tetrone (XII) as prepared above was not depressed.

**Acknowledgments.**—The authors wish to express their appreciation to Drs. Frank R. Mayo and Cheves Walling for their interest and suggestions.

NAUGATUCK, CONN. RECEIVED NOVEMBER 9, 1950

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[CONTRIBUTION FROM THE WORCESTER FOUNDATION FOR EXPERIMENTAL BIOLOGY]

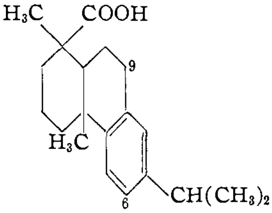
# The Preparation and Properties of Dehydroabietophenone (*nor*-Dehydroabietyl Phenyl Ketone) and 6-Hydroxydehydroabietophenone[1]

BY ROBERT P. JACOBSEN

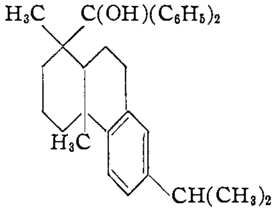
The preparation and properties of dehydroabietophenone and its 6-hydroxy derivative are described. The facile oxidation of the methylene group at $C_9$ in dehydroabietic acid and its derivatives is confirmed.

In view of reports[2,3] of the possible estrogenic activity of certain resin acid derivatives, it seemed of interest to prepare for pharmacological examination compounds related to dehydroabietic acid (I) in which the carboxyl and one or more of the alkyl groups were replaced by oxygen functions.

In this connection Zeiss[4] has reported the oxidation of non-crystalline material considered to be diphenyldehydroabietinol (II) with chromic acid at 80–90° forming benzophenone and a non-crystalline neutral product to which the structure III was assigned. Recently Brossi, Gutmann and Jeger[5] have prepared pure II, m.p. 139.5–140°, and have demonstrated that the compound undergoes decomposition, both during attempted distillation at 11 mm. and on heating 30 minutes at about 220° in vacuum, with the production of a mixture of $C_{19}H_{26-28}$ hydrocarbons together with benzophenone and benzhydrol. The principal hydrocarbon, IV, obtained in the pyrolysis of II was oxidized at 80° with chromic acid forming not III but a mixture of the 9-oxo derivatives, V and VI. These observations have been confirmed by Zeiss[6] so that the possible susceptibility of II to chromic acid degradation is still in question.



I



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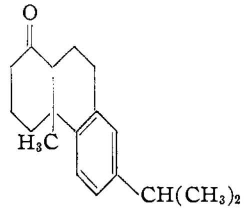
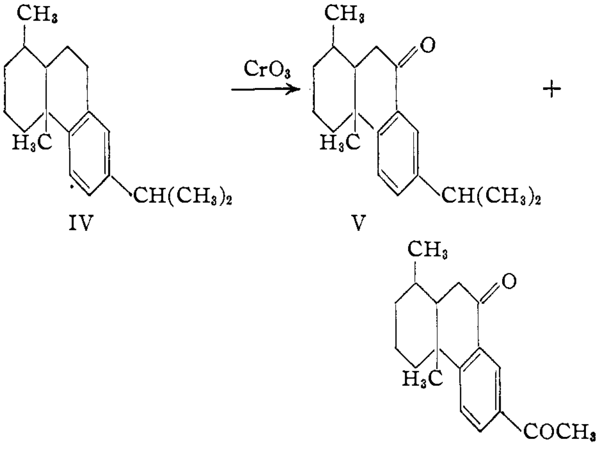


III



IV V VI

Brossi, Gutmann and Jeger succeeded in preparing III by the ozonolysis of the hydrocarbon mixture formed in the phosphorus pentachloride[7] dehydration–rearrangement of dehydroabietinol, a reaction sequence which achieves one of the aims mentioned above.

This report describes the properties of dehydroabietophenone (IX) prepared for a similar type of degradation. In the characterization of the resinous phenyl ketone several derivatives analogous to 9-oxodehydroabietic acid[8] and V were obtained by chromic acid oxidation at 20–35°.

