*Anal.* Calcd. for $C_{12}H_{18}O_5$: C, 59.49; H, 7.49. Found: C, 58.97, 59.80; H, 7.73, 7.84.

The acid was optically inactive and gave no methoxyl by Zeisel determination. It was soluble in alkali but precipitated on addition of carbon dioxide; neutral equivalent, 246–268. Titration of a purer sample with a Beckmann *p*H meter indicated a $pK_a$ of 10 ± 0.5 and a neutral equivalent of 230 ± 5. It gave no color with ferric chloride, sublimed unchanged and was recovered unchanged after boiling for one hour with alcoholic alkali, after refluxing with pyridine–acetic anhydride and after treatment with semicarbazide acetate for two days. The ultraviolet absorption at 2220 Å. had log $\epsilon$ = 2.38, decreasing steadily with increasing wave length. In alkaline solution the curve was shifted 350 Å. toward the visible, with a maximum between 2350–2450 Å.; log $\epsilon$ = 2.74. Work designed to elaborate the structure of this compound is in progress.

The crude cholesterol fractions contained a different neutral hapten, not yet isolated in pure form, but active in dilutions of 1:100,000. Perhaps these two substances are reponsible for two of the Rh subgroups.

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RECEIVED AUGUST 16, 1948

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[4] Eli Lilly and Company Fellows 1946–1948.

## THE CONFIGURATION OF ISOMERIC 1,2- AND 1,3-DICHLOROPROPENES

*Sir:*

Some question has recently arisen concerning the configuration of the isomeric 1,2- and 1,3-dichloropropenes. Huntress and Sanchez-Nieva[1] report the preparation of the lower-boiling isomer of the 1,2-compound (76° isomer) and state that the configuration of the two stereoisomers is still undetermined. (The other isomer boils at 93°.) In the case of the 1,3-dichloropropenes, the alpha or low-boiling isomer was assigned the trans configuration by Hatch and Roberts[2] due to the fact that, in the presence of cuprous chloride, it was more slowly hydrolyzed than was the beta or high-boiling isomer. Andrews and Kepner[3] questioned this choice, and indicated that no definite assignment could be made on the basis of available experimental evidence.

We wish to report results dealing with the dipole moments of these materials. The pertinent data is given in Table I.

TABLE I

DIPOLE MOMENT DATA FOR SOME ISOMERIC DICHLOROPROPENES AT 30°

| Isomer | $P_\infty$ (cc.)[a] | $\mu$(Debye units) | | |
|---|---|---|---|---|
| 1,2-Dichloropropene (76° isomer) | 43.4 | 0.84 | | |
| 1,2-Dichloropropene (93° isomer) | 123.0 | 2.20 | | |
| 1,3-Dichloropropene (alpha or 104° isomer) | 99.5 | 1.92 | 1.78[b] | 1.77[c] |
| 1,3-Dichloropropene (beta or 112° isomer) | 86.0 | 1.73 | 1.81[b] | 1.66[c] |

[a] Determined by the method of Rogers and Roberts, *ibid.*, **68**, 844 (1946). Benzene was used as solvent. [b] From vapor phase data by Oriani and Smyth, *J. Chem. Phys.*, **16**, 930 (1948). [c] From the "Data Sheet" on 1,3-dichloropropenes published by Shell Chemical Corporation, dated 8/4/47.

The dipole moments of the 1,2-compounds seem to indicate beyond any possible doubt that the 76° isomer is the *trans* form. The small dipole moment which it does have apparently arises from resonating structures involving the methyl group.[4]

The dipole moments for the 1,3-dichloropropenes, as listed in the table, are somewhat conflicting. It would appear that the moment of the *cis* compound could not be less than that of the *trans* form. Thus our data as well as that of the Shell Company support the assignment of the *cis* configuration to the alpha or low-boiling isomer, while the data of Smyth gives so little difference in the isomers that little choice is possible.

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RECEIVED SEPTEMBER 9, 1948

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[1] Huntress and Sanchez-Nieva, THIS JOURNAL, **70**, 2813 (1948).

[2] Hatch and Roberts, *ibid.*, **68**, 1196 (1946).

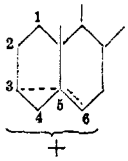
[3] Andrews and Kepner, *ibid.*, **69**, 2230 (1947).

[4] *Cf.* Rogers, THIS JOURNAL, **69**, 1243 (1947).

## EXCHANGE AT THE 6-POSITION OF *i*-CHOLESTERYL METHYL ETHER

*Sir:*

We have recently[1] suggested that the predominant mechanism which operates for the conversion of cholesteryl *p*-toluenesulfonate to the *i*-ether involves ionization to an intermediate ion I which has the cationic charge distributed between positions 3 and 6 and which reacts more rapidly with methanol at position 6 than 3.



I

Postulating the same ion I as an intermediate in the well-known[2] rearrangement of an *i*-compound to a normal one, one would expect, in the acid-catalyzed conversion of *i*-methyl to *n*-ethyl ether, prior formation, to a large extent, of the *i*-ethyl ether. This we have now been able to confirm.

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[1] Winstein and Adams, THIS JOURNAL, **70**, 838 (1948).

[2] McKennis, *ibid.*, **69**, 2565 (1947).

