where N is the Avogadro number; k, the Boltzmann constant; T, the absolute temperature, 293.2°; M, the molecular weight, 321.5; d, the density, 1.021; ϵ_0 the static dielectric constant; and ϵ_∞, that part of the dielectric constant due to atomic and electronic polarization.[21]

Acknowledgment.—I am indebted to Dr. J. D. Hoffman for the dielectric measurements and their interpretation, to Dr. J. R. Ladd for the chloromethyl compounds, to the Analytical Unit for the analytical and infrared data, and to Mr. E. M. Hadsell and Mrs. J. R. Ladd for distillation data.

SCHENECTADY, NEW YORK

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[21] J. D. Hoffman, THIS JOURNAL, **75**, 6313 (1953), has demonstrated that ϵ_∞ calculated from the usual equation $\epsilon_\infty = n^2$, is unsatisfactory for silicones because of the large atomic polarization. He has developed the equation $\epsilon_\infty = 1.177n^2$, and this value of ϵ_∞ was used above.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Some Organotin Compounds Containing Water-solubilizing Groups

BY HENRY GILMAN AND T. C. WU

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Methiodides and methosulfates of some organotin compounds containing tertiary amino groups have been prepared. A few of these compounds have remarkable solubilities in water. The solubility increases with an increase in the number of quaternary ammonium groups in the molecule. The methiodide of triphenyl-γ-diethylaminopropyltin is more soluble than that of triphenyl-*p*-dimethylaminophenyltin. Triphenyl-*p*-bromophenyltin was found to have a much lower melting point than that described in the literature.

The evaluation of an organotin compound as a chemotherapeutic agent would be rendered more feasible by adequate masking of the tin and the addition of water-solubilizing groups to the molecule.[1] Some organolead compounds containing tertiary amino groups have been converted into their methiodides and methosulfates, thus enhancing their solubility in water.[2] In this investigation a number of new organotin compounds were prepared and their solubilities were studied.

The organotin compounds containing one or more tertiary amino groups were prepared by treating an organotin halide with an organolithium compound containing a substituted amino group or by treating a dialkylaminoalkyl halide with triphenyltin–lithium.[3] The conversion of organotin compounds containing substituted amino groups to their methiodides or methosulfates was carried out by treating the organotin compounds with methyl iodide or with dimethyl sulfate. Tetra-*p*-dimethylaminophenyltin was treated with an excess of methyl iodide to give the tetramethiodide which could be recrystallized from water, but the product obtained from the reaction of tetra-*p*-dimethylaminophenyltin with dimethyl sulfate was too soluble in water to be purified from this solvent. Triphenyl-*p*-dimethylaminophenyltin gave the methiodide and the methosulfate in good yields, but they are only slightly soluble in hot water. Attempts to prepare diphenyldi-*p*-dimethylaminophenyltin resulted in an oily product, the identity of which was shown by its conversion to the methiodide derivative. The solubility of these quaternary ammonium salts appears to increase with an increase in the number of the quaternary ammonium groups. Also, the methosulfates seem to have a better solubility than the corresponding methiodides.

Organotin compounds containing dialkylaminoalkyl groups also were considered as possible intermediates for introducing water-solubilizing groups into the molecule. Triphenyl-γ-diethylaminopropyltin was obtained as an oily product from the reaction of triphenyltin–lithium with γ-diethylaminopropyl chloride. The methiodide of triphenyl-γ-diethylaminopropyltin is somewhat soluble in hot water while the methosulfate derivative is too soluble to be isolated. Here again, it appears that the methosulfate is more soluble than the corresponding methiodide.

As an illustration, the preparation of quaternary ammonium salts of triphenyl-*p*-dimethylaminophenyltin is outlined as

$$(C_6H_5)_3SnCl + LiC_6H_4N(CH_3)_2\text{-}p \longrightarrow (C_6H_5)_3SnC_6H_4N(CH_3)_2\text{-}p$$

$$(C_6H_5)_3SnC_6H_4N(CH_3)_2\text{-}p + CH_3I \longrightarrow [(C_6H_5)_3SnC_6H_4N(CH_3)_3\text{-}p]^+I^-$$

$$(C_6H_5)_3SnC_6H_4N(CH_3)_2\text{-}p + (CH_3)_2SO_4 \longrightarrow [(C_6H_5)_3SnC_6H_4N(CH_3)_3\text{-}p]^+[OSO_2OCH_3]^-$$

Some of these quaternary ammonium salts decompose on heating and it is difficult to judge the purity based on the melting point determination. A few methiodides can be recrystallized from water to give crystalline products.

