and a filtrate, which was saturated with sodium chloride, extracted several times with ether, the ether distilled and the residue fractionated to give 0.6 g. (16.6%) of *n*-butyric acid (formed by cleavage of $CF_3COC_3H_7$-*n*), b.p. 160–165°; anilide, m.p. 95–96°.[19]

Cleavage of α-Ethylbenzoyltrifluoroacetone (V) by Aqueous Alcoholic Sodium Hydroxide.—The previous reaction was repeated except that VI was replaced by an equivalent amount of its isomer, V. After the two-hour reflux period, during which no gas was evolved, 200 ml. of water was added, the basic aqueous phase extracted with three 50-ml. portions of ether and the extracts dried. After distilling the solvent, the residue was fractionated to give 5.3 g. (87.2%) of butyrophenone, b.p. 116–119° (20 mm.); 2,4-dinitrophenylhydrazone, m.p. 197–199°.[19] The basic aqueous phase was acidified with concentrated hydrochloric acid, extracted with ether and the extracts dried. After the solvent was removed only a small amount (0.2 g.) of a sharp smelling liquid (probably trifluoroacetic acid) remained. Thus, no benzoic acid was formed in this reaction.

The Acylation of Trifluoromethyl Benzyl Ketone with Benzoyl Chloride. The Synthesis of 2-(1-Phenyl-3,3,3-trifluoro)-Δ¹-propenyl Benzoate (VII).—To a suspension of 0.3 mole (17.1 g.) of sodium methoxide in 200 ml. of anhydrous ether was added 0.3 mole (56.4 g.) of trifluoromethyl benzyl ketone over a 30-minute period. The ether refluxed rapidly during the addition of the ketone. After stirring for one hour, the reflux condenser was replaced by a condenser for downward distillation, the ether was distilled and the residue heated in vacuum (20–40 mm.) for one hour to remove the methanol formed in the reaction. Anhydrous ether (250 ml.) was then poured into the reactor and then 0.3 mole (42.2 g.) of benzoyl chloride, dissolved in 50 ml. of anhydrous ether was added dropwise over a 30-minute period and the mixture stirred at room temperature for one hour. The contents of the flask was then poured onto crushed ice and worked up as described above for VI to give 73.3 g. (83.5%) of VII, b.p. 123–127° (1.3 mm.), m.p. 47–48° (from 95% ethanol). *Anal.* Calcd. for $C_{16}H_{11}O_2F_3$: C, 65.75; H, 3.79. Found: C, 65.92; H, 3.83. Compound VII gave a negative enol test and did not form a copper salt.

Cleavage of VII with Aqueous Alcoholic Sodium Hydroxide.—In the apparatus used to cleave VI were placed 0.0342 mole (10.0 g.) of VII, 50 ml. of 95% ethanol, 0.2 mole (8.0 g.) of sodium hydroxide dissolved in 50 ml. of water and the mixture was refluxed for two hours, during which time a gas, probably fluoroform, was evolved. Water (200 ml.) was then added and the basic reaction mixture was extracted with two 50-ml. portions of ether. When this extract was dried and distilled, no residue remained. The basic aqueous phase was acidified with a mixture of ice and hydrochloric acid and extracted with three 100-ml. portions of ether. The combined ether extracts were washed with several portions of saturated sodium bicarbonate solution until the acidification of the washings no longer gave a precipitate. The ether extract was then dried, the ether removed and the residue distilled to give 0.7 g. (10.9%) of trifluoromethyl benzyl ketone, b.p. 164–167°; ammonia addition compound (recrystallized from benzene), m.p. 73–74°.[20] The acidified bicarbonate washings were filtered and the dried precipitate weighed 2.3 g. (m.p. 114–120°). One recrystallization from petroleum ether (b.p. 60–70°) gave 2.1 g. (50.3%) of benzoic acid, m.p. 121–122° alone and when mixed with an authentic sample. The filtrate from the filtered acidified aqueous phase was then extracted with three 100-ml. portions of diethyl ether and the combined extracts were dried and the solvent distilled. The crystalline residue weighed 4.0 g. (m.p. 49–112°) and was recrystallized from petroleum ether (60–70°) to give 1.8 g. (38.6%) of phenylacetic acid (formed by cleavage of $CF_3COCH_2C_6H_5$), m.p. 75.5–77° alone and when mixed with an authentic sample. The mother liquor from this last recrystallization was evaporated and gave 1.9 g. of solid material, m.p. 35–105°, which was probably a mixture of benzoic and phenylacetic acids.

