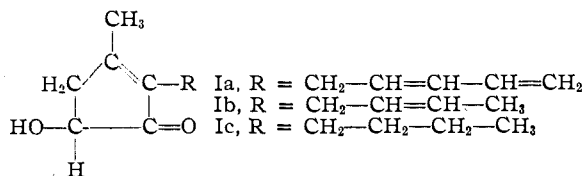


## COMMUNICATIONS TO THE EDITOR

## THE STRUCTURE OF DIHYDROCINEROLONE

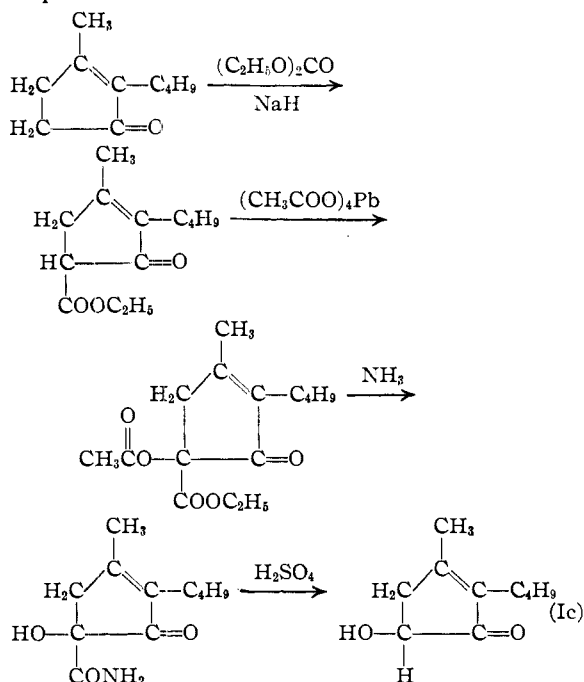
Sir:

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.<sup>1</sup> 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.

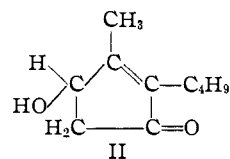
*Anal.* Calcd. for  $\text{C}_{10}\text{H}_{16}\text{O}_2$ : C, 71.39; H, 9.59. Found: C, 70.72; H, 9.65; average of four determinations. Calcd. for semicarbazone  $\text{C}_{11}\text{H}_{19}\text{O}_2\text{N}_3$ : C, 58.64; H, 8.50. Found: C, 58.27; H, 8.56; average of four determinations.

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,<sup>2</sup> 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).

DEPT. OF AGRICULTURE  
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S. B. SOLOWAY

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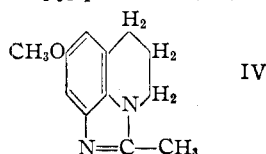
THE REACTION OF 6-METHOXY-8-AMINO-1,2,3,4-TETRAHYDROQUINOLINE WITH KETONES<sup>1</sup>

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,<sup>2</sup> 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 Herbrandson<sup>3</sup> 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 C<sub>7</sub>H<sub>17</sub>N·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 C<sub>8</sub>H<sub>20</sub>IN: 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 Wragg<sup>4</sup> 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.

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RECEIVED DECEMBER 18, 1946

(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 acids<sup>1</sup> 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  $\alpha,\beta$ -glycols,  $\alpha$ -hydroxyketones,  $\alpha,\beta$ -diketones and certain  $\beta$ -carbonyl compounds<sup>2,3</sup> 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.
$\beta$ -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
$\alpha$ -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 potential<sup>4</sup> 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).

methoxyl contents of the dark brown amorphous products were only a fraction of those of the original acids. That from ferulic acid contained 9.8% methoxyl after five minutes of oxidation, and after five hours of reaction the product from vanillic acid contained 6.5% methoxyl.

