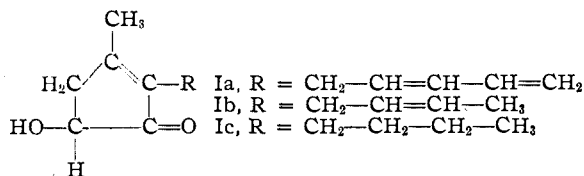


COMMUNICATIONS TO THE EDITOR

THE STRUCTURE OF DIHYDROCINEROLONE

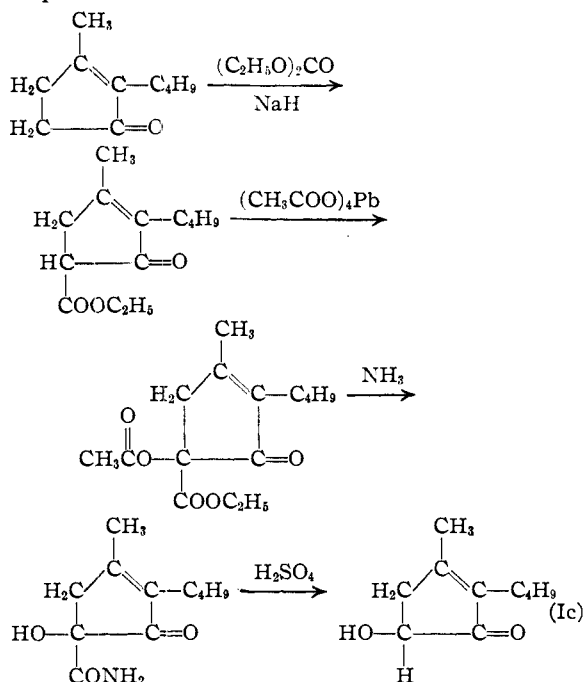
Sir:

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-



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_D^{27} 1.4930.

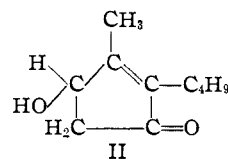
Anal. Calcd. for $\text{C}_{10}\text{H}_{16}\text{O}_2$: C, 71.39; H, 9.59. Found: C, 70.72; H, 9.65; average of four determinations. Calcd. for semicarbazone $\text{C}_{11}\text{H}_{19}\text{O}_2\text{N}_3$: C, 58.64; H, 8.50. Found: C, 58.27; H, 8.56; average of four determinations.

The hydroxyketone reduces Fehling solution vigorously, in contrast to the behavior of dihydrocinerolone, which shows only a slow reduction. It

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

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.



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.

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

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BELTSVILLE, MD.

F. B. LAFORGE
S. B. SOLOWAY

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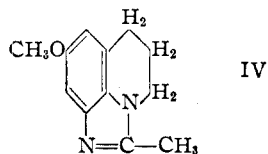
THE REACTION OF 6-METHOXY-8-AMINO-1,2,3,4-TETRAHYDROQUINOLINE WITH KETONES¹

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-diethylamino-pentanone-4 (II) with 6-methoxy-8-aminoquinone-

(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.

line (III), a case of direct rupture of a carbon-carbon bond under relatively mild conditions has been encountered. When either a mixture of II and III in methanol or the Schiff base from II and III are reduced catalytically over Raney nickel at temperatures between 100 and 160° and pressures of from 400 to 800 lb. per sq. in. the high boiling product was found to consist of about 25–29% of I and 50% of 2-methyl-8-methoxy-5,6-dihydro-4-imidazo[*ij*]quinoline (IV).



Compounds of the type of IV have been recorded as arising from the action of acetic acid or anhydride on 8-amino-1,2,3,4-tetrahydroquinoline,² a process which obviously proceeds by elimination of water from a tautomeric form of an acetamino derivative of the tetrahydroquinoline and which involves no rupture of a carbon-carbon linkage. In the present case final identification of IV was by mixed melting point with a sample prepared according to Price and Herbrandson³ whose note appeared after the structure of IV had been demonstrated by oxidative degradation. From the lower boiling products of the amination reaction *N,N*-diethyl-*n*-propylamine hydrochloride, m. p. 205.5–206.5, was isolated.

Anal. Calcd. for C₇H₁₇N·HCl: C, 55.4; H, 12.0. Found: C, 55.5; H, 12.2.

