COMMUNICATIONS TO THE EDITOR

EPI-ALLOCHOLESTEROL, A NEW ISOMER OF CHOLESTEROL

Sir:

The asymmetric nature of carbon atom 3 in the cholesterol molecule should permit the existence of a stereoisomer, differing from cholesterol only in the configuration of the hydrogen atom and hydroxyl group at carbon 3. Such epi-forms have already been obtained from the saturated sterols, dihydrocholesterol and coprosterol.

In a search for this compound we have prepared a new (epi) isomer of cholesterol by reducing cholestenone with aluminum isopropylate. The principal product of this reaction is a mixture of two isomeric sterols, one of which is precipitable by digitonin. The non-precipitable sterol is an alcohol of the composition $C_{27}H_{46}O$ (Found: C, 84.12; H, 11.97. Calculated: C, 83.86; H, 12.00), melting at 84°. The compound is strongly dextrorotatory: $[\alpha]^{24}_{D}$ +120.8 (2% in benzene), and forms an acetate melting at 82.5°. On catalytic hydrogenation a mixture of epi-dihydrocholesterol and epi-coprosterol is obtained. This is a clear indication that in the new compound the hydroxyl group at position 3 is *trans* to the methyl group at carbon 10. The formation of two compounds on hydrogenation (as occurs with allocholesterol) and an intense Rosenheim reaction point to the probability that the double bond is in position 4–5. The behavior of our compound is similar to that of the saturated epi-forms in that it fails to form an addition compound with digitonin. All of the evidence thus far obtained indicates that the new substance is epi-allocholesterol.

The compound is further distinguished by a reaction which, as far as we know, has no analogy in the behavior of other sterols. On refluxing for two hours with a dilute solution of hydrochloric acid in 95% ethyl alcohol, the compound is quantitatively dehydrated to a hydrocarbon $C_{27}H_{44}$ (Found: C, 87.67; H, 12.14. Calculated: C, 87.96; H, 12.04); melting point 79°; $[\alpha]^{23}_{D}$ −112.8 (2% in benzene). The melting point and levorotatory nature of this hydrocarbon would indicate that it is cholesterilene. Its absorption spectrum, however, shows maxima (244, 235, 229 mμ) at shorter wave lengths than reported for cholesterilene by Heilbron (*J. Chem. Soc.*, 47 (1928)).

The nature of the reduction product which is precipitable by digitonin is under investigation.

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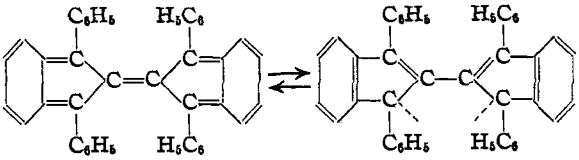
THE RUBRENE PROBLEM

Sir:

In a recent paper, J. C. Eck and C. S. Marvel [This Journal, **57**, 1898 (1935)] state: "The discoverers of rubrene [the literature of rubrene has been summarized by Dufraisse, *Bull. soc. chim.* [4] **53**, 789 (1933)] have considered it to be a difulvene of structure I, which may be in equilibrium with a diindenyl form containing two trivalent carbon atoms II. The diradical structure has also been advocated by Schönberg (*Ber.*, **67**, 633 (1934))."



I II

Formulas incorrectly printed in paper of Eck and Marvel

This must give the impression that I have advocated the theoretical speculations of the discoverer of rubrene. To establish my claim of priority, I would point out (1) that the discoverers of rubrene never considered the equilibrium I ⇄ II and (2) that prior to my publication [*Ber.*, **67**, 633 (1934)] no one had considered the transformation of I ⟶ II under any conditions [*cf.* also Schönberg, *Ann.*, **518**, 299 (1935); *Ber.*, **67**, 1404 (1934); **68**, 162 (1935)].

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PHOTOIODINATION OE THE ETHYLENIC BOND AT LOW TEMPERATURES

Sir:

To highly purified butene-1 (kindly furnished by Professor Kistiakowsky and Dr. Ruhoff of this