In order to synthesize some tetraaryltin compounds containing water-solubilizing groups in the *para* position of one of the aryl groups, triphenyl-*p*-bromophenyltin was considered as a possible intermediate compound. This compound was prepared in a high yield by the reaction of *p*-bromophenylmagnesium iodide with triphenyltin chloride. However, when *p*-bromophenyllithium was used instead of the Grignard reagent, no triphenyl-*p*-bromophenyltin was isolated. The failure to obtain the desired product probably is due to the cleavage of the carbon–tin bond of the organotin compound by the organolithium compound. It has been observed that tetraphenyltin[4] and tetraphenyllead[5] can be cleaved by *n*-butyllithium to give tetra-*n*-butyltin and tetra-*n*-butyllead, respectively. The corresponding metal–metal interconversion reaction with tetraphenyllead and *n*-butylmagnesium bromide does not occur in the same length of

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[1] H. Gilman and C. E. Arntzen, *J. Org. Chem.*, **15**, 994 (1950).

[2] H. Gilman and L. Summers, THIS JOURNAL, **74**, 5924 (1952).

[3] H. Gilman and S. D. Rosenberg, *ibid.*, **74**, 531 (1952).

[4] H. Gilman, F. W. Moore and R. G. Jones, *ibid.*, **64**, 2482 (1942).

[5] H. Gilman and F. W. Moore, *ibid.*, **62**, 3206 (1940).

time.[5] The melting point of triphenyl-*p*-bromophenyltin was found to be 133–135°, instead of 224° as reported in the literature.[6]

Experimental

The organotin compounds were analyzed by decomposing a sample with concentrated sulfuric acid followed by ignition to stannic oxide according to a recently described procedure.[7] The organotin compounds described in this paper gave a positive qualitative test for tin.[8] All melting points are uncorrected.

Tetra-*p*-dimethylaminophenyltin Tetramethiodide.—Three grams (0.005 mole) of tetra-*p*-dimethylaminophenyltin (prepared by the reaction of *p*-dimethylaminophenyllithium with stannic chloride in ether[9]), 27.4 g. (0.193 mole) of methyl iodide and 50 ml. of methanol were refluxed gently on a water-bath for 4 hours. There was obtained 5.4 g. (93%) of light brown solid by filtration. It melted at 190° dec. The crude product could be recrystallized from hot water to give colorless needles, but the decomposition temperature did not change by recrystallization. This compound is soluble in hot water, slightly soluble in hot methanol, and soluble in ethylene glycol at room temperature.

Anal. Calcd. for $C_{36}H_{52}I_4N_4Sn$: I, 43.50; Sn, 10.17. Found: I, 42.73, 42.79; Sn, 10.19, 10.03.

Tetra-*p*-dimethylaminophenyltin Tetramethosulfate.—A mixture containing 3.0 g. (0.005 mole) of tetra-*p*-dimethylaminophenyltin, 10.4 g. (0.082 mole) of dimethyl sulfate, and 20 ml. of methanol was refluxed on a water-bath for 1.5 hours. On cooling, a light violet precipitate formed. This product was too sticky to be placed in a capillary tube for a melting point determination. It was soluble in water and hot methanol, but insoluble in most other organic solvents. The product was partially purified by dissolving in hot methanol and then precipitated by the addition of a large amount of ether. The pale reddish-tan solid so formed was dried in a desiccator. There was obtained 3.1 g. of solid which softened at 180° and then evolved gas and finally turned black at 195°. Analyses showed that it contained 13.5% of sulfur and 13.1% of tin. No reasonable structure with this composition can be written. It appears to be a mixture.

Triphenyl-*p*-dimethylaminophenyltin Methiodide.—A mixture containing 4.7 g. (0.01 mole) of triphenyl-*p*-dimethylaminophenyltin (prepared by the reaction of *p*-dimethylaminophenyllithium with triphenyltin chloride in ether according to a published procedure[1]), 14.2 g. (0.10 mole) of methyl iodide, and 25 ml. of methanol was refluxed for 4 hours. The reaction mixture was cooled in an ice–water-bath and was filtered by suction. There was obtained 5.8 g. (95%) of colorless solid which melted at 167–169° with evolution of gas when it was heated at the rate of 6° per minute in a capillary tube. When it was heated at the rate of 2° per minute it melted at 164°. Recrystallization from methanol did not change the melting point. On exposure to light the compound turned yellow, but in the absence of light it remained colorless. The compound is slightly soluble in hot water and is quite soluble in chloroform, ethylene glycol, hot methanol and hot ethanol.