In the preparation of IX from dehydroabietyl chloride (VII) and diphenylcadmium the product was obtained in the form of a viscous resin soluble in pentane and showing no tendency to crystallize on fractional elution with pentane from a column of alumina. This product, on prolonged heating at 130° in methanolic hydroxylamine solution, formed an amorphous solid with only three-fifths the nitrogen content calculated for the oxime; attempts to prepare a dinitrophenylhydrazone were also unsuccessful.

The reduction of crude dehydroabietophenone with aluminum isopropoxide afforded a semicrystalline product from which crystalline phenyldehydroabietinol (XI) was isolated (about 40% yield based on the acid) by virtue of its slight solubility in pentane. The pentane-soluble fraction was heated with dinitrobenzoyl chloride in pyridine providing 7% (based on the acid) of the dinitro-

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[1] The work described in ths paper was supported by a grant from G. D. Searle & Company.

[2] L. F. Fieser and W. P. Campbell, THIS JOURNAL, **61**, 2530 (1939); M. M. Baizer, M. Karnowsky and W. G. Bywater, *ibid.*, **72**, 3800 (1950).

[3] C. W. Brandt and D. J. Ross, *Nature*, **161**, 892 (1948).

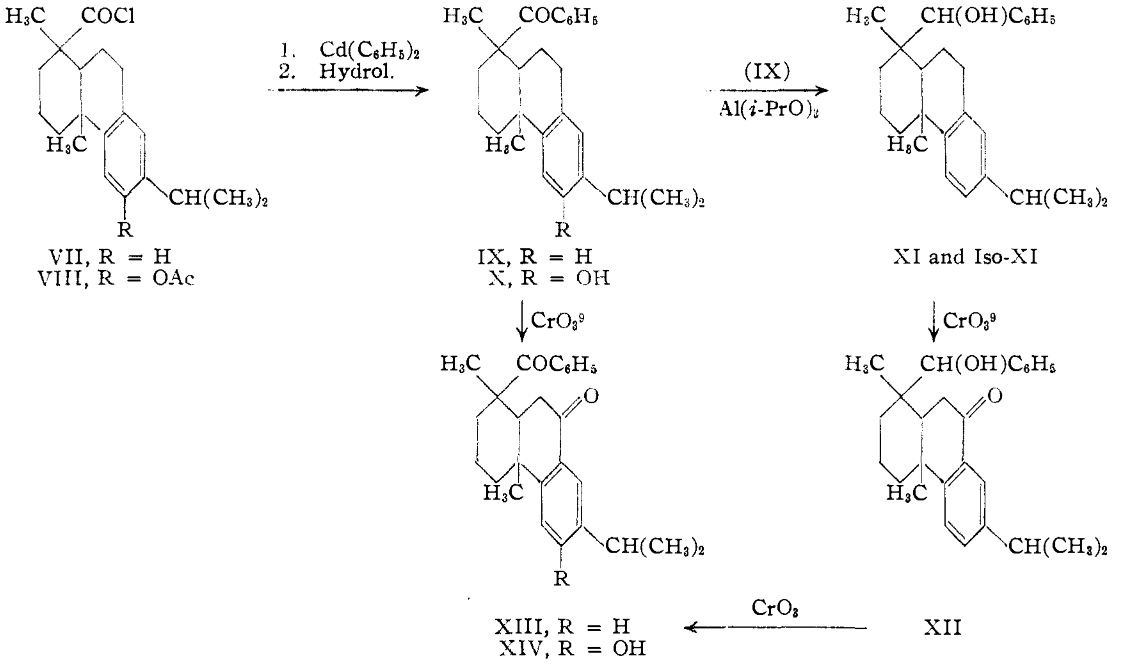
[4] H. H. Zeiss, THIS JOURNAL, **70**, 858 (1948); **69**, 302 (1947).

[5] A. Brossi, H. Gutmann and O. Jeger, *Helv. Chim. Acta*, **33**, 1730 (1950).

[6] H. H. Zeiss, THIS JOURNAL, **73**, 497 (1951).

[7] L. Ruzicka and J. Meyer, *Helv. Chim. Acta*, **5**, 589 (1922).

