Noller and Dinsmore,[9] in a recent study of the reaction of alkyl bromides with pyridine, have shown that the loss of hydrogen bromide and the formation of alkyl pyridinium bromides are distinct, but simultaneously occurring reactions. It is quite probable also that in the reaction of alkyl halides with secondary amines the relative rates of two independent reactions, the loss of halogen acid and tertiary amine formation, determine the course of the reaction, since the data for the reaction of alkyl bromides with piperidine in Table I appear, in general, to be quite similar to those reported by Noller and Dinsmore.

Summary

The isolation of four different N-butylpiperidine hydrochlorides from the reaction of piperidine with the butyl bromides has demonstrated that these bromides, in this reaction, do not rearrange previous to reaction. The difference between the behavior of cyclohexyl bromide and other secondary bromides has been found to be one of degree rather than kind.

[9] Noller and Dinsmore, THIS JOURNAL, 54, 1025 (1932).

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Diarsyls. V. Reactions of Tetraphenyldiarsyl

BY F. F. BLICKE, R. A. PATELSKI AND L. D. POWERS

Tetraphenyldiarsyl reacts with sulfur to form tetraphenylarsyl sulfide; with sulfur chloride, diphenylchloroarsine and sulfur were obtained; with thionyl chloride the reaction products were diphenylchloroarsine, sulfur dioxide and sulfur.

Bromocyanogen and the diarsyl yield diphenylbromoarsine; triphenylarsine is formed when the diarsyl reacts with phenylmagnesium bromide.

Interaction with arsenic trichloride proceeds rapidly with the formation of diphenylchloroarsine and arsenic in practically quantitative yield; when phenylarsine oxychloride was used the reaction products were diphenylchloroarsine and phenylarsine oxide.

Phosphorus trichloride and the diarsyl yield diphenylchloroarsine.

Tetraphenyldiarsyl, dissolved in benzene, was shaken with liquid sodium–potassium alloy. The colorless benzene layer soon became intensely yellow-brown in color and a very decided change was noticed in the appearance of the alloy, a change which we attribute to the formation of the potassium, or sodium derivative of diphenylarsine. Bromobenzene was added to the mixture and, after some time, evaporation of the benzene layer yielded oily triphenylarsine; the latter was isolated in the form of the methyl iodide addition product, methyltriphenylarsonium iodide, since this substance is easier to purify, in small amounts, than triphenylarsine.

Each of the following compounds which contain reactive halogen attached to carbon was mixed with tetraphenyldiarsyl, dissolved in benzene, and allowed to remain at room temperature for twelve hours: acetyl chloride, benzoyl chloride, benzophenone chloride, 2,4-dinitrobromobenzene and tetraphenyldichloroethane.[1] In each instance approximately 80% of unchanged diarsyl was recovered.

It was thought possible that ethylene oxide might react with tetraphenyldiarsyl, dissolved in benzene, to form diphenyldiphenylarsyloxyethylarsine, $(C_6H_5)_2As-CH_2CH_2-O-As(C_6H_5)_2$; the diarsyl, however, was recovered unchanged.

Tetraphenyldiarsyl is not affected by cold halogen acids or alkali.

Experimental Part

All of the reactions described below were carried out in a free-radical bulb in an atmosphere of nitrogen. Absolute grades of alcohol and ether were used and all solvents were saturated with nitrogen prior to use.

Unless otherwise indicated the tetraphenyldiarsyl was prepared from 3.56 g. (0.01 mole) of diphenyliodoarsine, 1 cc. of mercury and 90 cc. of dry benzene. The mixture was shaken for twelve hours and then siphoned through a filter into a radical bulb. It has been shown previously that by this method a yield of at least 90% of pure diarsyl is obtained. All of the yields of the various reaction products described below were calculated on the assumption that 0.01 mole of the iodoarsine yielded 0.009 mole of the diarsyl.

Sulfur.—To the diarsyl solution there was added 0.15 g. of sulfur, dissolved in carbon disulfide. After twenty-four hours the solvents were removed by distillation under reduced pressure, the oily residue dissolved in ether, the solution poured into a beaker and concentrated. Tetraphenylarsyl sulfide separated in crystalline condition. The yield was 1.9 g.; calcd. yield 2.2 g.; mixed m. p. 61–62°[2] after recrystallization from alcohol.