Anal. Calcd. for $C_{27}H_{28}INSn$: I, 20.73; Sn, 19.39. Found: I, 20.71, 20.43; Sn, 19.60, 19.59.

Triphenyl-*p*-dimethylaminophenyltin Methosulfate.—Two and one-half grams (0.02 mole) of dimethyl sulfate was added to 4.7 g. (0.01 mole) of triphenyl-*p*-dimethylaminophenyltin dissolved in 20 ml. of dry benzene. There was very little heat evolved and some white solid was formed slowly in the reaction mixture. The mixture was heated in a water-bath for 2 hours. On cooling, 5.1 g. (86%) of white solid melting at 229–233° with evolution of gas was obtained. This product was recrystallized from methanol. It was observed that the melting point of this purified product also varied with the rate of heating. When a sample was heated in a capillary tube at the rate of 3° per minute, it melted at 240–243°. When it was heated twice as fast, it melted at 244–246°. This compound is soluble in ethylene glycol, hot methanol, hot chloroform and only sparingly soluble in hot water.

Anal. Calcd. for $C_{28}H_{31}NO_4SSn$: Sn, 19.91. Found: Sn, 20.14, 20.09.

Diphenyldi-*p*-dimethylaminophenyltin Dimethiodide.—Fourteen and two-tenths grams (0.10 mole) of methyl iodide was mixed with 5.1 g. (0.01 mole) of diphenyldi-*p*-dimethylaminophenyltin prepared by the reaction of *p*-dimethylaminophenyllithium with diphenyltin dichloride. On standing at room temperature some white solid gradually formed from the light yellow liquid. After 3 hours the mixture solidified. This was crushed, washed with petroleum ether (b.p. 28–40°) and filtered. There was obtained 7.8 g. (98%) of light tan solid which melted at 164–168° with evolution of gas when it was heated at the rate of 4° per minute. It was recrystallized from methanol but the decomposition point of the recrystallized product also varied with the rate of heating. The product was practically insoluble in water and most other organic solvents except ethylene glycol and methanol.

Anal. Calcd. for $C_{30}H_{36}I_2N_2Sn$: I, 31.84; Sn, 14.89. Found: I, 32.32, 31.76; Sn, 14.63, 14.69.

Diphenyldi-*p*-dimethylaminophenyltin Dimethosulfate.—Ten grams (0.08 mole) of dimethyl sulfate was added to 5.1 g. (0.01 mole) of diphenyldi-*p*-dimethylaminophenyltin dissolved in 30 ml. of methanol with shaking. The solution turned green with evolution of heat. It was refluxed for two hours and cooled. Ether was added to the solution but no solid precipitated out from the two liquid layers thus formed. The mixture was distilled, and the residue was taken up with water. An excess of acetone was added to precipitate 0.9 g. of fine powder decomposing at 125°. Further addition of acetone resulted in an oil. This oil was insoluble in most organic solvents except methanol and ethylene glycol. Also, it was slightly soluble in water. Attempts to purify this product were unsuccessful.

Triphenyl-γ-diethylaminopropyltin.—In a 1000-ml. three-necked flask fitted with a glass stirrer, a dropping funnel and a nitrogen gas-inlet tube was placed 6.6 g. (0.035 mole) of finely ground anhydrous stannous chloride suspended in 300 ml. of ether. While this suspension was kept at −10°, 0.11 mole of phenyllithium was added dropwise, over a period of 1.5 hours, to the stannous chloride.[3] To this there was added 5.8 g. (0.039 mole) of γ-diethylaminopropyl chloride dissolved in 25 ml. of ether in a period of 15 minutes. After the addition, the reaction mixture was allowed to warm to room temperature and then was refluxed for 2 hours. The gray suspension thus formed was hydrolyzed with cold water and filtered. Seven-tenths gram of solid melting at 215–220° was obtained, which, after one recrystallization from benzene, was identified as tetraphenyltin by a mixed melting point determination. Following separation, drying and distillation of the ethereal solution from the filtrate, an oily residue weighing 14.5 g. was obtained. It solidified upon cooling in a Dry Ice–acetone-bath. However, attempts to purify the crude product by low temperature crystallization were unsuccessful. The crude product was used for the preparation of the methiodide and the methosulfate derivatives as such.

