sample. The reaction was shown to be quantitative by titration of the triphenyltin chloride formed with standard alkali. No evidence for any other halogen containing product was found.

Chloroform reacted more slowly. After twenty-four hours at 30° only about 20% hydrogenolysis had occurred. Methylene chloride was identified as one product by vapor phase chromatography, the other product being triphenyltin chloride. At reflux for eighteen hours the reduction was nearly quantitative.

The reaction of triphenyltin hydride with methylene chloride at room temperature for thirty hours gave triphenyltin chloride in only 2% yield. However, when the reaction mixture was heated at reflux for eighteen hours, a 92% yield of triphenyltin chloride was found. Methyl chloride was identified as the other product by vapor phase chromatography and by its infrared spectrum.

In summary, the hydrogenolysis of the halomethanes is increasingly facile in the order: methylene chloride < chloroform < carbon tetrachloride. It is also noteworthy that the reactivity of the chloromethanes to reduction by triphenyltin hydride is the reverse of their apparent reactivities toward lithium aluminum hydride.[4] There is a reasonable possibility that this synthetic method using a triaryltindeuteride might offer a convenient method of selectively introducing deuterium into a poly-halogen containing molecule.

Experimental

Triphenyltin Hydride and Carbon Tetrachloride.—Upon mixing 1.383 g. (9.00 mmoles) of carbon tetrachloride and 0.702 g. (2.00 mmoles) of triphenyltin hydride, an immediate reaction took place with generation of heat. The reaction mixture was allowed to cool to room temperature (15 min.) and then dissolved in 100 ml. of a 1:1 mixture of benzene–ethanol. Titration with 0.2000 *N* sodium hydroxide to a Thymol Blue end point required 10.00 ml. (100%).

In a separate experiment, 1.053 g. (3.00 mmoles) of triphenyltin hydride was mixed with 1.400 g. (9.09 mmoles) of carbon tetrachloride in a constant temperature bath at 30° and allowed to stand for 24 hr. The vapor phase chromatograph showed two peaks attributed to carbon tetrachloride and chloroform by comparison with known compounds. The n.m.r. spectrum showed a band at 2.96 τ which increased in intensity when chloroform was added to the reaction mixture and the n.m.r. was rerun.

Triphenyltin Hydride and Chloroform.—A solution of 1.076 g. (3.64 mmoles) of triphenyltin hydride and 1.071 g. (9.00 mmoles) of chloroform was allowed to stand at 30° for 24 hr. Titration with 0.2000 *N* sodium hydroxide as above required 4.16 ml. (22%).

When a solution of 0.702 g. (2.00 mmoles)triphenyltin hydride and 1.066 g. (8.90 mmoles) of chloroform was heated under reflux at 70° for 13 hr., the titration required 9.89 ml. (98.7%).

In a second experiment, 0.554 g. (1.58 mmoles) of triphenyltin hydride was mixed with 0.955 g. (8.00 mmoles) of chloroform and allowed to stand 24 hr. at room temperature. The vapor phase chromatograph showed two peaks attributed to chloroform and to methylene chloride as shown by comparison with standards.

Triphenyltin Hydride and Methylene Chloride.—A solution of 1.047 g. (2.98 mmoles) of triphenyltin hydride and 0.784 g. (9.22 mmoles) of methylene chloride was allowed to stand at 30° for 24 hr. Titration of the reaction mixture, as above, required 0.24 ml. of 0.2000 *N* sodium hydroxide (1.6%).

A mixture of 0.710 g. (2.02 mmoles) of triphenyltin hydride and 0.758 g. (8.90 mmoles) of methylene chloride was heated under reflux for 18 hr. Titration of the reaction mixture as above, required 9.25 ml. of 0.2000 *N* sodium hydroxide (92.0%).

In a separate experiment, 35.1 g. (0.1 mole) of triphenyltin hydride was mixed with 20.0 g. (0.24 mole) of methylene chloride and heated under reflux. The methyl chloride formed in the reaction was trapped in a tube cooled in a Dry Ice–acetone bath. The vapor phase chromatograph showed the presence of methyl chloride by comparison with a known sample. Further evidence for the presence of methyl chloride was obtained by collecting the gas in an infrared cell and comparing its spectrum with that known for methyl chloride, with which it was identical.

The Anomalous Hydrogenation of Carbomethoxyhydrazones[1]

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It has been reported[2] that monosubstituted hydrazines may be prepared in high yields from aldehyde or ketone carbethoxyhydrazones by catalytic hydrogenation, followed by hydrolyis of the resulting carbethoxyhydrazines. An attempt to apply this procedure to aldehyde carbomethoxyhydrazones led to unexpected results.