[8] A. E. Drake, U. S. Patent 2,434,643.



benzoate of phenylisodehydroabietinol (iso-XI). The two phenylcarbinols were characterized as described below while the remaining non-crystalline material was reserved for further study.

The acetate and benzoate of the phenylcarbinol were readily prepared but the dinitrobenzoate could be obtained only in the form of a colorless, semi-gelatinous solid which decomposed on attempted high-vacuum sublimation.

The pure phenylisocarbinol was first prepared by the high-vacuum sublimation of amorphous material regenerated from the purified dinitrobenzoate. In the manipulation of larger amounts of the substance it was isolated in the form of a crystalline methanol solvate which melted with decomposition below the boiling point of methanol re-forming the isocarbinol as a colorless resin.

Mild chromic acid oxidation of phenyldehydroabietinyl acetate afforded an amorphous solid which after saponification gave crystalline XII. This was formulated as the 9-oxocarbinol on the basis of its ultraviolet absorption spectrum as compared with that of the starting carbinol, and its resistance to oxidation with alkaline hypoiodite. Several unsuccessful attempts were made to prepare crystalline derivatives of XII; the acetate, benzoate, dinitrobenzoate and oxime appeared to be amorphous solids, while the dinitrophenylhydrazone was obtained only in poor yield under forcing conditions. However, further mild chromic acid oxidation of XII led to the formation of a crystalline product formulated as 9-oxodehydroabietophenone (XIII). This material was then used as reference compound for relating the two carbinols and their resinous precursor, IX.

The amorphous acetate prepared from pure iso-XI was oxidized with chromic acid and the saponified product corresponding to the epimer of XII was oxidized further. The final product proved to be identical with XIII prepared from the phenylcarbinol. Further, a sample of the resinous IX was oxidized at room temperature with chromic acid with the formation of XIII thus completing the characterization of the non-crystalline phenyl ketone and its crystalline reduction products.

Similar transformation products prepared from 6-hydroxydehydroabietic acid proved to be more readily characterized because of the phenolic hydroxyl group. Crystalline methyl 6-hydroxydehydroabietate[10] was converted to the amorphous acid acetate which with thionyl chloride provided the acid chloride VIII. This was treated with diphenylcadmium as before and the product was hydrolyzed affording X in 70% yield. The phenolic ketone was characterized through formation of an acetate and methyl ether. Oxidation of the former with chromic acid under mild conditions led to the 9-oxo derivative and, after saponification and acidification, to the corresponding free phenol, 6-hydroxy-9-oxodehydroabietophenone (XIV). The acetate, methyl ether and oxime of XIV were prepared.

The author wishes to express his thanks to Mr. I. E. Washburn and Mr. W. M. Selby for help in the preparation of intermediates, and to representatives of the Hercules Powder Company for technical data.

## Experimental[11]

**Dehydroabietophenone (IX).**—Crude dehydroabietyl chloride was prepared by dissolving 150 g. of the acid (dried at 100°, m.p. 172–172.5°) in 150 ml. of thionyl chloride and heating the solution for two hours at 30–35° (bath) under nitrogen.

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[9] Oxidized as the acetate followed by hydrolysis.

[10] L. F. Fieser and W. P. Campbell, THIS JOURNAL, **61**, 2532 (1939); W. P. Campbell and M. Morgana, *ibid.*, **63**, 1841 (1941).

[11] Microanalyses were performed by Dr. Robert T. Dillon and staff of the Analytical Division, G. D. Searle & Company, whose assistance in this work the author gratefully acknowledges. Melting points were taken in open Pyrex capillaries using totally immersed thermometers calibrated for total immersion. Rotations were measured in chloroform using a 2-dm. tube. Samples for analysis were dried at 110° and 0.05 mm. over phosphorus pentoxide except as otherwise noted

The product dissolved in ether–toluene mixture was then added with stirring to the reagent prepared from 14.6 g. of magnesium turnings, 62.8 ml. of bromobenzene and 60.5 g. of cadmium chloride in 600 ml. of 1:1 ether–toluene. After gently refluxing the mixture for 45 minutes it was cooled with ice and acidified with hydrochloric acid. The washed and dried solvent layer was concentrated to about 300 ml. and the volume adjusted with dry toluene to 360 ml. This solution containing an estimated 0.5 g./ml. of phenyl ketone was used directly for aluminum isopropoxide reduction.