Triphenyl-γ-diethylaminopropyltin Methiodide.—Fourteen and two-tenths grams of methyl iodide was mixed with 4.6 g. (0.01 mole) of the crude triphenyl-γ-diethylaminopropyltin prepared as above. A paste was formed with evolution of heat. After 30 minutes the excess of methyl iodide was evaporated to give a light yellow paste which was then washed with petroleum ether (b.p. 28-40°) and filtered. Six grams of solid melting at 153–158° was obtained. Two recrystallizations from a solution of ethanol and petroleum ether (b.p. 60–70°) gave 4.1 g. (68%) of colorless lustrous plates melting at 173–175°. This product was soluble in chloroform and hot ethanol. It could be recrystallized from hot water.

Anal. Calcd. for $C_{26}H_{34}INSn$: I, 20.94; Sn, 19.58. Found: I, 21.07, 21.37; Sn, 19.64, 19.72.

Triphenyl-γ-diethylaminopropyltin Methosulfate.—Three grams of dimethyl sulfate was added to 3.8 g. (0.0082 mole) of triphenyl-γ-diethylaminopropyltin dissolved in 30 ml. of benzene. A large amount of heat was evolved while the mixture solidified. After one hour of refluxing on a water-bath the reaction mixture was cooled and placed in a refrigerator. Four grams of white solid melting at 118–132° with evolution of gas was separated by filtration. This

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(6) E. Krause and K. Weinberg, *Ber.*, **62**, 2235 (1929).

(7) H. Gilman and S. D. Rosenberg, THIS JOURNAL, **75**, 3592 (1953).

(8) H. Gilman and T. N. Goreau, *J. Org. Chem.*, **17**, 1470 (1952).

(9) P. R. Austin, THIS JOURNAL, **54**, 3728 (1932).

product was very soluble in water, ethanol, methanol and acetic acid at room temperature. Purification of this crude product was unsuccessful. It either separated as a sticky solid or formed two liquid layers in a number of solvents.

Triphenyl-*p*-bromophenyltin.—Triphenyl-*p*-bromophenyltin was prepared by Krause and Weinberg[6] from the reaction of *p*-dibromobenzene, magnesium and triphenyltin bromide. No yield was given in this paper, and they reported the melting point of this compound to be 224°, which seemed to be abnormally high for compounds of this type. Accordingly, the preparation of triphenyl-*p*-bromophenyltin was reinvestigated.

Several attempts were first made to prepare triphenyl-*p*-bromophenyltin essentially using the published procedure for the preparation of the silicon analog.[10]

In one experiment 0.10 mole of *n*-butyllithium was added, over a period of 10 minutes, to 25.8 g. (0.11 mole) of *p*-dibromobenzene suspended in 50 ml. of ether at 0°. A negative Color Test II-A[11] was obtained immediately after the addition. Thirty-four and seven-tenths grams (0.09 mole) of triphenyltin chloride dissolved in ether was added to the organolithium compound thus formed. The reaction mixture was warmed by the heat of reaction while a large amount of white precipitate formed. After 2 hours of refluxing the reaction mixture was hydrolyzed with ammonium chloride solution and filtered by suction. There was obtained 20.5 g. of white solid melting at 190–212°. Two recrystallizations from benzene yielded 15.2 g. of tetraphenyltin (mixed melting point) melting at 223–225°. The ethereal solution from the reaction mixture was separated, dried over sodium sulfate, filtered, and distilled to give a yellow gummy residue. This was shaken with hot 95% ethanol, cooled, and filtered to separate 19.9 g. of cream-colored, sticky solid melting at 103–110°. Two recrystallizations from a mixture of benzene and ethanol raised the melting point to 117–119°. This product contained halogen and tin, but the structure was not investigated. The experiment was repeated twice under different conditions. In all these experiments no triphenyl-*p*-bromophenyltin was isolated.