Cleavage of VII by Ethereal Methanolic Sodium Methoxide.—To a suspension of 0.05 mole (12.9 g.) of sodium methoxide in 100 ml. of anhydrous ether were added successively 0.05 mole (1.6 g.) of absolute methanol and 0.05 mole (14.6 g.) of VII, dissolved in 100 ml. of anhydrous ether. After stirring at room temperature for two hours, the mixture was processed in the customary manner to give 5.4 g. (79.3%) of methyl benzoate, b.p. 90–91° (20 mm.), and 6.3 g. (67.0%) of trifluoromethyl benzyl ketone, b.p. 164–166°; ammonia addition compound, m.p. 75–76°.[20]

Acknowledgment.—The authors gratefully acknowledge the support of the United States Atomic Energy Commission during the course of this investigation.

(20) W. R. Nes and A. Burger, THIS JOURNAL, **72**, 5409 (1950).

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF IOWA STATE COLLEGE]

Organoplatinum Compounds[1]

BY HENRY GILMAN, MYRL LICHTENWALTER AND ROBERT A. BENKESER

RECEIVED NOVEMBER 22, 1952

The reaction of methylmagnesium iodide with anhydrous platinic chloride is complex, leading in part to the formation of tetramethylplatinum, trimethylplatinum iodide, dimethylplatinum diiodide and methylplatinum pentaiodide. Tetramethylplatinum can also be produced by the reaction of trimethylplatinum iodide and methylsodium. It does not react with benzoyl chloride or iodine, but is cleaved by hydrogen chloride forming trimethylplatinum chloride. Hexamethyldiplatinum, formed by the action of metallic potassium on trimethylplatinum iodide, reacts readily with iodine to form trimethylplatinum iodide.

The first organoplatinum compound, trimethylplatinum iodide, was synthesized by treating anhydrous platinic chloride with a large excess of methylmagnesium iodide[2]

$$PtCl_4 + 3\,CH_3MgI \longrightarrow (CH_3)_3PtI + 2MgCl_2 + MgI_2$$

Upon a careful study of this reaction it has been found far more complex than is indicated by the above equation. In addition to the trimethylplatinum iodide (I), there is formed tetramethylplatinum[3] (II), dimethylplatinum diiodide (VII) and methylplatinum pentaiodide (V). Two other platinum compounds were isolated which were not identified. It is noteworthy that with the possible exception of these unidentified products none of the haloplatinum compounds isolated contained chlorine. The following Flow Sheet illustrates the methods which were employed to isolate the products of this reaction.

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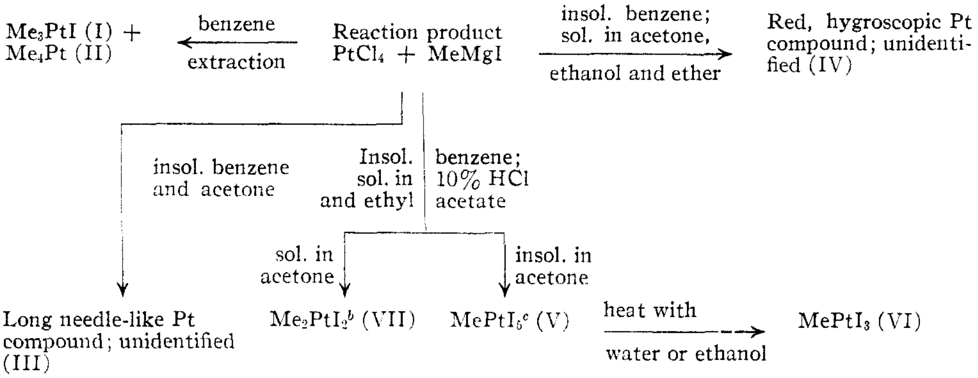
(1) Paper LXXII in the series: "Relative Reactivities of Organometallic Compounds." The preceding paper is H. Gilman, R. G. Jones and L. A. Woods, *J. Org. Chem.*, **17**, 1630 (1952).

(2) (a) W. J. Pope and S. J. Peachey, *Proc. Chem. Soc.*, **23**, 86 (1907); (b) *J. Chem. Soc.*, **95**, 571 (1909).

(3) See R. E. Rundle, THIS JOURNAL, **69**, 1327 (1947), and R. E. Rundle and J. H. Sturdivant, *ibid.*, **69**, 1561 (1947), for a determination of the crystal structure of this compound.

