

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 pH 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 responsible for two of the Rh subgroups.

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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-Nieva¹ 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 Roberts² 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 Kepner³ 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.

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

- (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).

TABLE I

DIPOLE MOMENT DATA FOR SOME ISOMERIC DICHLOROPROPENES AT 30°

Isomer	P_{∞} (cc.) ^a	μ (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.

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.

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

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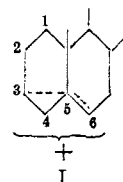
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EXCHANGE AT THE 6-POSITION OF *i*-CHOLESTERYL METHYL ETHER

Sir:

We have recently¹ 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 be-



tween positions 3 and 6 and which reacts more rapidly with methanol at position 6 than 3.

Postulating the same ion I as an intermediate in the well-known² 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.

- (1) Winstein and Adams, *THIS JOURNAL*, **70**, 838 (1948).
(2) McKennis, *ibid.*, **69**, 2565 (1947).