[Contribution from the Chemical Laboratory of the University of Kansas]

Anodic Reductions. I. Conversion of Benzophenone to Benzopinacol by Unipositive Magnesium

By Marvin D. Rausch, William E. McEwen and Jacob Kleinberg

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When electrolysis of pyridine containing sodium iodide as the electrolyte is carried out between magnesium electrodes in a divided cell, the magnesium is oxidized to the normal dipositive oxidation state. When an organic oxidant such as benzophenone is present, however, the initial mean valence number (V_1) of magnesium falls to between one and two, and a blue colored substance, which is sensitive to air and moisture, is formed in the anolyte. Hydrolysis of the *anolyte* in either 50% acetic acid or 18% hydrochloric acid produces benzopinacol as the only reduction product, which in quantity is directly related to the amount of unipositive magnesium produced during electrolysis. It is proposed that benzophenone is reduced in the anolyte by unipositive magnesium to a metal ketyl, which upon dimerization and hydrolysis gives benzopinacol. A deep blue-violet substance which likewise is air- and moisture-sensitive is produced in the catholyte during electrolysis; upon subsequent hydrolysis, however, no benzopinacol is formed. The reduction products isolated and identified are benzhydrol, dibenzhydryl ether and a small amount of 4,4′-dipyridyl. It is postulated that the electrolytic reduction in the catholyte proceeds through the formation of a dinegative benzhydrol anion. Similar electrolyses in which fluorenone is the organic oxidant present indicate the formation of fluorenopinacol in the anolyte. This substance is believed to be formed in a manner analogous to that proposed for benzopinacol.

In a recent communication from this Laboratory[1] on the anodic oxidation of magnesium in aqueous salt solutions, it was demonstrated that, on the basis of Faraday's law, the metal dissolves anodically with an initial mean valence number (V_1) considerably less than two. This dissolution is accompanied by anodic evolution of hydrogen, in amount corresponding to oxidation from the measured mean valence state to the common dipositive magnesium cation.

That the anodic oxidation of magnesium produces the unipositive state of this metal was further demonstrated by the reduction of permanganate ion to manganese dioxide and silver ion to elementary silver in the anolyte, under conditions which did not permit the oxidizing agent to come directly in contact with the anode.

Since the electrolytic reduction of various functional groups serves as an important method of synthetic organic chemistry, it was desired to ascertain whether organic oxidants could likewise be reduced in the anode compartment of an electrolytic cell when active metals such as magnesium, aluminum, zinc, etc., were used as anodes. It is entirely possible that the reducing action of unipositive magnesium, as produced by electrolysis, might parallel the reducing action of sodium, zinc, or magnesium plus magnesium(II) iodide on many organic compounds. For example, it is possible to produce a mixture of metallic derivatives of tetrahydrodipyridyls by the action of sodium or zinc on pyridine,[2,3] and benzopinacol can be produced by the action of sodium or the binary mixture, magnesium plus magnesium(II) iodide, on benzophenone.[4,5]

The present paper deals with the behavior of magnesium electrodes in solutions of electrolytes in anhydrous pyridine, both in the absence and presence of an organic oxidant, benzophenone. Anhydrous pyridine is highly suitable as a solvent for conducting these electrolyses, since no hydrogen ion is present which can be reduced in competition with the reduction of the organic oxidant.

Experimental

Materials.—The 8-mm. magnesium rod, from which all electrodes were cut, was of 99.8% purity and was furnished by the Aluminum Company of America.[6] The sodium iodide was Merck reagent grade, and benzophenone (m.p. 48°) was obtained from the Eastman Chemical Co. The pyridine was Mallinckrodt analytic reagent grade, and was dried over anhydrous barium oxide for several weeks, fractionally distilled through a 45-cm. packed column at atmospheric pressure, and stored over additional anhydrous barium oxide until used.

Apparatus and Procedure.—The source of direct current was a full-wave mercury tube rectifier, capable of supplying up to 1000 volts. The quantity of electricity passed through the circuit was determined by means of a silver coulometer. The electrolyses were carried out in a divided cell separated by a sintered glass disc, similar to the cell described and illustrated in a previous communication.[7] All reactions were run in a constant temperature bath maintained at 40 ± 0.5°.

