The Electrolytic Reduction of Ketones at a Mercury Cathode.—Preparation of Organomercuric Compounds

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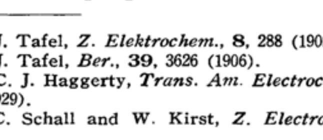
Tafel(1) reported that on an electrolytic reduction, acetone might be reduced to isopropyl alcohol at a mercury cathode, and later he reported(2) that methyl ethyl ketone was reduced to diisobutyl mercury at a mercury cathode, and acetone to diisopropyl lead at a lead cathode. Haggerty(3) investigated the possibility of preparing diisobutyl mercury from acetone in a sulfuric acid solution at a mercury cathode. Dimenthyl mercury(4) was also obtained from menthone in a strong sulfuric acid electrolyte at a mercury cathode at a higher temperature.

It has been thought that on electrolytic reduction of ketones in a sulfuric acid solution at a mercury cathode, organomercury compounds are produced according to the following formula:



$$2\,{}^{R}_{R}\!>\!C{=}O + 6H^+ + 6F + Hg \rightarrow {}^{R}_{R'}\!>\!CH{-}Hg{-}CH\!<\!{}^{R}_{R'} \qquad (1)$$

and when the organomercury compounds obtained are treated with mercuric halide in an alcoholic solution, organomercuric halides are prepared as follows:

$$R{-}CH_2{-}Hg{-}CH_2{-}R + HgX_2 \rightarrow 2R{-}CH_2{-}HgX \qquad (2)$$

It has been also recognized that when they are treated with hydrogen chloride gas in an alcoholic solution, organomercuric chloride and hydrocarbon are obtained:

$$R{-}CH_2{-}Hg{-}CH_2{-}R + HCl \rightarrow R{-}CH_2HgCl + R{-}CH_3 \qquad (3)$$

The author has investigated electrolytic reduction of aryl alkyl ketones and cyclic ketones and prepared organomercury compounds from several ketones by using a diluted sulfuric acid solution at a mercury cathode at a higher temperature. Phenylacetone, acetylbenzoyl(5), cyclopentanone, cyclohexanone, and methylcyclohexanone were reduced to organomercury compounds, and their halides were prepared. These organomercury compounds were shown in Table II. The preparation of other ketones, namely, acetophenone, propiophenone, *p*-methylacetophenone, *p*-bromoacetophenone, benzoin, benzil, 1-acetonaphthone, and dibenzyl ketone were tried in this experiment in the same way, but mercury compounds were not obtained, and corresponding pinacol and alcohol were produced.

In general, it is thought that ketones which have carbonyl radical adjacent to phenyl radical are not reduced to mercury compounds.

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1) J. Tafel, *Z. Elektrochem.*, **8**, 288 (1902).

2) J. Tafel, *Ber.*, **39**, 3626 (1906).

3) C. J. Haggerty, *Trans. Am. Electrochem. Soc.*, **56**, 421 (1929).

4) C. Schall and W. Kirst, *Z. Electrochem.*, **29**, 537 (1923).

5) T. Arai, unpublished.

Organomercury compounds were synthesized by many kinds of methods, and dicyclohexyl mercury and its halides were already obtained purely chemically[6,7], but other compounds obtained in this experiment, were not prepared by pure chemical methods. In this experiment the yield of organomercury compounds was not very good; this method, however, seems to be an easy and effective method of syntheses.

Experiment and Discussion

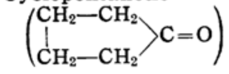
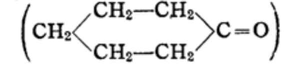
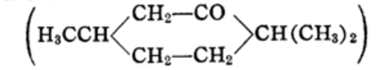
In most cases the cathodic solution consisting of 120 ml. of 5% sulfuric acid in which a ketone was suspended and alcohol was not used as electrolyte. A 5% solution of sulfuric acid served as an anodic solution and cylindrical lead was employed as anode. The anode was separated from the catholyte by means of porous pot. An electrical connection was made with the mercury at the bottom of a cathode by means of platinum wire sealed into a glass narrow tubing. Mercury was purified by washing with nitric acid. The electrolyte was first heated to 50° and during the electrolysis the catholyte was maintained at 50∼55° by the reaction heat. The electrolytic chamber was kept upright and the cathodic solution was stirred vigorously. After the current was passed for a short time, a black turbidity appeared in the catholyte. It has been thought[3] that this turbidity seemed to be due to finely divided mercury.