In a smaller experiment 15 g. of the acid treated as above followed by steam distillation of the concentrated toluene solution yielded 17.6 g. of resin. This was distilled in vacuum providing 11.8 g. (65%) of IX as a colorless stiff resin, b.p. 185–190° at 0.1 mm.

**Phenyldehydroabietinol (XI).**—In the aluminum isopropoxide reduction of IX 200 ml. of the concentrated toluene solution described above was mixed with the clear decantate prepared from 15 g. of aluminum turnings (trace of mercuric chloride) and 2500 ml. of commercial 99% isopropyl alcohol. After slow distillation of this solution for about 40 hours the residue (700–900 ml.) was cooled with ice and rendered acid to congo red. By maintaining this acidity while gradually diluting the stirred mixture with 1200–1500 ml. of water the product was obtained as a granular solid. In this manner 300 g. of dehydroabietic acid provided 271 g. of crude reduction product which after recrystallization from ether–pentane afforded 151 g. (42% based on the acid) of solid melting above 154° together with about 120 g. of pentane-soluble non-crystalline material. Repeated crystallization from ether–pentane of a sample of the solid product served to raise the melting point to 160–161°; $[\alpha]^{24}\mathrm{D}$ 0.2° ($\alpha$ 0.025°, *c* 6.66).

*Anal.* Calcd. for $C_{26}H_{34}O$: C, 86.13; H, 9.45. Found: C, 86.04; H, 9.49.

**The benzoate of XI** was prepared by heating for two hours on the steam-bath 0.20 g. of the phenylcarbinol with 0.5 ml. of benzoyl chloride in 2 ml. of pyridine. On recrystallization from acetone–methanol the product formed rosettes of small leaves melting at 151.5–152.5° after drying at 80°.

*Anal.* Calcd. for $C_{33}H_{38}O_2$: C, 84.93; H, 8.21. Found: C, 84.70; H, 8.18.

**The acetate of XI**, similarly prepared with acetic anhydride in pyridine, crystallized from methanol in clumps of short needles melting at 108–109° after drying at 80°.

*Anal.* Calcd. for $C_{28}H_{36}O_2$: C, 83.12; H, 8.97. Found: C, 83.21; H, 8.92.

**The Isolation of Phenylisodehydroabietinol (iso-XI).**—The isocarbinol was separated from the non-crystalline fraction accompanying XI by heating 0.78 g. of the material in a sealed tube with 1.5 g. of 3,5-dinitrobenzoyl chloride in 15 ml. of pyridine for five hours at 95°. Moistening the oily product with acetone-methanol caused the crystallization of 0.26 g. of pale yellow solid melting at 199–205°. In several experiments the weight of this solid was about one-third that of the material treated corresponding to a yield of 7% based on the starting acid. This **isocarbinyl dinitrobenzoate** was purified by recrystallization from acetone–methanol and acetone alone forming small medallion-shaped granules melting at 205.5–207°.

*Anal.* Calcd. for $C_{33}H_{36}O_6N_2$: C, 71.20; H, 6.52; N, 5.03. Found: C, 71.29; H, 6.63; N, 4.94.

**Anhydrous isocarbinol** was prepared by the saponification of 0.96 g. of the above dinitrobenzoate with 0.5 g. of sodium hydroxide in 40 ml. of 1:1 methanol–benzene. The product was obtained in the form of a powdery solid (0.59 g.) by pouring its methanol solution into stirred dilute saline. A portion of this solid was purified for analysis by sublimation at 90–135° (bath) and 0.001 mm. The glassy sublimate sintered at 45° becoming mobile enough to flow at 70°.

*Anal.* Calcd. for $C_{26}H_{34}O$: C, 86.13; H, 9.45. Found: C, 85.99; H, 9.30.