The magnesium electrodes (5.0 by 0.5 cm.) were thoroughly cleaned with dilute nitric acid, dried and weighed before use. The sodium iodide–pyridine solutions (0.5 *m*) were prepared in such a way as to minimize exposure to air and moisture. When electrolyses were carried out on solutions containing benzophenone, 6.00 g. of this substance was dissolved in 130 cc. of the sodium iodide solution. The 130-cc. portions of pyridine solution were divided equally and placed in the two compartments of the divided electrolytic cell. In all electrolyses, there was no noticeable change in height of the solution in either compartment. Dry oxygen-free nitrogen was passed through the pyridine solution prior to electrolysis and maintained over the surface of both anolyte and catholyte during electrolysis. All electrolyses were made at a potential of 20 to 30 v., the current density being between 0.003 and 0.004 amp. per sq. cm. After electrolysis, the magnesium electrodes were thoroughly cleaned with distilled water, dried and weighed.

Isolation of Products from the Anolyte.—The entire contents of the anode compartment from a run in which V_1 was equal to 1.834, consisting of a blue solid suspended in a blue solution, were added to 300 cc. of freshly boiled 18% hydrochloric acid. The blue color was discharged instantly. Upon standing at room temperature for 24 hours, a colorless crystalline material precipitated. This was collected by filtration, washed with water and dried, 1.66 g. of material being obtained. This solid was digested with 30 cc. of hot petroleum ether, and the insoluble residue was then dissolved in a minimum amount of chloroform. Addition of

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[1] R. L. Petty, A. W. Davidson and J. Kleinberg, This Journal, **76**, 363 (1954).

[2] B. Emmert, *Ber.*, **47**, 2598 (1914); **49**, 1060 (1916); **50**, 31 (1917); B. Emmert and R. Buchert, *ibid.*, **54**, 204 (1921).

[3] O. Dimroth and R. Heene, *ibid.*, **54**, 2934 (1921); O. Dimroth and F. Frister, *ibid.*, **55**, 1223 (1922).

[4] W. E. Bachmann, This Journal, **55**, 1179 (1933).

[5] M. Gomberg and W. E. Bachmann, *ibid.*, **49**, 236 (1927).

[6] The authors hereby express their appreciation for this courtesy.

[7] A. W. Davidson and F. Jirik, This Journal, **72**, 1700 (1950); Fig. 1.

an excess of 95% ethanol to the chloroform solution caused precipitation of 0.405 g. (98% current yield) of benzopinacol, m.p. 185–186°. Recrystallization from chloroform and ethanol yielded crystals, m.p. 187–188°[8] (reported m.p. 188–189°),[4] also in admixture with an authentic sample of benzopinacol prepared by the method of Gomberg and Bachmann.[5] The infrared spectra of the two samples (in chloroform solution) were identical. Also, the benzopinacol was rearranged to benzopinacolone, m.p. 180–181° (reported m.p. 179–180°),[5] by the method described by Fieser.[9]

Evaporation of the petroleum ether extract afforded 1.26 g. of benzophenone, m.p. 47–48°.

In another run, an attempt was made to achieve a quantitative recovery of organic material from the anolyte hydrolysate. From 3.00 g. of benzophenone originally present in the anode compartment, 2.51 g. of material precipitated from the acid solution on prolonged standing, from which benzopinacol and benzophenone could be obtained as described above. Saturation of the acid filtrate with sodium chloride caused an additional 0.14 g. of benzophenone to precipitate. Finally, ether extraction of the filtrate afforded an additional 0.07 g. of benzophenone, for a total recovery of 2.72 g. of organic material.

Several runs were carried out in which 6.00 g. of fluorenone was dissolved in 130 cc. of the sodium iodide solution, and the same general procedure was followed as described above for benzophenone. Following hydrolysis in freshly boiled 18% hydrochloric acid, fluorenopinacol separated together with a considerable amount of fluorenone; the similarity of solubility of these substances complicated isolation of the fluorenopinacol.

