford University Press, New York, N. Y., 1955, p. 12.

[12] B. Riniker, J. Kalvoda, D. Arigoni, A. Fürst, O. Jeger, A. M. Gold and R. B. Woodward, THIS JOURNAL, **76**, 312 (1954).

Chemical Co., St. Louis, Mo., for a supply of the starting ketone IV.

DEPARTMENT OF CHEMISTRY
WAYNE STATE UNIVERSITY
DETROIT 2, MICHIGAN

LEON H. ZALKOW
F. X. MARKLEY
CARL DJERASSI

RECEIVED APRIL 9, 1959

THE OUTER SPHERE ACTIVATED COMPLEX IN THE REDUCTION OF Co(III) SPECIES[1]

Sir:

In much of the work done on oxidation-reduction reactions of Cr(II), the role of the bridged activated complex has been emphasized.[2,3,4,5] In particular, when Co(III) or Cr(III) complexes are oxidizing agents, proof has been adduced that the reactions proceed through activated complexes in which there is interpenetration of coördination spheres. We now report the results of experiments using a complex of Cr(II) which reacts by means of activated complexes in which there is no interpenetration in the same sense.

The reaction of Cr^{++}aq. with $Co(NH_3)_6^{+++}$ is slow[2] and the specific rate at 25° at $\mu = 0.41$ (Cl^- as the anion) has now been measured as 0.16 $m.^{-1}$ $min.^{-1}$. However, when Cr^{++}aq. is converted to $Cr(dip)_3^{++}$ (dip = 2,2′ bipyridine), the rate of the reaction is much increased. Thus at $\mu = 0.20$ (NaCl) and 25°, the specific rate of the reaction between $Cr(dip)_3^{++}$ and $Co(NH_3)_6^{+++}$ is 1.5×10^4 $m.^{-1}$ $min.^{-1}$. The rate is independent of the concentration of 2,2′ pyridine as long as a sufficient excess is present, and it is independent of *p*H over a considerable range, 5.5 to 3.5. It has been shown that 3 bipyridine groups are associated with each Cr^{++} under these conditions, and that the chromium product is $Cr(dip)_3^{+++}$. At low *p*H, the rate of the reaction increases, presumably because $Cr(dip)^{++}$ or $Cr(dip)_2^{++}$ reacts with $Co(NH_3)_6^{+++}$ even more rapidly than does $Cr(dip)_3^{++}$.

The interest in the observation we report is not so much that 2,2′-bipyridine so markedly increases the reactivity of Cr^{++} for $Co(NH_3)_6^{+++}$, but rather that it opens up the possibility of studying the reduction of the large class of Co(III) complexes by a reagent which acts retaining an intact coördination sphere. Considerable work with Cr^{++}aq., which with all Co(III) complexes studied except $Co(NH_3)_6^{+++}$ and perhaps $Co(NH_3)_5OH_2^{+++}$ makes use of a bridged activated complex, has already been done. Thus a systematic study can be made of the influence on the rate by each of the distinct mechanisms of changing the composition of the oxidizing agents; furthermore the chemical and isotopic effects characteristic of each type of mechanism can now be assessed. It perhaps needs to be emphasized that Co(III) complexes qualify especially for these studies because they undergo substitution slowly.

It is interesting to note that even when a bridged activated complex is not involved, $Co(NH_3)_5OH_2^{+++}$ reacts with a reducing agent much more rapidly than does $Co(NH_3)_6^{+++}$, and the rate ratio using $Cr(dip)_3^{++}$ is *ca.* 90. On changing the solvent from H_2O to D_2O, the rate at which $Co(NH_3)_6^{+++}$ reacts with $Cr(dip)_3^{++}$ is reduced by less than 10%, but a slight decrease, *ca.* 30%, is noted when $Co(NH_3)_6^{+++}$ is used as oxidant. However, when $Co(NH_3)_5OD_2^{+++}$ reacts in D_2O the rate is decreased by a factor of *ca.* 2.5 from the rate for $Co(NH_3)_5OH_2^{+++}$ in H_2O (this rate ratio can be compared to the decrease of 3.9 observed[6] in making a similar comparison with Cr^{++}aq. as reductant). A striking difference between the two kinds of mechanisms is in the sensitivity to the change from $Co(NH_3)_5OH_2^{+++}$ to $Co(NH_3)_5OH^{++}$. This change occasions an increase in specific rate by a factor of *ca.* 10^7 when Cr^{++}aq. is the reductant,[6] but by less than 100, and perhaps by as little as 10, when $Cr(dip)_3^{++}$ reacts.

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[1] This work is supported by the Atomic Energy Commission under Contract #AT(11-1)-378.

[2] H. Taube and H. Myers, THIS JOURNAL, **76**, 2103 (1954).

[3] H. Taube and E. L. King, *ibid.*, **76**, 4053 (1954).

[4] D. L. Ball and E. L. King, *ibid.*, **80**, 1091 (1958).

[5] A. E. Ogard and H. Taube, *ibid.*, **80**, 1084 (1958).

[6] A. Zwickel and H. Taube, *ibid.*, **81**, 1288 (1959).

GEORGE HERBERT JONES LAB.
UNIVERSITY OF CHICAGO
CHICAGO, ILLINOIS

A. M. ZWICKEL
H. TAUBE

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BOOK REVIEWS

Nouveau Traitê de Chimie Minerâle. Tome IV. Group II: Glucinium – Magnesium – Calcium – Strontium – Baryum – Radium. PAUL PASCAL, Membre de l'Institut, Professeur honorâire à la Sorbonne. Masson et Cie., 120 Boulevard Saint-Germain, Paris 6, France. 1958. xxxix + 973 pp. 17 × 26 cm. Price: Broché, 7.500 fr., cartonné toilé, 8.500 fr.

The preparation of a systematic and encyclopaedic treatise on inorganic chemistry was no trifling job, seventy-five years ago; every decade that has passed since then has made it a progressively more daunting enterprise. The Arcadian simplicity of Roscoe and Schorlemmer and the earliest editions of Gmelin have given place to multi-volume productions of size and price so formidable as to restrict them almost automatically to the institutional market. The reviewer is inclined to regard the 1908–1937 edition of Abegg-Auerbach as the last comprehensive account of inorganic chemistry that had some claim to readability; those skeptical of the validity of such a claim are reminded of Donnan on copper. Mellor's treatise, staggering as the single-handled labor of a sexagenarian with little more than secretarial assistance, is known to all of us as a mine of information and references on early experimental observations but it is only intermittently readable. The gallant attempt of Yost and Russell to use a portion of the Periodic Table to illustrate how a modern systematic treatise on inorganic chemistry might be written has been much and justly admired; but their effort has, alas, provoked no "envious fever of emulation."

The encyclopaedic treatise is here to stay unless it is doomed to ultimate displacement by the punch-card. Since no such work is likely to complete a cycle of revision in less