Methoxyl groups previously reported lost during the periodate oxidation of purified ammonium lignin sulfonate<sup>1</sup> have been identified as methanol in the volatile products of the oxidation, as measured by the colorimetric method described by Simmons.<sup>5</sup>

The evidence cited here indicates an attack upon the aromatic nucleus in the lignin sulfonic acids. The absence of any easily discernible stoichiometry and failure to isolate definite products precludes any ready interpretation for the course of the reaction, without further investigation. Such a study is being undertaken in this Laboratory.

(5) Simmons, *Analyst*, **37**, 16 (1912).

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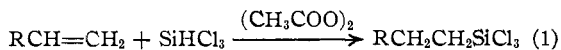
D. E. PENNINGTON  
D. M. RITTER

RECEIVED DECEMBER 16, 1946

#### PEROXIDE-CATALYZED ADDITION OF TRICHLOROSILANE TO 1-OCTENE

Sir:

The preparation of *n*-octyltrichlorosilane in 46% yield from silicon tetrachloride and *n*-octylmagnesium bromide has been reported.<sup>1</sup> We have now prepared this compound in excellent yield from 1-octene and trichlorosilane in the presence of diacetyl peroxide.



This new reaction of trichlorosilane is applicable to a wide variety of silicon hydrides and unsaturated compounds, and thus provides an important new synthesis for organosilicon compounds.<sup>2</sup>

Similar additions of chloroform and of bromoform to 1-octene and other olefins have been reported.<sup>3</sup>

1-Octene, 17.9 g., 0.16 mole, and trichlorosilane, b. p. 32°, 135.5 g., 1.0 mole, were placed in a three-necked flask with dropping funnel, thermometer, and a reflux condenser connected through a trap cooled in Dry Ice-acetone to a mercury seal of 20 cm. height. The system was swept with nitrogen for two hours, and the reaction mixture was heated to 45° under the slight extra pressure of the mercury. Crystalline diacetyl peroxide, 3 g., 0.025 mole, dissolved in 19.1 g., 0.17 mole, of 1-octene was then added during two hours. The mixture was heated at 50–63° for an additional nine hours.

After removal of excess trichlorosilane, the resi-

(1) Whitmore, Sommer, Di Giorgio, Strong, Van Strien, Bailey, Hall, Pietrusza and Kerr, *THIS JOURNAL*, **68**, 475 (1946).

(2) Cf. Rochow, "Introduction to the Chemistry of Silicones," John Wiley and Sons, New York, N. Y., 1946, pp. 18–30.

(3) Kharasch, Jensen and Urry, (a) *Science*, **102**, 128 (1945);

(b) *THIS JOURNAL*, **68**, 154 (1946).

due was distilled at reduced pressure and then redistilled at atmospheric pressure, giving 80.9 g. of clear colorless liquid, b. p. 231–232° at 728 mm., 99% yield.

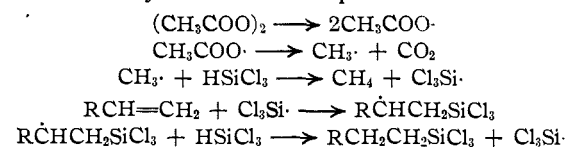
*Anal.* Calcd. for  $\text{C}_8\text{H}_{17}\text{SiCl}_3$ : Cl, 43.0. Found: Cl, 42.9, 43.0.

*n*-Octyltrichlorosilane from silicon tetrachloride and *n*-octylmagnesium bromide boils 233° at 731 mm.; 119° at 28 mm.<sup>1</sup>

Treatment of a portion of the product with ethanolic potassium hydroxide gave no hydrogen, indicating the absence of Si–H bonds.<sup>4</sup>

Reaction of the product, 24.8 g., 0.1 mole, with 0.35 mole of methylmagnesium bromide (using a procedure known to form the tetra-alkylsilane from *n*-octyltrichlorosilane)<sup>1</sup> gave 13.0 g. of *n*-octyltrimethylsilane, b. p. 201.5° at 733 mm.,  $n_D^{20}$  1.4242, 74% yield. Constants for this compound<sup>1</sup> are: b. p. 202° at 760 mm.,  $n_D^{20}$  1.4242. All the data thus conclusively confirm equation (1).