Isolation of Products from the Catholyte.—In a typical run, the entire contents of the catholyte were added to 300 cc. of freshly boiled 50% acetic acid. The deep blue-violet color was discharged instantly, but no solid product separated. About 100 cc. of concentrated hydrochloric acid was added, and the solution was extracted ten times with ether. The ether layer was washed with dilute sodium carbonate solution and dried over anhydrous calcium chloride. The ether was removed, and the solid residue, 1.65 g., dissolved completely in hot petroleum ether. Since no residue remained, no benzopinacol was present, as it is relatively insoluble in hot petroleum ether. The petroleum ether solution was cooled, and 1.35 g. (58% current yield), of crystals of benzhydrol separated, m.p. 64–66°. The benzhydrol was recrystallized from hot ligroin, m.p. 66.5–67.5° (reported m.p. 67–68°),[10] also in admixture with an authentic sample of benzhydrol. The infrared spectra of the two samples (in chloroform solution) were identical. Also, a derivative was prepared, benzhydryl N-phenylcarbamate, m.p. 138–140° (reported m.p. 139–140°).[11]

Evaporation of the petroleum ether extract afforded 0.30 g. of benzophenone, m.p. 47–48°.

In several runs, a second product was isolated in variable amounts from the ether extraction of the acidic catholyte hydrolysate. This product was less soluble than either benzophenone or benzhydrol in petroleum ether, and was recrystallized from hot ligroin, m.p. 108–110°. The product was identified as dibenzhydryl ether by a mixed melting point test with an authentic sample, m.p. 109–110°, prepared by the method of Knoevenagel and Heckel.[12] The infrared spectra of the two samples (in chloroform solution) were identical.

In contrast to the behavior of the anolyte, ether extraction of the catholyte solution, made basic by the addition of sodium hydroxide solution, produced still a third product. After distillation of the ether and pyridine, a small quantity of 4,4′-dipyridyl separated; 170 mg., m.p. 107–110° (reported m.p. 111–112°).[3] The dihydrate had a melting point of 69–72° (reported m.p. 73°).[3] Furthermore, the infrared spectrum (in chloroform solution) was identical with that of an authentic sample, prepared by the methods of Wibaut and Arens[13] and Dimroth and Heene.[3]

In another run, an attempt was made to achieve a quantitative recovery of organic material from the catholyte. After acidification with 18% hydrochloric acid, continuous ether extraction over a period of 24 hours produced 2.79 g. of material (from an original 3.00 g. of benzophenone), from which benzophenone, benzhydrol and dibenzhydryl ether could be obtained as described above. The catholyte hydrolysate was made basic with sodium hydroxide solution, and the pyridine removed by distillation with steam. Ether extraction produced 0.16 g. of a solid, from which 4,4′-dipyridyl could be isolated.

Results and Discussion

Anodic Oxidation of Magnesium in Sodium Iodide–Pyridine Solutions.—Initial experiments were conducted to find a suitable electrolyte. Fortunately, a considerable number of inorganic salts are soluble to some degree in anhydrous pyridine.[14] It was found that sodium iodide was best suited as an electrolyte, since it was moderately soluble and yielded solutions of fair conductance. It was necessary, however, that the potential be kept low enough to prevent anodic oxidation of the iodide ion. When oxidation of iodide ion occurred, the initial mean valence number (V_1) of the magnesium anode was always greater than two.

The extent of departure from normal current efficiency may be expressed by the initial mean valence number, V_1, of the magnesium cation produced. This has been calculated in conformity with the practice in previous communications,[1,15] by means of the equation

$$V_1 = \frac{\text{wt. of Ag deposited in coulometer} \times 24.32}{107.88 \times \text{wt. of Mg. lost from anode}}$$

It should be pointed out that control experiments were conducted under the same conditions of temperature and electrolyte concentration, and over the same time interval as the electrolyses. In every case, direct non-electrolytic reaction between magnesium and electrolyte was negligible. Further, measurements indicated that no loss in weight of the magnesium cathode occurred during the electrolyses.

A series of typical initial mean valence numbers is shown in Table I. These electrolyses were conducted for various time intervals, with magnesium anodes and cathodes in solutions of pyridine containing sodium iodide as the electrolyte.

TABLE I

ELECTROLYSES IN PYRIDINE

Electrolyte: 130 cc. of 0.5 *m* NaI in pyridine; Mg electrodes, 40°, 20–30 v., 0.003–0.004 amp. per sq. cm.