FLOW SHEET[a]



[a] The Roman numerals indicate the order in which the compounds were isolated. [b] Relatively pure dimethylplatinum diiodide is rather insoluble in ethyl acetate or acetone. [c] Pure methylplatinum pentaiodide is no longer easily soluble in ethyl acetate.

Tetramethylplatinum and hexamethyldiplatinum have been synthesized for the first time by the action of trimethylplatinum iodide on methylsodium and potassium metal, respectively

$$(CH_3)_3PtI + CH_3Na \longrightarrow (CH_3)_4Pt + NaI$$

$$2(CH_3)_3PtI + 2K \longrightarrow (CH_3)_3PtPt(CH_3)_3 + 2KI$$

Tetramethylplatinum is the first example of an organoplatinum compound in which all four valences of the metal are satisfied by organic radicals. The compound does not react with benzoyl chloride or iodine but is cleaved by dry hydrogen chloride to form trimethylplatinum chloride.

Hexamethyldiplatinum was shown by a cryoscopic molecular weight determination to be undissociated in benzene. It is cleaved by refluxing with iodine to form trimethylplatinum iodide.

Experimental

Trimethylplatinum Iodide (I). (a) From Platinic Chloride and Methylmagnesium Iodide.—This reaction was carried out using a modification of the method of Pope and Peachey. The conditions described are the most satisfactory for optimum yields.

A solution of methylmagnesium iodide, prepared from 15 g. (0.105 mole) of methyl iodide, 40 ml. of anhydrous ether and 2.5 g. (0.105 mole) of magnesium was diluted with 160 ml. of dry benzene. After filtering the solution through glass wool into a dry flask and cooling to −10°, 8.5 g. (0.025 mole) of anhydrous platinic chloride was added in small portions. Hydrolysis was effected, after stirring for four hours, by the addition of water while cooling in an ice-bath. The reaction products were extracted repeatedly with benzene; the benzene extracts were dried over sodium sulfate, filtered and concentrated to 50 ml. under reduced pressure. The heavy, reddish-brown powder which separated was filtered from the boiling solvent. The residue was extracted with a second 50-ml. portion of boiling benzene. The benzene extracts were combined and concentrated to 10 ml. followed by cooling in an ice-bath and filtering. The yield of trimethylplatinum iodide was 3.7 g. (45%).

Anal. Calcd. for C_3H_9PtI: Pt, 53.14; I, 34.6. Found: Pt, 53.20; I, 34.3.

A slight residue remaining from the last benzene extraction of the trimethylplatinum iodide concentrate was washed with hot acetone. A brick-red powder weighing 24 mg. remained which upon examination under a microscope was found to consist of long slender needles. It was practically insoluble in acetone, chloroform, ether, ethyl acetate and water, but slightly soluble in hot benzene, toluene and xylene. This material was not identified.

Anal. Found: Pt, 43.30; I, 47.93.

(b) From Hexamethyldiplatinum and Iodine.—To a solution containing 20 mg. of hexamethyldiplatinum in 10 ml. of ether was added 12.7 mg. of iodine. After refluxing the solution for several hours, the iodine color disappeared and a precipitate formed. This was filtered and crystallized from benzene. The yield of trimethylplatinum iodide was 12 mg. (45%).

Anal. Calcd. for C_3H_9PtI: Pt, 53.14; I, 34.6. Found: Pt, 53.07; I, 34.5.

Tetramethylplatinum (II).—The benzene from which the trimethylplatinum iodide was crystallized was evaporated leaving a slight residue. This was covered with 5 ml. of petroleum ether (b.p. 60–68°) and allowed to stand for 30 minutes. After filtering and concentrating slowly to about 1 ml., there was obtained 18 mg. (0.28%) of a crystalline material containing no halogen. Analysis indicated that it was tetramethylplatinum.

Anal. Calcd. for $C_4H_{12}Pt$: Pt, 76.48. Found: Pt, 75.46.

The residual hydrolysis products which were not extracted by benzene were washed with alcohol, acetone and finally ether until the washings were colorless. Concentration of these washings gave a small quantity of a red, hygroscopic platinum compound that was not identified.