According to Kharasch,<sup>3</sup> the addition of chloroform to olefins is a free-radical chain reaction, initiated by free methyl radicals generated in the reaction mixture by decomposition of the peroxide. A similar free-radical mechanism applies to our reaction, especially in view of the lower bond energy of Si–H (75.1 kcal./mole) as compared to that of C–H (87.3 kcal./mole).<sup>5</sup> Thus the addition may involve the steps



This work is being continued.

Trichlorosilane and 1-octene at 47–54° with a weak ultraviolet source give a 24% yield of *n*-octyl trichlorosilane corresponding completely to the product of the peroxide-catalyzed reaction. (Added to proof January 13, 1947.)

(4) Cf. Sauer, Scheiber and Brewer, *ibid.*, **68**, 962 (1946).

(5) Cf. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1942, p. 53.

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L. H. SOMMER  
E. W. PIETRUSZA  
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RECEIVED DECEMBER 17, 1946

#### THE REACTION OF AMINOALKYL HALIDES WITH DIPHENYLACETONITRILE. THE STRUCTURE OF AMIDONE

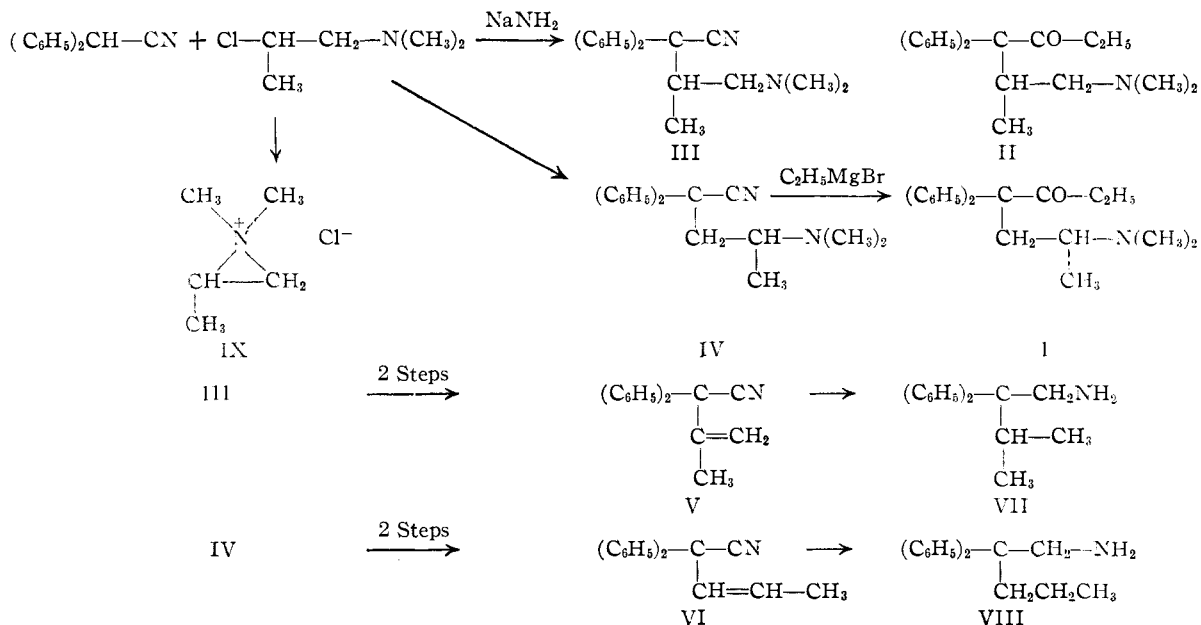
Sir:

Recent reports have indicated an uncertainty of the structure of the new German analgesic drug Amidone, or No. 10820.<sup>1,2</sup>

In this Laboratory, the preparation of this new drug by the German procedure led to the finding that the reaction between diphenylacetoneitrile and 1-dimethylamino-2-chloropropane results in a mixture containing equal amounts of two isomeric

(1) Office of the Publication Board, Department of Commerce, Report PB-981, p. 96-A.