Time of electrolysis, min.	V_1	Time of electrolysis, min.	V_1
30	1.98	30	2.01
20	2.00	20	2.00
15	2.03	25	2.03

The data demonstrate that when magnesium is oxidized in pyridine containing only sodium iodide, the V_1 is almost exactly 2.00, and that magnesium is converted therefore solely to its familiar dipositive state.

Anodic Oxidation of Magnesium in Solutions of Pyridine Containing Sodium Iodide and Benzophenone.—Since the anodic oxidation of mag-

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(8) All melting points are corrected.

(9) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1941, p. 204.

(10) J. F. Norris and C. Banta, THIS JOURNAL, **50**, 1807 (1928).

(11) E. Bergmann and D. Wagenberg, *Ber.*, **63**, 2587 (1930); note 7.

(12) E. Knoevenagel and W. Heckel, *ibid.*, **36**, 2827 (1903).

(13) J. P. Wibaut and J. F. Arens, *Rec. trav. chim.*, **61**, 59 (1942).

(14) L. F. Audrieth and J. Kleinberg, "Non-Aqueous Solvents," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 123.

(15) A. D. McElroy, J. Kleinberg and A. W. Davidson, THIS JOURNAL, **74**, 736 (1952).

nesium in solutions of pyridine containing sodium iodide alone appeared to proceed in a normal fashion, it was decided to study the effect of the presence of organic oxidants on the initial mean valence number. Accordingly, a series of organic compounds, *e.g.*, benzaldehyde, nitrobenzene, benzonitrile, etc., were added to the pyridine solutions containing sodium iodide, and the V_1 values in a number of cases were found to be appreciably less than two, suggesting the formation of unipositive magnesium.[16]

A unique result was encountered when benzophenone was the organic oxidant. Under conditions similar to those described above for solutions containing only sodium iodide and over varying time intervals, the V_1 was always between 1.30 and 1.85. Further, in a matter of seconds after the electrolysis was begun, a blue product began forming at the magnesium anode. Upon extended electrolysis, this blue color spread throughout the anode compartment. Control experiments indicated that in these electrolyses, also, direct non-electrolytic reaction between magnesium and the electrolyte was negligible. Moreover, the anolyte material did not atttack the magnesium electrode once electrolysis had been terminated. The blue solution in the anode compartment was quite sensitive to air and moisture, and the color was immediately discharged upon exposure to the atmosphere.

The color and behavior of the product in the anode compartment appeared to be quite analogous to the properties reported for metal ketyls.[4,5,17] Since it has been reported[5] that benzopinacol is formed upon the hydrolysis with 10% acetic acid of metal ketyl solutions derived from benzophenone, similar experiments were carried out on the anolyte to determine whether metal ketyl was indeed present. From the acid hydrolyzed anolyte, benzopinacol was actually isolated. Furthermore it has proved possible to correlate the quantity of magnesium oxidized to the unipositive state at the anode with the amount of benzopinacol isolated from the anode compartment on the assumption that the benzopinacol results from an initial reduction of benzophenone to a ketyl radical-ion by unipositive magnesium. Data and yields of benzopinacol are given in Table II for several electrolyses.

TABLE II

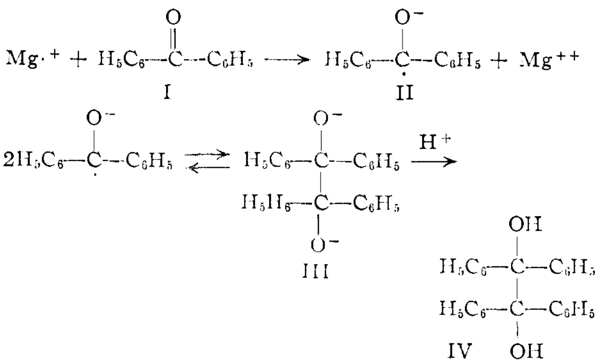
ANODIC BEHAVIOR OF MAGNESIUM IN PYRIDINE SOLUTIONS CONTAINING BENZOPHENONE

Electrolyte: 130 cc. of 0.5 *m* NaI in pyridine containing 6.00 g. of benzophenone; Mg electrodes. 40°, 20–30 v. 0.003–0.004 amp. per sq. cm.