Methylplatinum Pentaiodide (V).—The residue on the filter was treated with 10% hydrochloric acid which extracted a portion of this material and gave a black filtrate. This filtrate was extracted repeatedly with small portions of ethyl acetate. The combined extracts were dried over sodium sulfate, filtered, and the solvent removed under vacuum. The residue was washed with acetone until the washings were colorless. There remained 0.1 g. of black crystals which were no longer easily soluble in ethyl acetate or water. This compound was apparently methylplatinum pentaiodide.

Anal. Calcd. for CH_3PtI_5: Pt, 23.10; I, 75.10. Found: Pt, 23.32; I, 75.16.

Methylplatinum Triiodide (VI).—This compound was obtained by dissolving methylplatinum pentaiodide in water or alcohol and heating the solution on a steam-bath. A black amorphous powder was deposited. This apparently was methylplatinum triiodide.

Anal. Calcd. for CH_3PtI_3: Pt, 23.05; I, 64.41. Found: Pt, 33.20; I, 63.05.

The residue from the hydrochloric acid extraction upon examination seemed to consist largely of methylplatinum triiodide.

Dimethylplatinum Diiodide (VII).—The acetone-soluble portion of the ethyl acetate extracts was evaporated to dryness. The residue was dissolved in ether which was then allowed to evaporate slowly. There was obtained 2.15 g. of a black compound which was insoluble in ether, ethyl acetate, water or acetone. This was probably dimethylplatinum diiodide.

Anal. Calcd. for $C_2H_6PtI_2$: Pt, 40.75; I, 52.99. Found: Pt, 40.20; I, 51.42.

Hexamethyldiplatinum.—Two equivalents of powdered potassium was refluxed for ten hours with 0.6 g. of trimethylplatinum iodide dissolved in 20 ml. of dry benzene. After allowing the reaction mixture to stand for two days, the last traces of potassium were destroyed with a few drops of *n*-

amyl alcohol. After filtering and removing the solvent, the residue was washed with water to remove inorganic salts. The residue was extracted with ether and upon removal of this solvent pale yellow needles were deposited. After crystallization from a benzene–petroleum ether solution, 0.24 g. (60%) of colorless hexamethyldiplatinum crystals were obtained. This compound was very soluble in acetone, benzene or ether but insoluble in water and only slightly soluble in cold petroleum ether (b.p. 60–68°).

Considerable difficulty was experienced in the analysis of this compound. It exploded sharply on heating with a brilliant shower of sparks. Analysis for platinum was finally obtained by exploding the compound in a bulb with capillary openings. The capillaries were plugged with about one inch of glass wool to prevent the escape of platinum. After the compound was exploded, a slow current of air was passed through the bulb and it was burned to a constant weight. Analysis for carbon and hydrogen was obtained by scattering a weighed sample of the material over a length of about four inches in the combustion tube and igniting a few particles at a time. A constant series of small explosions accompanied the combustion.

Anal. Calcd. for $C_6H_{18}Pt_2$: Pt, 81.25; C, 14.95; H, 3.76; mol. wt., 480. Found: Pt, 81.13; C, 14.55; H, 3.92; mol. wt., 492.

Tetramethylplatinum.—To a suspension of methylsodium prepared from 4 g. of dimethylmercury in 60 ml. of benzene-free hexanes and 1.5 g. of sodium was added 1 g. of trimethylplatinum iodide. The mixture was stirred for 24 hours, and then hydrolyzed by the addition of 2 ml. of *n*-amyl alcohol followed by ethanol and finally water. The hexane layer was separated, dried over sodium sulfate, filtered, and evaporated to dryness. The residue was covered with 20 ml. of petroleum ether (b.p. 60–68°) and after standing for 30 minutes the mixture was filtered and concentrated slowly. There was deposited 0.32 g. (46%) of a colorless solid which was readily soluble in cold benzene, acetone, ether and petroleum ether (b.p. 60–68°) but less soluble in cold alcohol or chloroform. The compound does not melt but decomposes with a slight explosion when heated in an open flame.

Anal. Calcd. for $C_4H_{12}Pt$: Pt, 76.48; C, 18.80; H, 4.72. Found: Pt, 76.84; C, 18.32; H, 4.31.

When the above reaction was attempted using methyllithium instead of methylsodium, trimethylplatinum iodide was recovered unchanged after a reaction time of ten hours.

Benzoyl Chloride and Tetramethylplatinum.—A solution containing 0.2 g. of tetramethylplatinum and 1 ml. of benzoyl chloride in 10 ml. of benzene was refluxed 100 hours. The tetramethylplatinum was recovered unchanged.

