[Contribution from the Department of Chemistry of the University of Kansas]

Anodic Reductions. II. Conversion of 2-Methoxyphenyl Mesityl Ketone to 2,2'-Dimesitoylbiphenyl by Unipositive Magnesium

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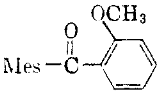
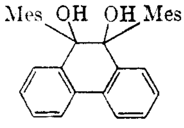
The anodic oxidation of magnesium in sodium iodide-pyridine solutions results in the conversion of the metal to the normal dipositive condition. In the presence of each of the organic oxidants, 2-methoxyphenyl mesityl ketone and 2,2'-dimesitoylbiphenyl, magnesium is anodically oxidized to a mixture of uni- and di-positive states. The unipositive magnesium brings about reduction of the organic oxidants. From 2-methoxyphenyl mesityl ketone there was obtained 2,2'-dimesitoylbiphenyl and a polymeric substance. 2,2'-Dimesitoylbiphenyl afforded only polymeric material.

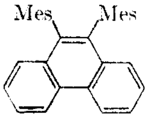
The reduction of 2-methoxyphenyl mesityl ketone (I) by the binary mixture magnesium-magnesium iodide has been shown by Fuson and coworkers to yield 9,10-dimesityl-9,10-dihydro-9,10-dihydroxyphenanthrene (II) and 9,10-dimesitylphenanthrene (III).[1,2] Although it is probable that 2,2'-dimesitoylbiphenyl (IV) was formed as an intermediate in this reduction, this compound was not isolated.



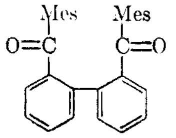
I



II



III



IV

Recently it has been demonstrated in this Laboratory[3] that benzophenone can be reduced to benzopinacol by unipositive magnesium generated by the anodic oxidation of the metal in sodium iodide-pyridine solutions. The present communication describes the reduction of 2-methoxyphenyl mesityl ketone (I) to 2,2'-dimesitoylbiphenyl (IV) by +1 magnesium produced anodically. Neither 9,10-dimesityl-9,10-dihydro-9,10-dihydroxyphenanthrene (II) nor 9,10-dimesitylphenanthrene (III) were found among the reduction products.

In the anodic oxidation of magnesium in sodium iodide-pyridine solutions containing 2-methoxyphenyl mesityl ketone (I) the metal enters solution with a V_i value (initial mean oxidation number) of 1.88–1.92; in the absence of the ketone a V_i value of two is obtained. The V_i value gives a measure of the extent of departure from normal current efficiency and is calculated from the loss in weight of the anode and the number of Faradays of electricity passing through the solution as determined by means of a silver coulometer. (See Experimental.). A V_i value lower than two for magnesium is taken as evidence that the metal enters solution as a mixture of the uni- and dipositive states. Since no unipositive magnesium is found in solution after electrolysis, it is considered that this species is oxidized to the common dipositive state by ketone I. Indeed, 2,2'-dimesitoylbiphenyl (IV), a reduction product of ketone I, is found when the anolyte is hydrolyzed after electrolysis. It is noteworthy that the reduction does not proceed as far as when the binary mixture magnesium-magnesium iodide is used as reducing agent.

In contrast to the previously reported[3] example of "anodic reduction," namely the conversion of benzophenone to benzopinacol, in which there was an excellent correlation between the quantity of magnesium oxidized to the unipositive state and amount of organic reduction product recovered from the anolyte, in the case herein reported the recovery of identifiable reduction product (IV) amounted to approximately 36–40% of that expected from the quantity of +1 magnesium formed. In addition to IV a relatively large amount of unidentified polymeric material was also isolated from the anolyte. It is highly probable that the polymeric material represents another reduction product, and one very likely derived from IV, in as much as an apparently identical polymeric substance was obtained upon the "anodic reduction" of IV.

In all the electrolyses the catholyte consisted merely of sodium iodide dissolved in pyridine. After electrolysis the catholyte solution was hydrolyzed and 4,4'-dipyridyl was isolated. This compound undoubtedly arose from air oxidation of tetrahydro-4,4'-dipyridyl, the conjugate base of which was formed by cathodic reduction of the solvent.