**The solvated isocarbinol** was encountered following the saponification of 16.8 g. of dinitrobenzoate with aqueous methanolic sodium hydroxide. The dry precipitated product obtained as above was moistened with methanol whereupon the chalky powder slowly changed to crystalline solid. This was recrystallized from methanol forming 11.0 g. of laths sintering at 52–56°: $[\alpha]^{23}\mathrm{D}$ -61° ($\alpha$ −7.36°, *c* 6.06). The sample for analysis was dried at 30°.

*Anal.* Calcd. for $C_{26}H_{34}O{\cdot}CH_3OH$: C, 82.18; H, 9.71. Found: C, 82.27; H, 9.61.

**Phenyl-9-oxodehydroabietinol (XII).**—A solution of 0.20 g. of XI acetate in 3 ml. of acetic acid was mixed with 0.6 ml. of a solution (0.25 g./ml.) of chromic anhydride in 80% acetic acid and allowed to stand four hours at 27°. After dilution of the oxidation mixture with water containing a little sodium sulfite the precipitated solid (0.19 g.) was collected. This was saponified with 0.5 *N* aqueous methanolic sodium hydroxide and crystallized from methanol forming 0.13 g. (70%) of thin needles melting at 204–208°. Repeated crystallization served to raise the melting point to 207.5–210.5°; $[\alpha]^{24}\mathrm{D}$ −15° ($\alpha$ −1.29°, *c* 4.24). The ultraviolet absorption spectrum of XII showed maxima at 265 mμ (log ε 4.03) and 305 mμ (log ε 3.30) while that of the starting carbinol, XI, exhibited maxima at 263 mμ (log ε 2.79), 271 mμ (log ε 2.90) and 278 mμ (log ε 2.81).

*Anal.* Calcd. for $C_{26}H_{32}O_2$: C, 82.93; H, 8.57. Found: C, 83.06; H, 8.61.

In order to ensure complete reaction in the oxidation of larger amounts of the phenylcarbinyl acetate the reaction conditions employed were five to seven hours at 30–35°; the yield was the same as above.

When a sample of XII was treated with alkaline hypoiodite no iodoform was produced and the test portion was recovered unchanged.

**9-Oxodehydroabietophenone (XIII) (a) From XI *via* XII.**—One-half gram of the 9-oxocarbinol in 7 ml. of acetic acid was treated with 1 ml. of chromic acid solution as for the oxidation of XI acetate and allowed to stand for 5.5 hours at 26°. The product crystallized from aqueous methanol in hexagonal tablets (0.26 g., 52%) melting at 100–101°. Since this material possessed a faint yellow color it was dissolved in carbon tetrachloride and decolorized by percolation through a small column of 48–100 mesh Alorco F-10 alumina. The colorless residue, after recrystallization from aqueous methanol, melted at 103–104°; $[\alpha]^{23}\mathrm{D}$ 24° ($\alpha$ 3.03°, *c*, 6.29).

*Anal.* Calcd. for $C_{26}H_{30}O_2$: C, 83.38; H, 8.07. Found: C, 83.39; H, 7.98.

(b) **From Iso-XI.**—A 2 g. sample of the methanol solvated iso-XI was fused at 70° (bath) in a stream of dry nitrogen. The resulting anhydrous resin was heated on the steam-bath for two hours with 5 ml. of acetic anhydride and 4 ml. of pyridine. One-half (1 g.) of the crude acetylated material in 15 ml. of acetic acid was oxidized as above and the product saponified providing 0.81 g. of impure 9-oxoisocarbinol. The further oxidation of 0.5 g. of this material at 23° provided 0.14 g. (24% based on the solvated iso-XI) of crude XIII which melted at 101.5–102.5° after one crystallization from aqueous methanol.

(c) **From Crude IX.**—To a solution of 8.48 g. of dehydroabietophenone (b.p. 185–190° at 0.1 mm.) in 100 ml. of acetic acid was gradually added at 15–20° a solution of 8.75 g. of chromic anhydride in 35 ml. of 80% acetic acid. The oxidation was allowed to proceed for six hours at 35° after which the product was crystallized from carbon tetrachloride–hexane mixture affording in several crops 6.12 g. (50% as the carbon tetrachloride solvate melting in the range 80.5–85.5°) of thin yellow blades containing carbon tetrachloride of crystallization (Calcd. for $C_{26}H_{30}O_2{\cdot}CCl_4$: Cl, 26.84. Found: Cl, 25.91). Decolorization as above followed by recrystallization from aqueous methanol afforded pure XIII, m.p. 103–104°.