Thus, in a typical experiment, 2.00 g. of *i*-cholesteryl methyl ether, m. p. 79.0–79.5°, was subjected to a one-half hour reflux period in absolute ethanol to which was added ethanolic *p*-toluenesulfonic acid (total volume of final solution 37 ml.) 0.001 *M* in excess of the slight potassium acetate impurity present in the *i*-methyl ether as usually prepared.[3] The acid was neutralized, the solvent was evaporated, and the organic material was taken up in hexane. Systematic separation of the products by chromatography with the aid of alumina gave rise to 1.09 g. of *i*-ethyl ether, m. p. 45.0–45.5° (reported[4] 47°), mixed m. p. with authentic material, 45.5–46.0°, $[\alpha]^{25}\text{D}$ (chloroform) +47.10° (1 dcm., $c = 2.65$) (reported[4] $[\alpha]^{20}\text{D}$ +49.78° ($c = 1.607$)), 0.18 g. of *i*-methyl ether, m. p. 78.5–79.5° and 0.48 g. of *n*-ethyl ether, m. p. 88.0–89.0°. Thus, under these conditions, the ethyl ether product was 68% *i*-ethyl. The latter ether is converted to *n*-ethyl at a very appreciable rate, but the results serve to indicate the initial conversion of *i*-methyl ether predominantly to *i*-ethyl.

The *i*-ethyl ether product was indistinguishable in melting point and optical rotation from authentic *i*-ethyl ether and has, therefore, the same configuration as that of the product of the first reaction of ion I with ethanol under the usual conditions of preparation of *i*-ethyl ether. As far as we are aware this represents the first demonstration of exchange at the 6-position of *i*-compounds and suggests that, with care, it can be general.

The present work strengthens the case for an intermediate ion I in certain forward and reverse *i*-sterol rearrangements. It supplies evidence neither for nor against some contribution of bimolecular type mechanisms, and these remain possibilities for some rearrangements.

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RECEIVED AUGUST 30, 1948

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(3) Stoll, *Z. physiol. Chem.*, **207**, 147 (1932).

(4) Beynon, Heilbron and Spring, *J. Chem. Soc.*, 907 (1936).

(5) National Institute of Health Postdoctoral Fellow, 1947-1948.

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# NEW BOOKS

**Biochemistry.** Part I. FIAT Review of German Science, 1939–1946. Senior Author, RICHARD KUHN, Kaiser-Wilhelm-Institut für Medizinische Forschung, Heidelberg; Co-authors, H. FISCHER, H.-J. BIELIG, H. VON DOBENECK, D. JERCHEL, W. SIEDEL, M. STRELL, K. THOMAS, O. WARBURG AND G. WEITZEL. Published by Offices of Military Government for Germany, Field Information Agencies Technical, British, French, U. S. Printed under supervision of Dieterich'sche Verlagsbuchhandlung, Inhaber W. Klemm, Wiesbaden, Germany, 1947. 218 pp. Illustrated. 15 × 22.5 cm.

This volume, the first of a series of four devoted to biochemistry, consists of six review articles, respectively entitled: "**Fat and Fat Metabolism**," by K. Thomas and G. Weitzel (51 pp.); "**Invert Soaps and Tetrazolium Salts**," by D. Jerchel (7 pp.); "**Natural Pigments I**," by H. J. Bielig (42 pp.); "**Natural Pigments II, Syntheses of Pyrroles and Bile Pigments**," by H. Fischer and W. Siedel (19 pp.); "**Natural Pigments III, Syntheses of Porphyrins, Pentdyopent**," by H. Fischer and H. v. Dobeneck (18 pp.); "**Natural Pigments IV, Chlorophyll**," by H. Fischer and M. Strell (11 pp.). In addition, the book contains three original articles on carboxyhemoglobin and on the photochemical assimilation of carbon dioxide, by O. Warburg.

Much of the research work carried out during the war years was inevitably of a highly technical and utilitarian character, and in most instances the individual reports demand detailed study only by specialists. These review articles accordingly constitute a useful readers' guide for biochemists to whom the journals published in Germany in 1939 to 1946 are only now becoming available.

There are, however, several discussions of subjects of general interest. The section on fats and fat metabolism contains a stimulating account of fundamental work by Treibs (1942–1946) on the chemical reactions involved in the autoxidation of unsaturated fats, which must be carefully considered both by biochemists and by organic chemists. The same applies to the accounts of methods for the production of fatty acids from hydrocarbons and the studies of the metabolism and nutritional value of glycerides of these acids. The first section on natural pigments includes reviews, of more than ephemeral interest, of developments in the fields of carotenoids, flavines, pyrones and quinones. Of outstanding excellence are the reasoned discussions, by the late Hans Fischer and his associates, of the chemistry of porphyrins and other pigments related to pyrrole. The sections devoted to these topics resemble, in scope, articles in our own *Chemical Reviews*, and may well take a place in the permanent literature on the subject.

HANS T. CLARKE

**Electrochemical Analysis with Graded Cathode Potential Control.** By HARVEY DIEHL, Ph.D., Professor of Chemistry, Iowa State College, Ames, Iowa. Published by The G. Frederick Smith Chemical Co., 867 McKinley Ave., Columbus, Ohio, 1948. vii + 56 pp. 15 × 23 cm. Price, bound copies, $1.00 each; paper back copies free on request.

Professor Diehl most appropriately has dedicated this booklet to the late Henry J. S. Sand, who, forty years ago, introduced the technique of controlling the cathode potential in electrolytic separations and electrogravimetric determination of metals. In spite of its obvious advantages the controlled potential method did not become generally popular because of the tedium associated with the manual control of the potential. Recently, however, potentiostats which automatically perform this