(2) Scott and Chen, *J. Pharmacol.*, **57**, 63 (1946).



aminonitriles III (m. p. 66–67°. *Anal.* Calcd. for  $\text{C}_{19}\text{H}_{22}\text{N}_2$ : C, 81.97; H, 7.97; N, 10.06. Found: C, 81.89; H, 7.71; N, 10.01) and IV (m. p. 90–91°. Found: C, 82.03; H, 8.04; N, 10.04). The high-melting nitrile (IV) reacted with ethylmagnesium bromide to yield a product that possessed all of the properties reported for Amidone.

The methiodide of each of the aminonitriles was converted to its quaternary base and the bases heated to yield isomeric unsaturated nitriles, V (m. p. 63–64°. *Anal.* Calcd. for  $\text{C}_{17}\text{H}_{15}\text{N}$ : C, 87.52; H, 6.55. Found: C, 87.58; H, 6.56) and VI (b. p. 133–137° (1 mm.),  $n_D^{20}$  1.5750. Found: C, 87.66; H, 6.36). Hydrogenation of these nitriles using Raney nickel catalyst in methanolic ammonia yielded the isomeric amines, VII (b. p. 144–145° (2 mm.),  $n_D^{20}$  1.5830. *Anal.* Calcd. for  $\text{C}_{17}\text{H}_{21}\text{N}$ : C, 85.36; H, 8.85; N, 5.85. Found: C, 85.07; H, 8.78; N, 5.84) and VIII

(b. p. 142° (2 mm.),  $n_D^{20}$  1.5753. *Anal.* Found: C, 85.07; H, 8.71; N, 5.91). These amines were characterized through the benzoyl, phenylthiourea or ethylurea derivatives and by comparison with the amines prepared from diphenyl-isopropyl-acetonitrile and from diphenyl-*n*-propylacetonitrile.

From these data, it appears that Amidone possesses the structure I although the structure II should result if the reaction followed a normal course. It seems probable that the reaction proceeds through the ethyleneimmonium ion (IX) in a manner similar to that demonstrated for other reactions of halogenated alkylamines.<sup>3</sup>

MEDICAL RESEARCH DIVISION EVERETT M. SCHULTZ  
DEPARTMENT OF ORGANIC CHEMISTRY CHARLES M. ROBB  
SHARP AND DOHME, INC. JAMES M. SPRAGUE  
GLENOLDEN, PENNA.

RECEIVED DECEMBER 14, 1946

(3) Gilman and Philips. *Science*, **103**, 409 (1946).

## NEW BOOKS

**Textbook of Physical Chemistry.** By SAMUEL GLASSTONE, D.Sc., Ph.D., Formerly Research Associate of Princeton University and Professor of Chemistry in the University of Oklahoma. Second Edition. D. Van Nostrand Company, Inc., 250 Fourth Avenue, New York, N. Y., 1946. xiii + 1320 pages. 15.5 × 23.5 cm. Price, \$12.00.

Definite need exists for textbooks on a more advanced level than that of a number of well-known texts for first-year physical chemistry, and yet not as monumental as, for instance, Taylor's *Treatise on Physical Chemistry*. In a general way Glasstone has accomplished this objective and his book is decidedly useful for an advanced course in

general physical chemistry. It deals with a wide range of physico-chemical topics. The first two chapters, covering some 180 pages, are devoted to the presentation of the theory of atomic and molecular structure, quantum mechanics being discussed to an extent which should give the student some idea as to what it is all about, without getting him into the position of carrying out any quantum mechanical calculations. The contents of the following chapters are best indicated by their titles: First and Second Laws of Thermodynamics; The Gaseous State; The Solid State; Changes of State; The Liquid State; Physical Properties and Molecular Structure; Dilute Solutions; Phase Equilibria; Chemical Equilibrium and Free Energy; Electrochemistry; Chemical Kinetics; Surface Phenomena.