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EXPERIMENTAL

The electrolyses were carried out in a divided cell between magnesium electrodes, as described in a previous com-

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(1) Fuson and Hornberger, *J. Org. Chem.*, 16, 637 (1951).

(2) Fuson and Kerr, *J. Org. Chem.*, 19, 373 (1954).

(3) Rausch, McEwen, and Kleinberg, *J. Am. Chem. Soc.*, 76, 3622 (1954).

munication.[3] The initial mean oxidation number, V_i, was calculated by use of the equation[4,5]

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

A study was made of the anodic behavior of magnesium in sodium iodide-pyridine solutions containing 2-methoxyphenyl mesityl ketone (I) in the anolyte. The results are shown in Table I. It is apparent from the data cited that the presence of I causes a marked lowering of the V_i from a normal value of 2. It should be emphasized that control experiments showed that there was no non-electrolytic attack on magnesium by the anolyte mixture.

TABLE I

ANODIC OXIDATION OF MAGNESIUM IN NaI-PYRIDINE SOLUTIONS CONTAINING 2-METHOXYPHENYL MESITYL KETONE

Anolyte: 65 ml. of 0.5 *m* NaI in pyridine, also containing 400 mg. of 2-methoxyphenyl mesityl ketone

Catholyte: 65 ml. of 0.5 *m* NaI in pyridine

Temp. 40°: 20–40 v; 0.002–0.015 amp. per sq. cm.

Time of electrolysis, hr.	V_i[a]
6	1.87
11.5	1.88
20	1.89
21	1.91
22.5	1.92
27	1.92
60	1.90

[a] V_i in NaI-pyridine solutions in absence of ketone: 1.98, 2.00, 2.03, 2.01, 2.00, 2.03.

After an electrolysis in which the V_i was equal to 1.92, the entire contents of the anolyte compartment were added to 300 ml. of freshly boiled 18% hydrochloric acid. After the hydrolysate had stood for 24 hr., a solid material which had precipitated was collected by filtration. The filtrate was extracted with ten 50-ml. portions of ether. The original precipitate was dissolved in the ether extract, which was then washed with dilute sodium carbonate solution, dilute sodium thiosulfate solution and water, after which it was dried over sodium sulfate. The ether was removed by distillation, and the residue was dissolved in the minimum amount of hot ethanol. From the cooled solution, 75 mg. of a solid, m.p. 175–190°, crystallized. Fractional crystallization of this solid from ligroin gave 10 mg. of 2,2′-dimesitoylbiphenyl (IV), m.p. 226–228°; reported 228°.[4] The m.p. of an authentic sample[6] of 2,2′-dimesitoylbiphenyl was not depressed upon admixture of the material of m.p. 226–228°. The infrared spectra of the two samples in chloroform solution were identical.

Because of the similar solubilities of 2-methoxyphenyl mesityl ketone (I) and 2,2′-dimesitoylbiphenyl (IV) in organic solvents, it proved impossible to achieve quantitative separation of these compounds by fractional crystallization. Therefore, as a means of analyzing the solid mixture resulting from hydrolysis of the anolyte, an ultraviolet spectrophotometric determination was employed. Compound I in 95% ethanol solution exhibited absorption maxima at 255 and 317 mμ with ϵ_{max} value of 10,500 and 4380, respectively. Compound IV gave an absorption maximum at 255 mμ (ϵ_{max} 19,600) and an absorption shoulder extending from 280 to 300 mμ. It was found possible to analyze synthetic mixtures of the two compounds with an accuracy of ±5% by solving two simultaneous equations of the type

$$D = \epsilon_I C_I l + \epsilon_{IV} C_{IV} l$$

(l = cell length; C_I = molar concentration of compound I; C_{IV} = molar concentration of compound IV; D = optical density)

the optical density and ϵ_{max} values at 255 and 317 mμ being employed.