Sulfur Chloride.—The diarsyl solution was mixed with 0.67 g. of sulfur chloride dissolved in 20 cc. of benzene. The mixture became opalescent at once and a tan-colored precipitate of sulfur soon formed. After twenty-four hours the benzene solution was rose colored, due probably to the presence of sulfur in a colloidal state. The mixture was filtered, all of the solvent removed and the crystalline residue dissolved in alcohol. Upon concentration of the alcoholic solution 1.8 g. of diphenylchloroarsine was obtained; calcd. yield 2.4 g.; m. p. 42–43°.[3]

The reaction takes place equally well in ether but in this instance the solution does not become pink in color.

Thionyl Chloride.—Six-tenths of a gram of thionyl chloride, dissolved in 20 cc. of benzene, was allowed to react with the diarsyl solution. The same observations were made as recorded in the preceding experiment. There was obtained 1.8 g. of diphenylchloroarsine; calcd. yield 2.4 g.; m. p. 42–43°.

Bromocyanogen.—The solution of the diarsyl was treated with 1.06 g. of bromocyanogen,[4] dissolved in 20 cc. of benzene. After four days a small amount of a tan-colored precipitate, presumably polymerized cyanogen, had formed. The mixture was filtered, the solvent removed from the filtrate and the residue recrystallized from alcohol.

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(1) Finkelstein, *Ber.*, **43**, 1533 (1910).

(2) Michaelis, *Ann.*, **321**, 141 (1902).

(3) Blicke and Smith, THIS JOURNAL, **51**, 1564 (1929).

(4) "Organic Syntheses," John Wiley and Sons, Inc., New York, 1931, Vol. XI, p. 11.

The product, diphenylbromoarsine, melted at 52–53°.[3] The yield was 2.2 g., calcd. yield 2.8 g.

Phenylmagnesium Bromide.—Phenylmagnesium bromide, obtained from 4.81 g. of bromobenzene, 0.72 g. of magnesium and 20 cc. of ether, was added to the diarsyl solution. After twelve hours the mixture was removed from the radical bulb and decomposed with ice and ammonium chloride. The benzene–ether layer was shaken with sodium hydroxide solution, the aqueous layer separated and the organic solvents removed. The gummy residue was triturated with petroleum ether (30–60°) in order to dissolve the triphenylarsine and the solvent allowed to evaporate from the petroleum ether extract. The residue was treated with warm 95% alcohol, the alcoholic solution concentrated and inoculated with a crystal of triphenylarsine. After the material had become crystalline it was recrystallized from alcohol; m. p. 60–61°;[5] yield 1 g.

Arsenic Trichloride.—A solution prepared from 0.70 g. of arsenic trichloride and 20 cc. of benzene, was added to the diarsyl solution. The mixture became cloudy immediately and a red brown, amorphous precipitate of arsenic formed.[6] After twelve hours the mixture was filtered, the solvent removed from the filtrate and the residue recrystallized from alcohol. The product, diphenylchloroarsine, melted at 41–42°; yield 2.3 g.; calcd. yield 2.4 g.

Phenylarsine Oxychloride.—One and two-tenths grams of phenylarsine oxychloride,[7] dissolved in 90 cc. of dry benzene, was added to the diarsyl. A transitory lavender color was noticed. After several hours the solution was concentrated, poured into a beaker and all of the solvent removed. When the oily residue was rubbed under ether it became crystalline and the diphenylchloroarsine dissolved in the solvent while the phenylarsine oxide remained undissolved. The ether solution was decanted and the process repeated until a complete separation had been effected. There was obtained 1.9 g. of diphenylchloroarsine; m. p. 41–42°; calcd. yield 2.4 g. The phenylarsine oxide weighed 0.73 g.; m. p. 144–147°; calcd. yield 0.74 g.

Phosphorus Trichloride.—The benzene was removed from the diarsyl solution and after the solid material had been dissolved in 90 cc. of carbon tetrachloride there was added 0.46 g. of phosphorus trichloride, dissolved in 20 cc. of carbon tetrachloride. After twelve hours the solvent was removed, the yellow, oily residue treated with ether and after some time the solution was filtered from insoluble material. The diphenylchloroarsine obtained from the ether solution was recrystallized from alcohol; yield 0.6 g.; mixed m. p. 37–41°.