As the electrolysis continued, the cathodic solution gradually cleared up. The amount of electric current passed was about one and a half of the theoretical one. After the electrolysis, a heavy viscous oil floated on the surface of the mercury. The catholyte was placed in a separate funnel, the oil was removed, the residue was extracted with ether, the ether extracts were evaporated under reduced pressure and a solid residue or a viscous oil was obtained. It was mercury compound and the yield of crude product was about 25∼30% of the theoretical amount. As the compounds was unstable,

TABLE I

ELECTROLYTIC CONDITIONS

Cathode: Hg 15.2 cm^2; anode: Pb, cylindrical; anolyte: 5% H_2SO_4

Ketones	wt. (g.)	Elect. current		Temp. °C	Catholyte	Products
		amp.	hours			
Phenylacetone ($C_6H_5CH_2COCH_3$)	7	2	6	18°	5% H_2SO_4 120 ml.	Recovered
〃	10	2	6	20°	30% H_2SO_4 120 ml.	Hg Compd.
〃	10	3	4	55°	5% H_2SO_4 120 ml.	〃
〃	10	2	6	18°	6 N HCl 60 ml. glac. HAc 60 ml.	〃
Cyclopentanone 	12	2	8.5	16°	5% H_2SO_4 120 ml.	〃
〃	15	3	5	50°	5% H_2SO_4 120 ml.	〃
〃	10	3	5	20°	6 N HCl 60 ml. 50% H_2SO_4 60 ml.	〃
〃	10	3	5	21°	6 N HCl 60 ml. glac. HAc 60 ml.	〃
Cyclohexanone 	20	4	6	55°	5% H_2SO_4 120 ml.	〃
〃	50	4	15	55°	5% H_2SO_4 90 ml.	Pinacol and Hg Compd.
〃	12	3.5	5	16°	30% H_2SO_4 120 ml.	Hg Compd.
2-Methylcyclohexanone	10	3	4	55°	5% H_2SO_4 120 ml.	〃
3-Methylcyclohexanone	10	3	4	55°	5% H_2SO_4 120 ml.	〃
4-Methylcyclohexanone	10	3	4	55°	5% H_2SO_4 120 ml.	〃
Menthone 	10	3	4	60°	50% H_2SO_4 120 ml.	Recovered
Cyclohexanol	10	6	8	60°	50% H_2SO_4 120 ml.	〃
Dibenzylketone ($C_6H_5CH_2COCH_2C_6H_5$)	8	6	6	60°	50% H_2SO_4 120 ml.	〃

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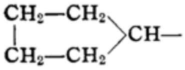
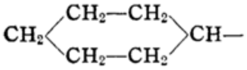
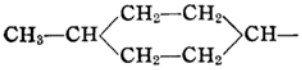
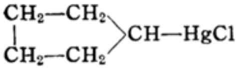
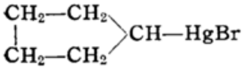
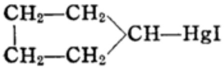
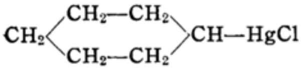
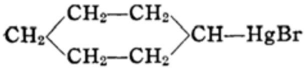
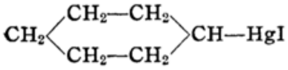
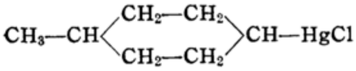
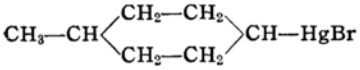
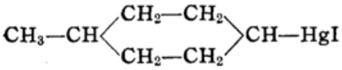
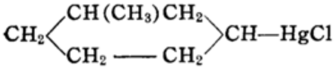
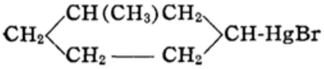
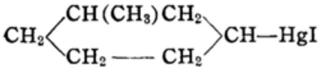
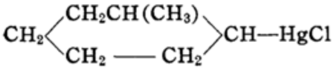
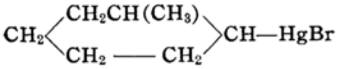
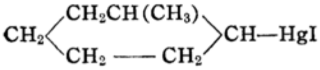
[6] G. Gruttner, *Ber.*, **47**, 1651 (1914).

[7] O. Tiffeneau and O. Gannage, *Chem. Zentr.*, 1, 766 (1921).

TABLE II

PROPERTIES OF ORGANOMERCURY COMPOUNDS

R—Hg—R (Group I)

R—	m.p. °C	Appearance	Solvent	Hg %		References
				Calcd.	Found	
$C_6H_5CH_2CH(CH_3)$—	69~71°	needles	Et-OH	48.25	48.45	
	106~108°	needles	50% Et-OH	59.20	59.51	
	149~151°	needles	50% Et-OH	54.68	54.45	6,7
	172~174°	needles	Et-OH	50.80	50.41	7
R—Hg—X (Group II)						
$C_6H_5CH_2CH(CH_3)$—HgCl	80~81°	needles	Et-OH	56.47	56.49	
$C_6H_5CH_2CH(CH_3)$—HgBr	88°	needles	Et-OH	50.19	50.05	
$C_6H_5CH_2CH(CH_3)$—HgI	90°	needles→ pale yellow	Et-OH	44.91	44.71	
	106~107°	needles	Et-OH	65.73	65.58	10
	108~109°	leaflets	Et-OH	57.37	56.37	
	117~118°	needles→ pale yellow	Et-OH	50.57	50.40	
	158°	needles	50% Me_2CO	62.84	61.90	7,9
	141~142°	leaflets	50% Me_2CO	55.16	54.79	6,9
	142~144°	needles→ pale yellow	Et-OH	48.85	48.75	7
	161~162°	plates	Et-OH	60.56	60.62	7
	157°	leaflets	80% Et-OH	53.39	53.17	7
	144°	plates	80% Et-OH	47.26	46.86	
	86~87°	needles	50% Et-OH	60.56	60.51	
	87~89°	plates	50% Et-OH	53.39	53.02	
	85~86°	plates	Et-OH	47.26	46.28	
	66~67°	needles	Et-OH	60.56	60.35	
	64~65°	leaflets	50% Et-OH	53.39	53.10	
	68~69°	plates	50% Et-OH	47.26	46.95	