Triphenyl-*p*-bromophenyltin can be prepared by first converting *p*-bromophenyllithium into the Grignard reagent prior to the reaction with triphenyltin chloride. Thus, to 11.8 g. (0.05 mole) of *p*-dibromobenzene was added 0.05 mole of *n*-butyllithium at 0°. Ten minutes later 0.05 mole of magnesium iodide (prepared by treating magnesium with iodine in anhydrous ether) was added rapidly to the organolithium compound and was stirred for 10 minutes; meanwhile, the reaction mixture was cooled to −20°. Then 19.3 g. (0.05 mole) of triphenyltin chloride dissolved in 75 ml. of dry benzene was added rapidly to the Grignard reagent thus prepared. Color Test I[12] at the end of the addition was negative. Three minutes later the reaction mixture was hydrolyzed with cold, aqueous ammonium chloride solution. The ethereal solution was separated, dried over sodium sulfate, filtered and distilled to give 21.7 g. (86%) of white solid melting at 132–135°. One recrystallization from a solution containing 150 ml. of ethanol and 50 ml. of benzene gave 18.1 g. (72%) of colorless crystals melting at 133–135°. Further recrystallizations from a solution of ethanol and benzene or from ethanol alone did not change the melting point. Since the melting point found was very different from that described in the literature,[6] the compound was analyzed.

Anal. Calcd. for $C_{24}H_{19}BrSn$: Br, 15.79; Sn, 23.46. Found: Br, 15.64, 15.70; Sn, 23.58, 23.64.

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[10] H. Gilman and H. W. Melvin, This Journal, **72**, 995 (1950).

[11] H. Gilman and J. Swiss, *ibid.*, **62**, 1847 (1940).

[12] H. Gilman and F. Schulze, *ibid.*, **47**, 2002 (1925).

[Contribution from the Chemical Laboratories of Purdue University]

Reduction of Organic Compounds by Lithium in Low Molecular Weight Amines. I. Selective Reduction of Aromatic Hydrocarbons to Monoölefins

By Robert A. Benkeser, Robert E. Robinson, Dale M. Sauve and Owen H. Thomas

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Lithium in low molecular weight aliphatic amines is uniquely suited for reducing aromatic hydrocarbons selectively to monoölefins. Thus, naphthalene and tetralin are reduced in a one-step operation in 50 to 70% yield to $\Delta^{9,10}$- and $\Delta^{1,9}$-octalins (50:1 ratio) by lithium in methyl-, ethyl- or *n*-propylamine. The small amount of $\Delta^{1,9}$-octalin formed can be isomerized to the 9,10-isomer with phosphorus pentoxide. Benzene is reduced similarly to cyclohexene and cyclohexane; biphenyl to a mixture of 1-cyclohexylcyclohexene and bicyclohexyl. Ethylbenzene at 17° is reduced to 1-ethylcyclohexene and ethylcyclohexane, while at −78°, 1-ethylcyclohexene is formed. It is proposed that these reactions involve a rapid 1,4-reduction, with isomerization of the resulting dihydro compound to a conjugated system. The final 1,2-reduction is slow, thus permitting good yields of monoölefins.

In a previous communication from this Laboratory,[1] the absorption of large quantities of lithium by various aromatic compounds dissolved in anhydrous ethylamine was reported. The formation of an organolithium intermediate is strongly suggested by the definite ratio of lithium absorbed to aromatic compound even in the presence of excess lithium; the intensely colored solutions which result; the fact that hydrolysis of the reaction mixtures did not result in the evolution of hydrogen. If an organolithium intermediate is involved, the hydrolysis product should be an extensively reduced hydrocarbon. Thus, naphthalene in ethylamine was observed to absorb eight atoms of lithium per mole of hydrocarbon. The expected reduction product should thus be one or more of the isomeric octahydronaphthalenes. In accord with this prediction we were able to isolate a mixture of $\Delta^{9,10}$- and $\Delta^{1,9}$-octalin (50:1 ratio) from this reaction.

In view of the encouraging results obtained with naphthalene, we became interested in exploring the applicability and limitations of lithium in ethylamine as a reducing agent. An excellent and very convenient procedure now has been developed whereby extensive reductions may be carried out in this system. The purpose of this paper is to report the selective nature of this reduction in producing monoölefins from aromatic hydrocarbons.

Naphthalene and Tetralin.—Naphthalene and tetralin are reduced by lithium in ethylamine to a mixture of $\Delta^{9,10}$- and $\Delta^{1,9}$-octalin (50:1 ratio). A small amount of decalin also is produced (see Table I). Identification of the olefins was accomplished by way of the nitrosochloride derivatives.

Biphenyl.—Employing similar techniques, biphenyl was reduced to a mixture of 1-cyclohexyl-

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[1] R. A. Benkeser, R. E. Robinson and H. Landesman, This Journal, **74**, 5699 (1952).