

was, of course, assigned the *syn-anti* structure (IIc). The remaining fluorine had an F^{19} peak at $\phi -36.0$. In both IIa and IIc it appears that the aromatic ring would shield the fluorine atom to a considerable extent, and on the basis of the evidence on hand no further assignment of structure can be made.⁹

Experimental Section

Preparation of meso- and dl- α,α' -Bis(difluoramino)bibenzyl.²—The procedure was close to that used by Cerfontain.¹ Chlorobenzene was the solvent and the mixture was flushed with nitrogen prior to adding tetrafluorohydrazine from a pressurized cylinder. Thus, 10.0 g of *trans*-stilbene in 70 ml of chlorobenzene was stirred under 1 atm (600–800 mm) of tetrafluorohydrazine. The solution was warmed and stirred magnetically; at 75° a noticeable uptake of N_2F_4 occurred. The mixture was stirred 4 hr at 75°, but tetrafluorohydrazine uptake was complete in 3 hr. The chlorobenzene solution and an insoluble solid were washed from the reaction flask with methylene chloride. Methylene chloride was removed at reduced pressure, and the residual chlorobenzene solution was chilled in ice-water. Filtration gave 4.78 g of solid, mp 158–159°. The filtrate was reduced to dryness *in vacuo* and the residue was recrystallized from ligroin three times to give an additional 1.04 g of meso- α,α' -bis(difluoramino)-bibenzyl, mp 157–158°.

Anal. Calcd for $C_{14}H_{12}N_2F_4$: C, 59.15; H, 4.26; N, 9.86. Found: C, 59.60; H, 4.48; N, 9.88.

The combined ligroin filtrates were reduced in volume and chilled; 5.94 g of material, mp 107–110°, was obtained. When this material was again dissolved in ligroin, 0.06 g of material, mp 156–157°, remained. Two additional crops of dl- α,α' -bis(difluoramino)bibenzyl were obtained from the filtrate of the 5.94-g crop; the first weighed 2.42 g, mp 111.5–113°, and the second weighed 0.57 g, mp 110–112°.

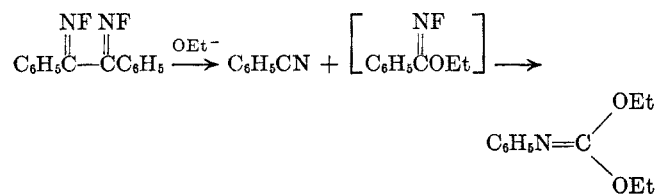
Anal. Calcd for $C_{14}H_{12}F_2N_2$: C, 59.15; H, 4.26; N, 9.86. Found: C, 59.03; H, 4.63; N, 10.22.

Dehydrofluorination of the Stilbene-Tetrafluorohydrazine Adduct.—The adduct from 5 g of *trans*-stilbene and excess N_2F_4 was dissolved in 100 ml of methylene chloride. Then 8.3 ml (60 mmoles) of triethylamine in 25 ml of methylene chloride was added dropwise. After 3 hr at 35°, the mixture was washed with water, dilute aqueous hydrochloric acid, and water. Evaporation of the methylene chloride left 6.9 g of residue. This residue was chromatographed on silica gel; elution was carried out with pentane-methylene chloride (1:20 to 1:1). In fractions 8–23, 6.00 g of α,α' -bis(fluorimino)bibenzyl was eluted.

Anal. Calcd for $C_{14}H_{10}F_2N_2$: C, 68.84; H, 4.13; N, 11.47. Found (for fraction 9): C, 68.73; H, 4.34; N, 11.68. (F^{19} nmr spectrum showed singlet, $\phi -36.$) Found (for fraction 13): C, 68.58; H, 4.11; N, 11.45. (F^{19} nmr spectrum showed doublets, $\phi -36.6$, $\phi -28.4$, $J_{FF} = 20$ cps.) Found (for fraction 19, a solid which was recrystallized from hexane, mp 62–63°): C, 68.38; H, 3.82; N, 11.36. (F^{19} nmr spectrum showed a single peak, $\phi -35.5.$)

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(9) Although the mixture of the fluorimines II was stable to alcohol, exposure to excess sodium ethoxide in ethanol produced benzonitrile and



N-phenyl diethylimidocarbonate. This is an example of a Beckmann cleavage reaction under basic conditions.