**6-Hydroxydehydroabietophenone (X).**—Crystalline methyl 6-hydroxydehydroabietate[10] (6.17 g., m.p. 156.5–157.5°) was saponified with 25% methanolic potassium hydroxide and the precipitated acid was acetylated to provide 6.8 g. of amorphous material. This crude acetoxy acid was converted to the acid chloride with thionyl chloride and the product treated with diphenylcadmium reagent prepared from 1.0 g. of magnesium, 4.4 ml. of bromobenzene and 4 g. of cadmium chloride. The solid product was saponified by refluxing for one hour with 100 ml. of methanol containing 10 ml. of 50% aqueous potassium hydroxide after which the diluted alkaline solution was poured into an excess of cold hydrochloric acid. The resulting precipitate (7.15 g.) was crystallized from aqueous methanol providing 4.8 g. (70% based on the phenolic methyl ester) of product in the form of small leaves melting at 155–156.5°. Purified material melted at 160.5–161.5°: $[\alpha]^{24}\mathrm{D}$ 55° ($\alpha$ 4.71°, *c* 4.29).

*Anal.* Calcd. for $C_{26}H_{32}O_2$: C, 82.93; H, 8.57. Found: C, 82.73; H, 8.74.

In a second run using twice the above amounts the yield was 71%. The phenolic phenyl ketone formed leaflets from aqueous methanol melting as above, and rods or platelets from methanol alone, m.p. 168.5–170.5°. The lower melting modification when rubbed with a trace of the latter was observed to melt at 167.5–170°.

**The acetate of X** was prepared from 3.80 g. of the phenol and 6 ml. of acetic anhydride in 10 ml. of pyridine by heating the mixture on the steam-bath for two hours. The product crystallized from methanol in glistening leaves melting at 162.5–163.5°.

*Anal.* Calcd. for $C_{28}H_{34}O_3$: C, 80.34; H, 8.19. Found: C, 80.11; H, 8.31.

**The methyl ether of X** was obtained by the portionwise addition of 2 ml. of dimethyl sulfate[12] to the hot (70–80°) stirred suspension of 0.42 g. of the compound in 10 ml. of 25% sodium hydroxide. The neutral product (0.28 g.) after recrystallization from methanol and drying at 80° melted at 134.5–136.5°.

*Anal.* Calcd. for $C_{27}H_{34}O_2$: C, 83.03; H, 8.78. Found: C, 82.90; H, 8.91.

**6-Hydroxy-9-oxodehydroabietophenone (XIV).**—A suspension of 1.05 g. of X acetate in 15 ml. of acetic acid was oxidized as described above. Following saponification of the product the free phenol was crystallized from acetone or acetone–methanol forming 0.74 g. (75%) of needles melting at 230–236°. The sample purified for analysis melted at 233.5-236.5°; $[\alpha]^{26}\mathrm{D}$ 53° ($\alpha$ 1.22°, $c$ 1.15 in dioxane). The larger needles decrepitated explosively on vacuum drying.

*Anal.* Calcd. for $C_{26}H_{30}O_3$: C, 80.08; H, 7.74. Found: C, 79.97; H, 7.90.

**The acetate of XIV** was formed by heating a sample of the above with acetic anhydride in pyridine. The ester crystallized from aqueous methanol in leaves melting at 114–115.5 after drying at 80°.

*Anal.* Calcd. for $C_{28}H_{32}O_4$: C, 77.75; H, 7.46. Found: C, 77.99; H, 7.73.

In the preparation of the **methyl ether of XIV**, 0.15 g. of the dioxophenol suspended in 8 ml. of 25% sodium hydroxide was shaken at 50–60° with 2 ml. of dimethyl sulfate added in 0.25-ml. portions. The product crystallized from aqueous methanol in leaves melting at 125.5–127.5° after drying at 80°.

*Anal.* Calcd. for $C_{27}H_{32}O_3$: C, 80.16; H, 7.97. Found: C, 80.36; H, 8.18.