The structure of the latter was confirmed by comparison with a sample synthesized for the purpose as well as by comparison of the methiodides of the amine from the two sources. The methiodide melted at 243–244°.

Anal. Calcd. for C₈H₂₀IN: C, 37.4; H, 7.8. Found: C, 37.6; H, 8.1.

Further examination of the reaction showed that IV is formed when 6-methoxy-8-aminotetrahydroquinoline (V) is merely heated with a variety of ketones at 150–200°. Thus with octanone-2, hexane was eliminated and with methyl benzyl ketone, toluene was eliminated and IV remained. Barber and Wragg⁴ have recently described a condensation product of V with acetone to which the structure of 2,2-dimethyl-8-methoxy-1,2,5,6-tetrahydro-4-imidazo[*ij*]quinoline is assigned. This substance on heating likewise yields IV.

Details of the above observations will be published shortly.

DEPARTMENT OF CHEMISTRY
COLUMBIA UNIVERSITY
NEW YORK 27, NEW YORK
SHARPLES CHEMICALS, INC.
WYANDOTTE, MICHIGAN

ROBERT C. ELDERFIELD
FRANK J. KREYSA
JAMES H. DUNN
DAVID D. HUMPHREYS

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(2) Hazlewood, Hughes and Lions, *J. Proc. Roy. Soc. N. S. Wales*, **71**, 467 (1937–1938).

(3) Price and Herbrandson, *THIS JOURNAL*, **68**, 910 (1946).

(4) Barber and Wragg, *J. Chem. Soc.*, 610 (1946).

PERIODATE OXIDATION OF PHENOLS

Sir:

As part of an investigation of periodic acid oxidation of lignin sulfonic acids¹ there have been examined a number of compounds of structure possibly related to lignin. It has been found that under conditions previously considered specific for the oxidation of α,β -glycols, α -hydroxyketones, α,β -diketones and certain β -carbonyl compounds^{2,3} some substituted phenols are attacked by periodic acid. Table I lists the consumption of periodate by several phenols and aromatic amines. The reactions carried out at room temperature in dilute aqueous solution were essentially complete in a few hours. In all cases, except those of resorcinol and phloroglucinol, oxidations were accompanied by appearance of yellow to red colorations.

TABLE I
REDUCTION OF PERIODATE BY PHENOLS AND AMINES
(TIME OF REACTION TWO AND ONE-HALF HOURS)

	Moles of periodic acid consumed per mole of substrate	Critical oxidation potential, volts
Phenol	0.0	1.089
Vanillin	0.1	1.080
Resorcinol	0.5–1.0	1.043
<i>p</i> -Cresol	0.1	1.038
<i>p</i> -Aminocinnamic acid	2.0	1.020 estd.
β -Naphthol	1.8	1.017
<i>p</i> -Anisidine	1.2	0.892
5-Chlorovanillic acid	2.5	.870 estd.
Guaiacol	3.0	.868
Vanillic acid	3.0	.865
Acetylvannillic acid	0.0	...
Vanillyl alcohol	3.6	.831 estd.
Cresol	3.1	.825
Phloroglucinol	0.5	.799
α -Naphthol	2.5	.797
Ferulic acid	3.1	.757 estd.
Catechol	3.7	.742
Hydroquinone	1.1	.715

Although it appears that to be oxidized by periodic acid a phenol must have a critical oxidation potential⁴ of less than approximately 1.04 volts, this is not the only factor determining the rate and degree of oxidation. For example, resorcinol is oxidized more readily than the cresols, while phloroglucinol with a low oxidation potential is oxidized but slowly. Orthodiphenols consume appreciably more periodate than monohydric phenols or meta or para diphenols.

Attempts to isolate and characterize definite products from the periodate oxidation of vanillic acid and ferulic acid were unsuccessful. The

(1) Pennington and Ritter, *THIS JOURNAL*, **68**, 1391 (1946).

(2) Jackson, in Adams, "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., Vol. II, 1946, p. 341.

(3) Sprinson and Chargaff, *J. Biol. Chem.*, **164**, 433 (1946); Huebner, Ames and Bubl, *THIS JOURNAL*, **68**, 1621 (1946).

(4) Fieser, *ibid.*, **52**, 5204 (1930); Ritter, *ibid.*, **69**, 46, (1947).