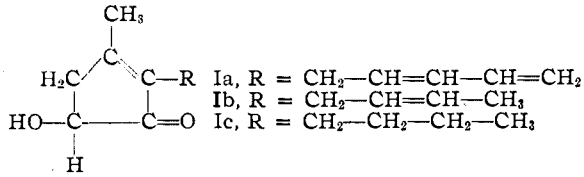
COMMUNICATIONS TO THE EDITOR

THE STRUCTURE OF DIHYDROCINEROLONE

Sir:

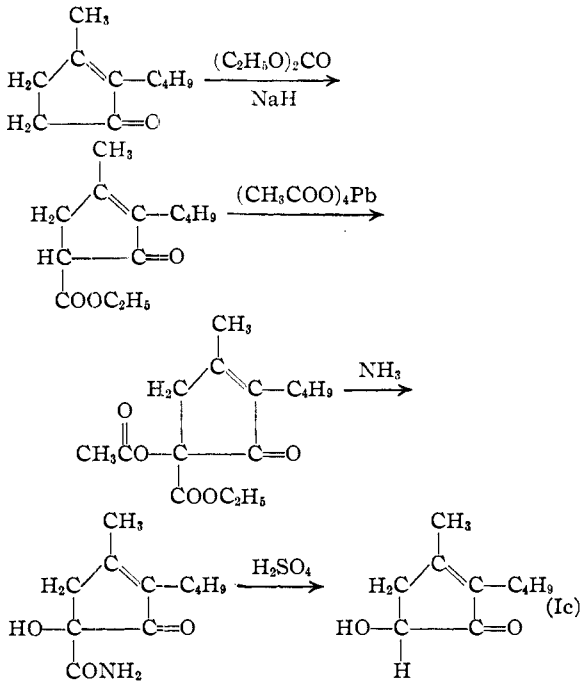
The alcoholic–ketonic components of the pyrethrins have been shown to consist of pyrethrolone and cinerolone for which the structures Ia and Ib, respectively, have been accepted.[1] These compounds on hydrogenation furnish the respec-



Ia, R = CH_2—CH=CH—CH=CH_2
Ib, R = CH_2—CH=CH—CH_3
Ic, R = CH_2—CH_2—CH_2—CH_3

tive tetrahydro and dihydro derivatives with saturation of the side chains.

We have now synthesized 2-butyl-3-methyl-4-hydroxycyclopentenone (Ic) through the following steps

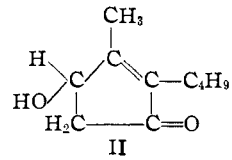


The final product (Ic) distilled at 92° (0.3 mm.); $n^{27}D$ 1.4930.

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 70.72; H, 9.65; average of four determinations. Calcd. for semicarbazone $C_{11}H_{19}O_2N_3$: C, 58.64; H, 8.50. Found: C, 58.27; H, 8.56; average of four determinations.

The hydroxyketone reduces Fehling solution vigorously, in contrast to the behavior of dihydrocinerolone, which shows only a slow reduction. It readily yields a phenylosazone, m. p. 147°, whereas dihydrocinerolone does not yield this derivative. The semicarbazone of synthetic 2-butyl-3-methyl-5-hydroxycyclopentenone melts at 169°; the semicarbazone of racemic dihydrocinerolone melts at 185°. Racemic dihydrocinerolone is therefore not identical with the synthetic hydroxyketone (Ic), and this fact necessitates a revision of its formula and hence that of cinerolone.

We suggest formula II for dihydrocinerolone, and in all probability a corresponding revision applies to pyrethrolone.



II

The expected properties of a compound of structure II would not be at variance with those characteristic of dihydrocinerolone. With the location of the hydroxyl in position 4, allylic to the double bond in positions 2–3, the esters and ethers of dihydrocinerolone, in accordance with the facts, would be especially subject to cleavage on hydrogenation, with the formation of dihydrocinerone. It would not yield a phenylosazone and probably would not reduce Fehling solution vigorously. The 4-chloro compound obtained by substitution of the hydroxyl would be very reactive, which is also in agreement with the facts. Structure II involves no disagreement with observed spectrographic data.

The original location, by Staudinger and Ruzicka,[2] of the hydroxyl group in pyrethrolone in position 5 is based solely on the formation of a compound which they assumed to be a *p*-nitrophenylosazone, but the nature of which seems to us to be doubtful.

(1) F. B. LaForge and W. F. Barthel, *J. Org. Chem.*, **10**, 114 (1945).

(2) H. Staudinger and L. Ruzicka, *Helv. Chim. Acta*, **7**, 212 (1924).

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THE REACTION OF 6-METHOXY-8-AMINO-1,2,3,4-TETRAHYDROQUINOLINE WITH KETONES[1]

Sir:

During the course of an investigation of the synthesis of Plasmochin (Pamaquin), 6-methoxy-8-(4-diethylamino-1-methylbutylamino)-quinoline (I), by reductive amination of 1-diethylaminopentanone-4 (II) with 6-methoxy-8-aminoquino-

(1) The work described in this communication was done in part under contracts recommended by the Committee on Medical Research between the Office of Scientific Research and Development and Columbia University and Sharples Chemicals, Inc.