The hydrogenation of heptaldehyde carbomethoxyhydrazone in acetic acid produced an unknown crystalline solid, I, m.p. 71–72°, in addition to the desired substituted hydrazine. Catalytic reduction of acetaldehyde carbomethoxyhydrazone afforded similar results, and a compound, m.p. 111–112°, was formed along with crude 1-ethyl-2-carbomethoxyhydrazine.

Compound I, $C_{16}H_{34}N_2O_2$, was not attacked readily by 5% alcoholic potassium hydroxide solution, but was hydrolyzed to a chlorine containing substance, $C_{14}H_{33}ClN_2$, by refluxing with concentrated hydrochloric acid. This was shown to be 1,1-diheptylhydrazine hydrochloride by comparison with an authentic sample of the material which was prepared by the alkylation of hydrazine with *n*-heptyl chloride. These results suggested that I is 1-carbomethoxy-2,2-diheptylhydrazine.

In order to substantiate this structure, the

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(1) This research was supported through Research Grant CY-4662 from the Cancer Chemotherapy National Service Center, National Cancer Institute, U.S. Public Health Service.

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synthesis of I was undertaken by the reaction of 1,1-diheptylhydrazine with methyl chloroformate. There were obtained two products: the first was identical with I, and the second was found to be 1,1,5,5-tetraheptylcarbohydrazide, $[(C_7H_{15})_2NNH]_2CO$. An authentic sample of the latter was synthesized from 1,1-diheptylhydrazine and phosgene.

When a methanol solution of heptaldehyde and 1-heptyl-2-carbomethoxyhydrazine was shaken with hydrogen in the presence of platinum, compound I was isolated in 63% yield. It seems reasonable that I was formed during the hydrogenation of heptaldehyde carbomethoxyhydrazone in a similar fashion. The required heptaldehyde might have arisen from hydrolysis of the hydrazone. The intermediate condensation product of heptaldehyde and 1-heptyl-2-carbomethoxyhydrazine then could have suffered hydrogenolysis to afford I and water.

Although the structure of the compound, m.p. 111–112°, obtained from the hydrogenation of acetaldehyde carbomethoxyhydrazone was not determined, analytical data are in agreement with the formula $(C_2H_5)_2NNHCO_2CH_3$.

Experimental[3]

n-Heptaldehyde Carbomethoxyhydrazone.—A mixture of 36 g. (0.4 mole) of methyl carbazate, 51.3 g. (0.45 mole) of n-heptaldehyde, 100 ml. of methanol, and 0.5 ml. of acetic acid was heated to reflux and allowed to stand overnight. The solvents were removed under reduced pressure, and the residue was crystallized from ethyl acetate. There was obtained 67.5 g. (91%) of colorless needles, m.p. 55–58°. After repeated recrystallizations from petroleum ether (b.p. 86–100°), a sample melted at 62–63°.

Anal. Calcd. for $C_9H_{18}N_2O_2$: C, 58.03; H, 9.74. Found: C, 58.37; H, 9.46.

Acetaldehyde Carbomethoxyhydrazone.—This compound was prepared in 88% yield from acetaldehyde and methyl carbazate in the manner described above. The product was recrystallized from a mixture of ether and petroleum ether (b.p. 86–100°) and found to melt at 120–121°.

Anal. Calcd. for $C_4H_8N_2O_2$: C, 41.37; H, 6.94. Found: C, 41.59; H, 7.11.

Hydrogenation of n-Heptaldehyde Carbomethoxyhydrazone.—A solution of 25.4 g. (0.14 mole) of n-heptaldehyde carbomethoxyhydrazone in 50 ml. of acetic acid was shaken with hydrogen, at an initial pressure of 50 p.s.i., for 4 hr. in the presence of 0.5 g. of platinum oxide catalyst. The reaction mixture was filtered and the filtrate was diluted with water to the cloud point. A solid, I, (4.2 g.) precipitated, and after repeated recrystallizations from petroleum ether (b.p. 60–68°) gave fluffy white needles; m.p. 71–72°.

Anal. Calcd. for $C_{16}H_{34}N_2O_2$: C, 67.09; H, 11.96; N, 9.78. Found: C, 67.34; H, 11.80; N, 9.94.

The filtrate from the reaction mixture was extracted repeatedly with ether and the ether extracts were combined, washed with sodium bicarbonate solution, water, dried over anhydrous sodium sulfate, and concentrated. The residue (16.7 g.) was dissolved in dry ether and the solution was saturated with dry hydrogen chloride. There was obtained 14 g. (45%) of 1-heptyl-2-carbomethoxyhydrazine hydrochloride which melted at 126–127° dec. after recrystallization from ethyl acetate.