In a typical electrolysis in which the V_i value was 1.90 the anolyte was added to 300 ml. of freshly boiled 18% hydrochloric acid. The solid material which precipitated was collected and dissolved in ether. The filtrate was extracted with ether in a continuous extraction apparatus and the extract was combined with the ether solution of the original solid. The ethereal solution was washed with dilute sodium carbonate solution, dilute aqueous sodium thiosulfate, and water, after which it was dried over magnesium sulfate. Distillation of the ether left a residue which was extracted with 95% ethanol. A significant quantity of a polymeric material remained undissolved. The ethanol extract was analyzed by the spectrophotometric method described above. A 38% current yield (in terms of the amount of unipositive magnesium produced) of 2,2′-dimesitoylbiphenyl (IV) was obtained. As a check, an ultraviolet absorption spectrum was taken on a synthetic mixture of I and IV containing the latter in the percentage found above. This spectrum was superposable with the one obtained with the material from the anolyte. Furthermore, infrared spectra of the anolyte and synthetic mixtures in chloroform solution were essentially identical. These facts would appear to show that the ethanol-soluble material from the anolyte consisted solely of a binary mixture of the reduction product, 2,2′-dimesitoylbiphenyl (IV), and the starting compound, 2-methoxyphenyl mesityl ketone (I).

A survey was next made of the anodic behavior of magnesium in sodium iodide-pyridine solutions containing 2,2′-dimesitoylbiphenyl (IV) in the anolyte. A summary of the V_i values found is given in Table II. In as much as control experiments showed that magnesium was not attacked non-electrolytically by the anolyte mixture, and since no +1 magnesium was found after electrolysis, the V_i values obtained demonstrate that 2,2′-dimesitoylbiphenyl is reduced by unipositive magnesium produced anodically. After an electrolysis in which the V_i value was 1.95, the entire contents of the anolyte were added to 300 ml. of freshly boiled 20% hydrochloric acid. After the hydrolysate had stood for 24 hr., a solid material which had precipitated was collected. The filtrate then was extracted with ether in

TABLE II

ANODIC OXIDATION OF MAGNESIUM IN NaI-PYRIDINE SOLUTIONS CONTAINING 2,2′-DIMESITOYLBIPHENYL

Anolyte: 65 ml. of 0.5 *m* NaI in pyridine, also containing 400 mg. of 2,2′-dimesitoylbiphenyl

Catholyte: 65 ml. of 0.5 *m* NaI in pyridine

Temp. 40°: 20–40 v; 0.002–0.015 amp. per sq. cm.

Time of electrolysis, hr.	V_i
2	1.94
7	1.93
9	1.96
12	1.93
22	1.95

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(4) Petty, Davidson, and Kleinberg, *J. Am. Chem. Soc.*, **76**, 363 (1954).

(5) McElroy, Kleinberg, and Davidson, *J. Am. Chem. Soc.*, **74**, 736 (1952).

(6) We are indebted to Professor R. C. Fuson for supplying us with this compound.

a continuous extractor, and the extract was washed with dilute sodium carbonate solution, dilute sodium thiosulfate solution, and water, after which it was dried over magnesium sulfate. Distillation of the ether left a solid residue which was combined with the original precipitate to give a total of 397 mg. of solid. (The amount of 2,2′-dimesitoylbiphenyl originally in the anolyte was 400 mg.). The solid was extracted with chloroform, leaving about 80 mg. of insoluble material which appeared to be polymeric in nature and which resembled the polymeric substance obtained in the experiments with 2-methoxyphenyl mesityl ketone. It seems highly probable that the polymer results from an initially formed reduction product of 2,2′-dimesitoylbiphenyl. The infrared spectrum of the chloroform extract was identical with that of the starting material, and evaporation of the chloroform solution gave pure 2,2′-dimesitoylbiphenyl.

In all the electrolyses the catholyte consisted merely of sodium iodide dissolved in pyridine. It is interesting that the only reduction product identified after hydrolysis of the catholyte solution was 4,4′-dipyridyl, which was obtained in 20–30% current yield. This product was undoubtedly formed by the hydrolysis and air oxidation of some reduction product of the solvent, probably the conjugate base of tetrahydro-4,4′-dipyridyl.[3] In addition to the dipyridyl, a relatively large quantity of high molecular weight substances containing nitrogen (polypyridyls?) was obtained from the catholyte.

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