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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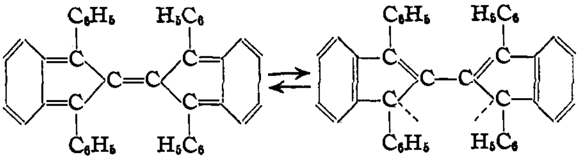
Received December 20, 1935

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 $\rightleftarrows$ 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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Received November 21, 1935

PHOTOIODINATION OE THE ETHYLENIC BOND AT LOW TEMPERATURES

Sir:

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

Laboratory) 0.01 *M* in redistilled CH_2Cl_2 or $CHCl_3$ was added iodine in equimolar quantity. Six solutions thus prepared were illuminated through 10 cm. of water by high efficiency incandescent lamps. After three hours, 90% of the iodine disappeared in CH_2Cl_2 at -60 to $-90°$ and 98% disappered in $CHCl_3$ at -60 to $-70°$. Iodine did not react photochemically with either solvent. Three such solutions of photoiodinated butene were illuminated in quartz by a spark between high tungsten steel electrodes. Each evolved its iodine quantitatively within an hour as proved by titration with 0.01 *N* thiosulfate in three stages. Another kept at 20° for one hundred hours had already evolved 84% of the original iodine, also in stages. The cycle involving visible and ultraviolet light was repeated several times in a fresh sample. Six preliminary photolyses of less pure material had yielded similar results; one reverse thermal reaction was practically complete in four days. Experiments on quantum yields at various temperatures and wave-lengths, and the thermal reaction rates (Polissar, THIS JOURNAL, **52,** 956 (1930)) are being undertaken, using butene-1 and related compounds.

HARVARD UNIVERSITY GEORGE S. FORBES
CAMBRIDGE, MASSACHUSETTS ARTHUR F. NELSON
RECEIVED DECEMBER 21, 1935

ε-CAPROLACTONE

Sir:

Stoll and Rouvé [*Helv. Chim. Acta* **18,** 1087 (1935)] have recently reported the isolation of pure ε-hydroxycaproic acid and its conversion to the corresponding lactone by application of the high dilution technique. The same lactone was obtained by us previously [Van Natta, Hill and Carothers, THIS JOURNAL, **56,** 455 (1934)] from a sample of the acid admitted to be impure. Under the conditions described we concluded that the lactone is the principal primary product of the self-esterification of ε-hydroxycaproic acid. Stoll and Rouvé conclude that heating of the pure acid yields chiefly polyesters and very little if any of the monomeric lactone.

We do not doubt the correctness of their conclusions, but we maintain also that the results of our own experiments need not be doubted either. Stoll and Rouvé state (footnote, p. 1091) that since we obtained the lactone by an impossible method its identity may be doubted in spite of the correct physical constants, especially since it was not identified by means of known derivatives. As to the impossibility of the method used, our description is an exact record of an actual experiment and it is incomplete in only one point of detail that seems of any likely significance. Our acid was obtained after ether-extraction mixed with water and acetic acid. To remove these impurities under the mildest possible conditions the mixture was allowed to stand for four days (time not given in the text of our paper) at room temperature while connected directly to an evacuated receiver kept at $-80°$. It is quite likely that a large portion of the observed lactonization occurred under these conditions (titration indicated 20% lactone assuming that *all* the acetic acid had been removed). In any event it is evident that our conditions of temperature, catalysis and possible dilution were such that they might easily yield a result different from that reported by Stoll and Rouvé. We have already (*loc. cit.*) pointed out that the ε-hydroxy acid is a transition case where the choice between intra- and intermolecular reaction may be expected to be especially sensitive to experimental conditions.

As to the identity of our lactone, we *did* prepare and describe a derivative. The same crystalline hydrazide was obtained from: (1) the crude acid, (2) the monomeric lactone, (3) the dimeric lactone, (4) the polyester and (5) the (crude) ethyl ester of the hydroxy acid made by an independent method. Mixed melting points showed no depressions.

EXPERIMENTAL STATION F. J. VAN NATTA
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RECEIVED DECEMBER 6, 1935