Tetramethylplatinum and Iodine.—A solution containing 0.1 g. of tetramethylplatinum and 0.1 g. of iodine in 10 ml. of chloroform was refluxed 24 hours. The tetramethylplatinum was recovered unchanged.

Tetramethylplatinum and Hydrogen Chloride.—Dry hydrogen chloride was bubbled through a refluxing solution containing 0.1 g. of tetramethylplatinum in 10 ml. of petroleum ether (b.p. 60–68°). White crystals of trimethylplatinum chloride soon began to separate and after 15 minutes the precipitation was complete.

Anal. Calcd. for $(CH_3)_3PtCl$: Pt, 70.75; Cl, 12.90. Found: Pt, 70.20; Cl, 13.10.

AMES, IOWA

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

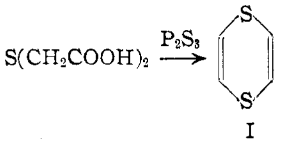
Heterocyclic Vinyl Ethers. III. The Synthesis of 1,4-Dithiadiene and 1,4-Dithiadiene Disulfone[1-3]

BY WILLIAM E. PARHAM, HANS WYNBERG AND FLOYD L. RAMP

RECEIVED DECEMBER 6, 1952

The synthesis and proof of structure of 1,4-dithiadiene and 1,4-dithiadiene disulfone are described.

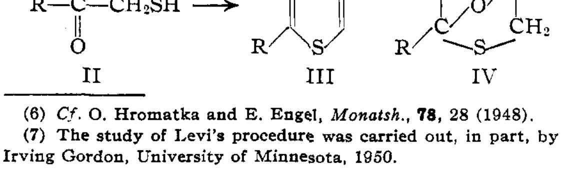
In 1890, Levi[4] reported that the action of phosphorus trisulfide and thiodiglycolic acid resulted in an oil which he formulated as 1,4-dithiadiene (I).



I

Evidence cited for the structure of I was: (1) sulfur analysis, (2) positive indophene test with isatin and sulfuric acid, and (3) conversion of I, by procedures involving Friedel–Crafts reactions with aluminum chloride, into the corresponding methyl ketone[5] (b.p. above 300°, phenylhydrazone m.p. 128°) and phenylketone[5] (b.p. 241°, mononitro derivative, m.p. 112°). With the exception of the boiling point (165–170°), no physical properties of I were reported. Other attempts to prepare 1,4-dithiadiene by Levi's procedure have been unsuccessful.[6,7] In our laboratories Levi's procedure was modified by the use of P_4S_7 and P_2S_5 in place of P_2S_3, by the use of petroleum ether and absolute ether in place of U.S.P. diethyl ether, and further by temperature variations. Only small quantities of distillable oils were obtained, which in no case gave derivatives as reported by Levi.[7]

With the exception of the thianthrenes (dibenzo-1,4-dithiadienes), there have been relatively few compounds prepared which contain the 1,4-dithiadiene ring system. A series of 2,5-diaryl-1,4-dithiadienes (III) have been prepared[8] by the self-condensation of α-mercaptoketones; however, this scheme is apparently not applicable to reactions in which R is aliphatic. The compound reported to



II III IV

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[1] This work was supported by the Office of Ordnance Research, Contract Number DA-11-022-ORD-571.

[2] Presented at the 122nd Meeting of the American Chemical Society, September, 1952.

[3] For the preceding paper of this series, see W. E. Parham, T. M. Roder and W. R. Hasek, THIS JOURNAL, **75**, 1647 (1953).

[4] L. E. Levi, *Chem. News*, **62**, 216 (1890). Levi called his product biophene. *Cf.* R. K. Summerbell and R. R. Umhoefer, THIS JOURNAL, **61**, 3020 (1939), for a discussion of 1,4-dioxadiene.

[5] Analytical data were not reported for the ketones.

[6] *Cf.* O. Hromatka and E. Engel, *Monatsh.*, **78**, 28 (1948).

[7] The study of Levi's procedure was carried out, in part, by Dr. Irving Gordon, University of Minnesota, 1950.

[8] T. B. Johnson, J. C. Moran and E. I. Kohmann, THIS JOURNAL, **35**, 447 (1913); (b) B. Groth, *Chem. Zentr.*, **95**, I, 1036 (1924); (c) R. H. Baker and C. Barkenbus, THIS JOURNAL, **58**, 262 (1936).