Time of electrolysis, hr.	Hydrolysis medium	Wt. of Mg dissolved, g.	V_1	Benzopinacol, mg. Calcd.	Benzopinacol, mg. Found	Yield, %
10.5	50% HAc	0.3787	1.63	1050	820	82
12.0	18% HCl	.3252	1.67	806	740	92
12.0	18% HCl	.3290	1.83	412	405	98

The data for the formation of the benzopinacol can most reasonably be interpreted by the mechanism of reaction

$$\mathrm{Mg} \longrightarrow \mathrm{Mg}\cdot^{+} + e^{-}$$



The magnesium anode is oxidized in part to unipositive magnesium ion. This potent reducing agent reacts with benzophenone (I) to form the colored ketyl radical-ion II and thereby is oxidized to the normal dipositive magnesium cation. Two ketyl radicals formed in this manner dimerize to form the dinegatively charged pinacolate ion III, which after hydrolysis in either 50% acetic acid or 18% hydrochloric acid yields benzopinacol (IV).[18] The yield of benzopinacol therefore is directly dependent upon the amount of unipositive magnesium ion produced.

Further support for such a mechanism of benzopinacol formation is indicated by the following observations: (1) The *sole reduction product* isolated from the anode compartment was benzopinacol. (2) In none of the electrolyses was more benzopinacol isolated than that amount theoretically calculated on the basis of the mechanism proposed. (3) The nearly quantitative recovery of organic material from each of the anolyte and catholyte in the various electrolyses showed that no appreciable transference of organic material from one compartment to the other had occurred. (4) The blue color which formed at the anode was visible within 10 to 15 seconds following the application of the current. This fact, together with those listed above, would rule out the formation of benzopinacol in the anode compartment by a mechanism involving the prior migration of an organic anion, such as V (discussed below), to the anode compartment. (5) The anolyte following electrolysis did not attack magnesium. Since, in such an experiment following electrolysis, both magnesium and magnesium(II) iodide would be present in pyridine solution together with benzophenone, there is no reduction of benzophenone to benzopinacol by a process such as that described for the binary mixture, magnesium plus magnesium(II) iodide.[5] This fact therefore would eliminate also such a process as a possibility during the electrolysis itself.

Products Obtained from the Cathode Compartment.—In the cathode compartment during the electrolysis of pyridine containing sodium iodide and benzophenone, a deep blue color developed at the cathode immediately upon application of the current. A deep blue-violet layer formed at the top of the catholyte after several hours, and upon

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(16) M. D. Rausch, W. E. McEwen and J. Kleinberg, unpublished information.

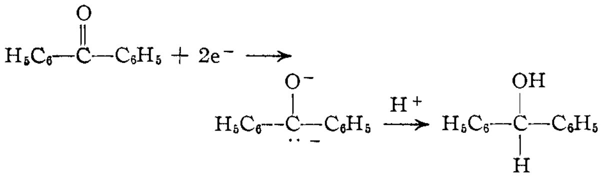
(17) E. Beckmann and T. Paul, *Ann.*, **266**, 1 (1891); W. Schlenk and T. Weickel, *Ber.*, **44**, 1182 (1911); W. Schlenk and A. Thal, *ibid.*, **46**, 2840 (1913).

[18] It was found that a better yield of benzopinacol was obtained when the hydrolysis was carried out in 18% hydrochloric acid rather than aqueous acetic acid, as recommended by Bachmann.[4]

extended electrolysis this color diffused throughout the catholyte, stopping at the glass disc separating the two compartments.

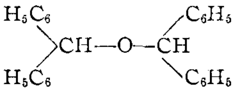
Since electrolytic reduction occurs at the cathode, and since a color is formed resembling that developed in the anolyte, it was anticipated that acid hydrolysis of the catholyte might likewise produce an excellent yield of benzopinacol. In every case, however, hydrolysis of the deep blue-violet catholyte did not produce any detectable amount of this product. Instead, three different products resulting from electrolytic reduction were isolated. By far the major product obtained was benzhydrol (VI), which was isolated in 50–60% current yields. A second neutral product was isolated in variable yield; this substance proved to be dibenzhydryl ether (VII). Formation of this product is not unreasonable, since it is known that benzhydrol can be converted readily to dibenzhydryl ether.[19] A third basic product containing nitrogen proved to be 4,4′-dipyridyl (VIII), which was isolated in only small amounts. This undoubtedly arose by air oxidation of initially formed tetrahydro-4,4′-dipyridyl.