Sodium–Potassium Alloy.—Liquid sodium–potassium alloy, prepared under xylene from 1.2 g. of sodium and 1.0 g. of potassium, was washed free from the liquid medium and added to the diarsyl solution. After the mixture had been shaken for twelve hours it consisted of a yellow-brown benzene layer, black, suspended particles and unchanged alloy. There was then added 12.2 g. of bromobenzene. The mixture became warm and after it had been shaken for three hours it was filtered, the solvent removed from the filtrate and the red-brown gummy residue subjected to steam distillation in order to remove biphenyl. Since the product could not be obtained in a solid state it was refluxed with 3 cc. of methyl iodide for several hours in order to convert the triphenylarsine into methyltriphenylarsonium iodide. The latter was obtained in the form of crystals contaminated by an oil. The material was extracted with hot water and the aqueous solution boiled with charcoal. The methyltriphenylarsonium iodide obtained from the filtrate weighed 1.6 g.; mixed m. p. 72–73°.[8]

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(5) Sachs and Kantorowicz [*Ber.*, **41**, 2768 (1908)] recorded the melting point as 60.5°.

(6) The precipitate was dissolved in nitric acid, the solution evaporated to dryness and the residue treated with hydrochloric acid; when hydrogen sulfide was passed into the solution yellow arsenious sulfide was obtained.

(7) Michaelis, *Ann.*, **201**, 202 (1880).

(8) Michaelis, *ibid.*, **321**, 166 (1902).

Summary

It has been shown that tetraphenyldiarsyl reacts readily with the following substances: sulfur, sulfur chloride, thionyl chloride, bromocyanogen, phenylmagnesium bromide, arsenic trichloride, phenylarsine oxychloride, phosphorus trichloride and sodium–potassium alloy.

Compounds which contain reactive halogen attached to carbon, such as acetyl chloride, benzoyl chloride, benzophenone chloride, 2,4-dinitrobromobenzene and tetraphenyldichloroethane, as well as ethylene oxide, do not react with the diarsyl, in benzene solution, at ordinary temperature.

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A Study of Phenyl- and Diphenylarsine

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Phenylarsine, dissolved in bromobenzene, absorbs oxygen very rapidly at first; the absorption then proceeds at a slower rate until the material has absorbed approximately one molecular equivalent of the gas. When the arsine was exposed to air we obtained the same oxidation products mentioned by Dehn[1] but the relative amounts varied in different experiments. Phenylarsine and sulfur react to form phenylarsine sulfide and hydrogen sulfide.

It has been reported[2] that phenylarsine reacts with iodine, dissolved in potassium iodide solution, to yield phenylarsonic acid and phenyldiiodoarsine. It has been shown that two molecular equivalents of this arsine, dissolved in ether, reacts instantly with four molecular equivalents of iodine to form phenyldiiododiarsine in quantitative yield. However, when only two molecular equivalents of iodine are used arsenobenzene is formed and by the use of three equivalents diphenyldiiododiarsyl is obtained.

Equimolecular quantities of phenylarsine and triphenylarsine dichloride react in accordance with the following equation

$$2C_6H_5AsH_2 + 2(C_6H_5)_3AsCl_2 = 2(C_6H_5)_3As + C_6H_5As{=}AsC_6H_5 + 4HCl$$

Dehn and Wilcox[3] reported that diphenylarsine, when allowed to oxidize in air, was converted almost completely into diphenylarsinic acid; a very small amount of tetraphenylarsyl oxide was also obtained. We found that diphenylarsine, dissolved in bromobenzene, absorbs oxygen as rapidly as a solution of triphenylmethyl or tetraphenyldiarsyl. The quantity of oxygen absorbed was approximately that required for the interaction of the arsine

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(1) Dehn, *Am. Chem. J.*, **33**, 149 (1905).

(2) Dehn, *ibid.*, **33**, 151 (1905); Fleury, *Bull. soc. chim.*, [4] **27**, 490 (1920).

(3) Dehn and Wilcox, *Am. Chem. J.*, **35**, 47 (1906).