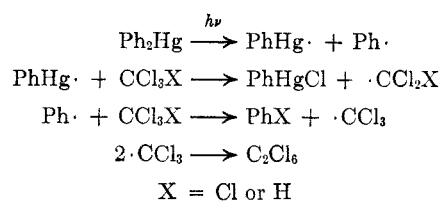
The Electrolytic Reduction of Organomercuric Acetates in the Presence of Carbon Tetrachloride

KUNIHISA YOSAHIDA AND SHIGERU TSUTSUMI

Department of Chemical Technology, Faculty of Engineering, Osaka University, Miyakojima-ku, Osaka, Japan

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The photolysis of organomercury compounds occurs by initial fission to form organomercury radical and organo radical. Diphenylmercury¹ reacts with carbon tetrachloride or chloroform to form phenylmercuric chloride, hexachloroethane, and chlorobenzene or benzene, respectively; the reactions are represented by the following scheme. Namely, the phenylmercury



radical abstracts the chlorine atom of the solvent. Phenylmercuric chloride is also formed by pyrolysis of diphenylmercury in the presence of carbon tetrachloride.² Moreover, dibenzylmercury³ is photolyzed in chloroform to produce bibenzyl and mercurous chloride. On this occasion, it is not certain whether the benzylmercury radical abstracts the chlorine atom of the solvent to form intermediately benzylmercuric chloride.⁴

Besides, it is known that organomercury radicals disproportionate to diorganomercury compounds and mercury⁵ or dissociate to organo radicals and mercury.⁶

With these in view, the electrolytic reduction of organomercuric acetates was conducted to investigate the behavior of organomercury radicals in the presence of carbon tetrachloride.

A solution of organomercuric acetate (0.01 mole) and carbon tetrachloride (30 ml) in methanol (60 ml) was electrolyzed. The results are summarized in the Table I.

TABLE I
REACTION PRODUCTS

—RHgOAc—	Products, g					Recovered RHgOAc, g
	R	Wt, g	RHgCl	R ₂ Hg	Hg	
Ph	3.37	1.21	0.46	0.41	0.85	
PhCH ₂	3.51	0.05	0.87	0.50	1.02	
C ₆ H ₁₁	3.43	1.05	0.11	0.40	0.49	

These are consistent with the following reactions (eq 1–4). It is not certain whether the reduction occurs directly (eq 1) or *via* the preionization followed by

(1) G. A. Razuvaev and Yu. A. Ol'dekop, *Zh. Obshch. Khim.*, **19**, 736 (1949).

(2) G. A. Razuvaev and Yu. A. Ol'dekop, *ibid.*, **23**, 587 (1953).

(3) G. A. Razuvaev and Yu. A. Ol'dekop, *ibid.*, **19**, 1487 (1949).

(4) (a) It has been supposed that the benzylmercury radical abstracts the iodine atom from benzyl iodide.^{4b} (b) N. S. Hush and K. B. Oldham, *J. Electroanal. Chem.*, **6**, 39 (1963).

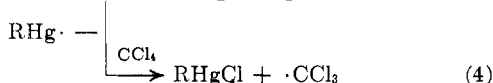
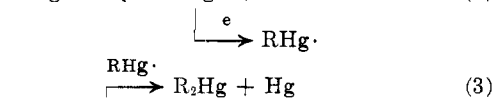
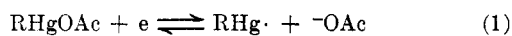
(5) (a) J. L. Maynard and H. C. Howard, Jr., *J. Chem. Soc.*, 960 (1923);

(b) B. G. Gowenlock and J. Trotman, *ibid.*, 2114 (1957); (c) ref 4b;

(d) R. E. Dessy, W. Kitching, T. Psarras, R. Salinger, A. Chen, and T. Chivers, *J. Am. Chem. Soc.*, **88**, 460 (1966).