crude product was dissolved in alcohol and the solution was used to prepare organomercuric halides. The product was crystallized from dilute alcohol, but some mercury compounds were difficult to crystallize.

The compound in the product was heated with alcoholic solutions of mercuric chloride, mercuric bromide, or mercuric iodide and white precipitates were formed as shown by Eq. 2. These substances were organomercuric halides; they were recrystallized from alcohol or acetone, and fine crystals were obtained. A quantitative yield was obtained.

The crude products were dissolved in alcohol and hydrogen chloride was passed into the solution and the hot reddish solution was cooled in an ice bath. Precipitates were produced as seen in Eq. 3; they were filtered and recrystallized from dilute alcohol containing charcoal. Fine crystals were obtained. It was organomercuric chloride and was identical with the compound obtained by treating the crude organomercury compound with mercuric chloride.

The analysis of mercury was carried out according to the convenient thiocyanate method recommended by Kharasch and Flenner (cited by Hillebrand and Lundell8)) and good results were obtained.

The influence of various electrolytic conditions on the reduction of several ketones are shown in Table I. Phenyl acetone was not reduced to mercury compound in 5% sulfuric acid solution at a low temperature; it was recovered almost intact, and was not reduced to secondary alcohol or pinacol. It was mercurised in 30% sulfuric acid or in a mixture of glacial acetic acid and 18% hydrochloric acid solution at a low temperature; however, it was mercurised even in 5% sulfuric acid solution at a high temperature. Cyclohexanone behaves similarly to phenylacetone. Cyclopentanone was easily mercurised at a low temperature in various cathodic solution. By the use of 50 g. of cyclohexanone, in catholyte, pinacol11) (dihydroxy-dicyclohexyl) was produced by about half the amount.

The ketones mentioned above were reduced to mercury compound even in a mild condition; however, in the case of menthone, it was reported4) that menthone was reduced to dimenthyl mercury only in a strong sulfuric acid at 77∼80° with a high current density and to methone or menthol in a weak sulfuric acid electrolyte at a mercury cathode.

Dibenzyl ketone, which was expected to be reduced to organomercury compound and tried in this experiment, was not reduced to mercury compound.

The formation of these mercury compounds is not a continuation of a secondary-alcohol formation because secondary alcohol was not reduced by electrolytic methods under various conditions; namely, cyclohexanol was reduced under the same conditions as above mentioned, but it was recovered almost as it was.

Dialkyl mercuries are volatile liquids and miscible with organic solvents, practically insoluble in water, decompose on standing at room temperature and are sensitive to light. Diaryl mercuries are solid and stable. The mercury compounds obtained in this experiment were also solid and soluble in ether and hot alcohol, but less soluble in cold alcohol and insoluble in water. Dicyclohexyl mercury was unstable and changed its color from white to gray slowly in several hours after recrystallization. It was reported6) that dicyclohexyl mercury was unstable and decomposed to black oil after 25 hours in a vacuum desiccator over phosphrous pentoxide. Dicyclopentyl mercury was stable as compared with the former, but both compounds turned from gray to black in a few days and at last they decomposed to yellow liquid and black residue. These compounds, above mentioned, were very unstable in the pure and dried state, but comparatively stable in sulfuric acid, ether, and alcohol. Dicycloalkyl mercury has a strong specific odor like camphor and diisopropylmercury like aromatic hydrocarbon.

It was reported7) that di-4-methylcyclohexyl mercury was a liquid, but this compound is a crystal and di-3-methyl, and di-2-methylcyclohexyl mercury might be solid; however, they were not obtained crystalline in this experiment and it seems that they have a lower melting point compared with the melting point of its halides, and di-4-methylcyclohexyl mercury and its halide have a high melting point owing to its symmetric structure.

Organomercuric halides are exceedingly stable, and are fine crystals with sharp melting points without odor; they are soluble in pyridine, hot alcohol, and acetone, less soluble in alcohol and insoluble in water. Iodides are white crystals, but their color changes to yellow on standing very slowly.

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8) W. F. Hillebrand and G. E. F. Lundell, "Applied Inorganic Analysis," John Wiley & Sons, New York, (1953).

9) E. L. Hill, *J. Am. Chem. Soc.*, **50**, 167 (1928).

10) N. Turkiewitz and St. Pilat, *Ber.*, **71**, 284 (1938).

11) 1,1-dihydroxydicyclohexyl, m. p. 129∼130°, plates.

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