A solution of 0.15 g. of XIV in methanolic hydroxylamine solution was heated in a sealed tube at 100° for three hours. The resulting **oxime** crystallized from aqueous methanol in short rods melting at 234–238° dec. (bath preheated to 210°), the melt effervescing and becoming dark red in color.

*Anal.* Calcd. for $C_{26}H_{31}O_3N$: N, 3.45. Found: N, 3.54.

ADDED IN PROOF.—Since this paper was submitted M. S. Kharasch and R. M. Acheson, *J. Org. Chem.*, 16, 447 (1951), have described the oxidative degradation of pure II to benzophenone and a mixture of ketonic substances containing little or no III.

SHREWSBURY, MASS.

RECEIVED JANUARY 24, 1951

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[12] H. H. Zeiss, U. S. Patent 2,450,706.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

# Hot Radical Reactions in the Photolysis of Methyl and Ethyl Iodides in the Liquid Phase[1,2]

BY WILLIAM H. HAMILL AND ROBERT H. SCHULER

The photolysis of liquid methyl and ethyl iodides at 2537 Å. with added radioiodine is accompanied by isotopic exchange. The photolysis of methyl iodide in cyclohexane produces cyclohexene and cyclohexyl iodide. The experimental results are consistent with a mechanism in which the primary process involves separation into an iodine atom and a hot alkyl radical. A fraction of the radicals then undergo secondary chemical reactions before they have been reduced to thermal energies. The fraction undergoing each hot radical reaction is independent of light intensity. At this wave length there appears to be no primary recombination of iodine atoms and methyl radicals.

This work was prompted by a need for information regarding the photolysis of alkyl iodides in the liquid phase at high light intensity and at high iodine concentrations in order to facilitate comparison with analogous radiolysis experiments at high fluxes of energetic X-rays and electrons.[3] The crucial postulate common to most mechanisms[4] of these photolyses is that the recombination (1) of the

$$R + I \longrightarrow RI \qquad (1)$$

alkyl radical and the iodine atom occurs by virtue of the Franck–Rabinowitch principle and that recombination with molecular iodine (2) is relatively unimportant because of the observed absence of retardation by iodine, even at appreciable

$$R + I_2 \longrightarrow RI + I \qquad (2)$$

concentrations. The absence of such retardation has been even more clearly demonstrated by the present work. If the back reaction were, indeed, due to such a cage effect then it is not evident how one is to account for a hundred-fold increase in the quantum yield for iodine formation from methyl iodide caused by a small amount of dissolved oxygen.[5]

## Experimental

Edwal Laboratories C.P. grade methyl and ethyl iodides were fractionally distilled and, except as noted, were vacuum-distilled from phosphorus pentoxide into the irradiation vessel and sealed. Eastman Kodak best grade cyclohexane was similarly treated for experiments with solutions.

The source of illumination was a Hanovia SC 2537 low pressure mercury discharge lamp in the form of a helical grid, used without filters or collimation, and operated at 350 watts. The lamp was housed in a ventilated box and the light intensity was maintained approximately constant by manual adjustment of the primary current to the high voltage transformer. Samples were exposed to illumination after the lamp had reached a steady temperature.

The 15-mm. diameter quartz tubes in which 5-ml. samples were illuminated were placed reproducibly 3 cm. from the periphery of the lamp. Any changes in geometry that occurred during this work were allowed for by using ethyl iodide itself as an actinometer.

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[1] Presented at the 115th Meeting of the American Chemical Society in San Francisco, March, 1949. From the doctoral dissertation of Robert H. Schuler, University of Notre Dame.

[2] This work was supported, in part, under contract N6 ori 165, T.O. II with the Office of Naval Research.

[3] W. H. Hamill and R. H. Schuler, to be published.

[4] For reviews see E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Corporation, New York, N. Y., 1946, p. 237, and G. K. Rollefson and M. Burton, "Photochemistry and the Mechanism of Chemical Reactions," Prentice Hall, Inc., New York, N. Y., 1939, p. 355.

[5] W. West and B. Paul, *Trans. Faraday Soc.*, **28**, 688 (1932).