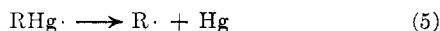
(6) (a) Reference 4b; (b) C. H. Wang, *J. Am. Chem. Soc.*, **85**, 2339 (1963);

(c) G. N. O'Connor, J. V. Crawford, and C. H. Wang, *J. Org. Chem.*, **30**, 4090 (1965).

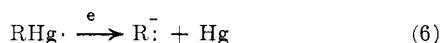


electron transfer from electrode to cation (eq 2).^{4b} In any case, several possible fates await the organomercury radical produced at a platinum electrode.

As the second bond dissociation energy of diorganomercury compounds is thought to be very low (the bond dissociation energy of the methylmercury radical is approximately 7 kcal/mole⁷ and that of phenyl- or benzylmercury radical will be lower⁸), dissociation 5



would be favored. Moreover, in the polarographic study of organomercuric salts^{4b} it is observed that the organomercury radical is reduced further to form carbanion and mercury (eq 6). However, the previous



observations^{5a,d} and an experiment of ours⁹ have shown that during the electrolysis of organomercuric salts the disproportionation reaction of organomercury radicals occurs predominantly to form diorganomercury compounds and mercury, and that reactions 5 and 6 can participate to a small extent only.

On the other hand, the present studies have shown that, when the reaction is carried out in the presence of carbon tetrachloride, the organomercury radical, especially phenyl- and cyclohexylmercury radical, abstracts predominantly the chlorine atom to form organomercuric chloride (eq 4), and the disproportionation reaction (eq 3) is suppressed. Although the benzylmercury radical can also abstract the chlorine atom to some extent, the disproportionation reaction is predominant. The fate of trichloromethyl radical is not established.

Finally, it is not clear why the reduction of phenylmercuric cation by means of ferrocene^{6b} furnishes the phenyl radical (eq 5) and the reduction by chromous ion¹⁰ or electrolytic method does not. At present it is not certain as well why the benzylmercury radical does not abstract the chlorine atom strongly.

Experimental Section

Materials.—Methanol was refluxed in the presence of calcium oxide and was purified by fractional distillation. Carbon tetrachloride and phenylmercuric acetate (mp 149°) were commercial products. Phenylmercuric chloride (mp 251°),¹¹ diphenylmercury (mp 125°),¹² benzylmercuric acetate (mp 126°),¹³ benzylmercuric chloride (mp 103°),¹³ dibenzylmercury (mp

(7) (a) C. M. Laurie and L. H. Long, *Trans. Faraday Soc.*, **53**, 1431 (1957); (b) S. J. U. Price and A. F. Trotman-Dickenson, *ibid.*, **53**, 939 (1957); (c) B. G. Gowenlock, J. C. Polanyi, and E. Warhurst, *Proc. Roy. Soc. (London)*, **A218**, 264 (1953).

(8) The average bond dissociation energy of dialkylmercury compounds decreases with increasing stability of the alkyl radical: B. G. Gowenlock, R. M. Haynes, and J. R. Majer, *Trans. Faraday Soc.*, **58**, 1905 (1962).

(9) The electrolysis of phenylmercuric acetate in methanol leads to a quantitative production of diphenylmercury and mercury; it does not produce benzene or biphenyl as would be expected if reactions 5 or 6 occur (a small amount of benzene was detected by ultraviolet spectroscopy).

(10) R. J. Ouellette and B. G. van Leuwen, *J. Org. Chem.*, **30**, 3967 (1965).

(11) A. N. Nesmeyanov, *Ber.*, **62**, 1013 (1929).

112°),¹³ cyclohexylmercuric acetate (mp 92°),¹⁴ cyclohexylmercuric chloride (mp 163°),¹⁵ and dicyclohexylmercury (mp 78°)¹⁵ were prepared according to known procedures.