Since no evidence was found in any of the electrolyses for the formation of benzopinacol, it is postulated that the primary reaction occurring in the catholyte is

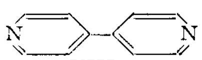


$$H_5C_6-\overset{\overset{O}{\|}}{C}-C_6H_5 + 2e^- \longrightarrow H_5C_6-\underset{\cdot\cdot\ -}{\overset{\overset{O^-}{|}}{C}}-C_6H_5 \xrightarrow{H^+} H_5C_6-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-C_6H_5$$

V VI



VII

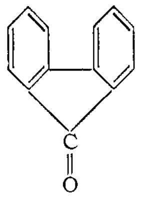


VIII

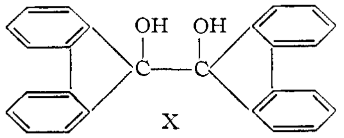
Benzophenone accepts two electrons from the electron-rich cathode and a dinegative benzhydryl anion V is formed; acid hydrolysis of this anion yields benzhydrol (VI). Such an anion as V has been reported to be formed by the action of sodium on benzophenone in ether–benzene solutions.[4,20] This anion has also been reported in the reduction of benzophenone by sodium in liquid ammonia.[21] The solutions formed in these reductions were blue-violet in color.

The small quantity of 4,4′-dipyridyl isolated in several of the electrolyses indicates that solvent pyridine molecules are reduced to only a slight extent in the cathode compartment when benzophenone is present, the latter evidently being preferentially reduced.

Anodic Oxidation of Magnesium in Solutions of Pyridine Containing Sodium Iodide and Fluorenone.—Several electrolyses were carried out in which the organic oxidant present was fluorenone (IX). Again, the V_1 was less than two, falling to between 1.60 and 1.80. From the acid-hydrolyzed anolyte small amounts of fluorenopinacol (X) were isolated.



IX



X

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[19] G. Oddo, *Gazz. chim. ital.*, **37** (2), 362 (1907); G. Stadnikov, *J. Russ. Phys. Chem. Soc.*, **47**, 1124 (1915); *Ber.*, **57**, 7 (1924).

[20] W. Schlenk and E. Weickel, *Ann.*, **464**, 25 (1928).

[21] C. B. Wooster, THIS JOURNAL, **50**, 1388 (1928).

LAWRENCE, KANSAS

[CONTRIBUTION FROM DANIEL SIEFF RESEARCH INSTITUTE, WEIZMANN INSTITUTE OF SCIENCE]

Studies in the Alicyclic Series. Part II.[1] Synthesis and Reactions of 2-Phenylcyclopent-2-enone

BY YAACOV AMIEL,[2a] ALFRED LÖFFLER AND DAVID GINSBURG[2b]

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2-Phenylcyclopent-2-enone has been prepared through the nitrosochloride of 1-phenylcyclopentene. The ketone undergoes Michael condensation to yield adducts which may be used for the clarification of certain stereochemical problems.

The value of 2-arylcyclohex-2-enones as intermediates in the synthesis of morphine has been demonstrated,[3] and the use of 2-phenylcyclohept-2-enone in the synthesis of compounds structurally related to colchicine has been reported.[4] In this communication, the synthesis of 2-phenylcyclopent-2-enone (I) through the nitrosochloride of 1-phenylcyclopentene is reported. The ketone has been employed in a number of transformations, permitting clarification of certain stereochemical problems.

The nitrosochloride of 1-phenylcyclopentene was prepared by treatment of the olefin with *n*-amyl nitrite in the presence of hydrochloric acid. The nitrosochloride was a colorless micro-crystalline product which was very unstable, and care must be taken in order to avoid its spontaneous decompo-

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[1] D. Ginsburg, Part I, *J. Chem. Soc.*, 2361 (1954).

[2] (a) Part of this work forms a portion of a thesis presented by Y. Amiel in partial fulfillment of the requirements of the Ph.D. degree, Hebrew University, Jerusalem. (b) Present address: Israel Institute of Technology, Haifa, Israel. Inquiries should be referred to this author.

[3] D. Ginsburg and R. Pappo, *J. Chem. Soc.*, 516, 938 (1951).

[4] D. Ginsburg and R. Pappo, THIS JOURNAL, **75**, 1094 (1953).