Electrolysis of Phenylmercuric Acetate.—The electrolysis was carried out by using two platinum plate electrodes (15 × 20 mm²), of which a space was 4 mm. At the beginning of the electrolysis a potential of 150 v produced a current of 0.01 amp. This of course fell off as the concentration of the phenylmercuric salt in the solution decreased. In order to maintain the current (0.01 amp), voltage was gradually shifted from 150 to 1000 v. A solution of phenylmercuric acetate (3.37 g, 0.01 mole) and carbon tetrachloride (30 ml) in methanol (60 ml) was electrolyzed in a nitrogen atmosphere for 13 hr. During this time, the internal temperature remained between 10 and 15°, and a white crystal was formed. Filtration of the reaction mixture afforded 0.75 g of solid (mp 253–255°). This material was identified as phenylmercuric chloride by mixture melting point measurement.

The clear filtrate was distilled at atmospheric pressure. After removal of methanol and carbon tetrachloride, the distillation residue was separated by fractional crystallization. It consisted of 0.85 g of phenylmercuric acetate, 0.46 g of diphenylmercury, and 0.46 g of phenylmercuric chloride. Phenylmercuric acetate was isolated owing to its solubility in hot water. The latter two compounds were separated by fractional crystallization from ethanol. Phenylmercuric acetate and diphenylmercury were identified by mixture melting point measurements.

The mercury deposited to cathode was dissolved in nitric acid and titrated (0.41 g).¹⁶

Electrolysis of Benzylmercuric Acetate.—A solution of benzylmercuric acetate (3.51 g, 0.01 mole) and carbon tetrachloride (30 ml) in methanol (60 ml) was electrolyzed at 7–12° for 13 hr (0.01 amp, 100–200 v). The resulting solution was worked up as above to give mercury (0.50 g), benzylmercuric acetate (1.02 g), benzylmercuric chloride (0.05 g), and dibenzylmercury (0.87 g). The latter two compounds were separated by fractional crystallization from carbon tetrachloride. These products were identified by mixture melting point measurements.

Electrolysis of Cyclohexylmercuric Acetate.—A solution of cyclohexylmercuric acetate (3.43 g, 0.01 mole) and carbon tetrachloride (30 ml) in methanol (60 ml) was electrolyzed at 7–10° for 13 hr (0.01 amp, 100–250 v). The resulting solution was distilled at atmospheric pressure. After removal of methanol and carbon tetrachloride, the distillation residue was separated by a combination of column and thin layer chromatography (benzene on silica gel). Dicyclohexylmercury (0.11 g), cyclohexylmercuric chloride (1.05 g), and cyclohexylmercuric acetate (0.49 g) were isolated. These products were identified by mixture melting point measurements. The amount of mercury was 0.40 g.

(12) H. O. Calvery, "Organic Syntheses," Coll. Vol. I, H. Gilman and A. H. Blatt, Eds., John Wiley and Sons, Inc., New York, N. Y., 1941, p 228.

(13) P. Wolff, *Ber.*, **46**, 64 (1913).

(14) M. C. Sneed and J. L. Maynard, *J. Am. Chem. Soc.*, **44**, 2946 (1922).

(15) G. Grüttner, *ibid.*, **47**, 1655 (1914).

(16) F. P. Treadwell and W. T. Hall, "Analytical Chemistry," Vol. 2 John Wiley and Sons, Inc., New York, N. Y., 1955, p 649.

Halomethyl-Metal Compounds. XI. The Reaction of Phenyl(trihalomethyl)mercury Compounds with Tertiary Amines¹

DIETMAR SEYFERTH,² MICHAEL E. GORDON,^{3a} AND
(in part) ROBERT DAMRAUER^{3b}

Department of Chemistry, Massachusetts Institute of Technology,
Cambridge, Massachusetts 02139

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The recent communication by Parham and Potoski⁴ concerning the reaction of phenyl(trichloromethyl)-

(1) Part X: D. Seyferth, J. M. Burlitch, H. Dertouzos, and H. D. Simons, Jr., *J. Organometal. Chem.*, in press.

(2) Alfred P. Sloan Foundation Fellow, 1962–1966.

(3) (a) National Institutes of Health Predoctoral Fellow, 1963–1966; (b) National Institutes of Health Predoctoral Fellow, 1964–1966.

(4) W. E. Parham and J. R. Potoski, *Tetrahedron Letters*, 2311 (1966).