Anal. Calcd. for $C_9H_{21}ClN_2O_2$: C, 48.10; H, 9.42; Cl, 15.78. Found: C, 48.30; H, 9.55; Cl, 16.15.

The free base was liberated from the hydrochloride by treatment with sodium hydroxide solution; b.p. 89–90°/0.25 mm., m.p. 39–40°.

Anal. Calcd. for $C_9H_{20}N_2O_2$: C, 57.41; H, 10.71; N, 14.88. Found: C, 57.41; H, 10.84; N, 14.62.

Hydrogenation of Acetaldehyde Carbomethoxyhydrazone.—The hydrogenation of 20 g. (0.17 mole) of acetaldehyde carbomethoxyhydrazone was carried out in the same manner as described in the preceding experiment. After removing the catalyst, the solvent was evaporated under reduced pressure and the residue was dissolved in ether. The latter solution was washed with small portions of 10% sodium bicarbonate solution and then with water. The ether solution was dried over anhydrous magnesium sulfate and evaporated to give 1 g. (7%) of a white solid which melted at 111–112° after recrystallization from petroleum ether (b.p. 60–68°).

Anal. Calcd. for $C_6H_{14}N_2O_2$: C, 49.30; H, 9.65. Found: C, 49.20; H, 10.00.

The compound was found to be quite water-soluble and apparently a fair amount was lost during its isolation. The filtrate from the reaction mixture was not investigated further.

Hydrolysis of Compound I.—A mixture of 1.85 g. of I and 20 ml. of concentrated hydrochloric acid was heated in oil bath at 130° for 12 hr. On cooling, a brown upper layer separated which solidified upon the addition of a little water. There was obtained 1.74 g. of material, m.p. 135–144°, which was recrystallized from aqueous methanol and finally from ethyl acetate, m.p., 147–148°. This was shown to be identical with the 1,1-diheptylhydrazine hydrochloride prepared in the next experiment.

Anal. Calcd. for $C_{14}H_{33}ClN_2$: C, 63.00; H, 12.46; Cl, 13.29. Found: C, 63.29; H, 12.26; Cl, 13.55.

Reaction of n-Heptyl Chloride with Hydrazine.—The general procedure of Westphal[4] was followed. A mixture of 44.8 g. (0.33 mole) of n-heptyl chloride, 42.7 g. (1.3 moles) of anhydrous hydrazine, and 25 ml. of anhydrous ethanol was heated at reflux for 16 hr. The reaction mixture was treated with aqueous alkali and extracted with ether. The ether extract was dried over anhydrous potassium carbonate, concentrated, and the residue distilled. There were obtained two main fractions: (1) b.p. 69–71° (2 mm.), 17.8 g. and (2) b.p. 95–97° (0.4 mm.), 16.7 g. Redistillation of fraction 1 gave a product with $n^{25}D$ 1.4440.

Anal. Calcd. for $C_7H_{18}N_2$: C, 64.56; H, 13.93. Found: C, 64.94; H, 13.64.

Redistillation of fraction 2 afforded the dialkylated hydrazine; $n^{25}D$ 1.4453, m.p. 15–16°.

Anal. Calcd. for $C_{14}H_{32}N_2$: C, 73.61; H, 14.12. Found: C, 73.43; H, 14.10.

The hydrochloride of the latter melted at 147–148° and did not depress the melting point of the degradation product obtained above.

Reaction of 1,1-Deheptylhydrazine with Methyl Chloroformate.—A mixture of 2.28 g. (0.01 mole) of 1,1-diheptylhydrazine, 6 ml. of pyridine, and 25 ml. of water was stirred vigorously while 0.95 g. (0.01 mole) of methyl chloroformate was added dropwise. After stirring for an additional 10 min., the precipitate which had formed was removed by filtration. The product (2.27 g.) on crystallization was found to contain two compounds. The first separated as white crystals from methanol. It was purified further by

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[3] All melting points are uncorrected. The elementary analyses were performed by the Weiler and Strauss Laboratories, Oxford, England.

[4] O. Westphal, *Ber.*, **74B**, 759 (1941).

repeated recrystallizations from 90% methanol and pentane; m.p., 95–96°.

Anal. Calcd. for $C_{29}H_{62}N_4O$: C, 72.16; H, 12.95; N, 11.61. Found: C, 72.01; H, 12.88; N, 11.68.

This compound was identical with 1,1,5,5-tetraheptylcarbohydrazide which was synthesized as described below.

The major component of the reaction remained in the mother liquors. After several recrystallizations from petroleum ether (b.p. 60–68°), it melted at 70–72° and did not depress the melting point of I. The infrared spectra of the two materials were identical.

1,1,5,5-Tetraheptylcarbohydrazide.—A solution of 1.14 g. (0.005 mole) of 1,1-diheptylhydrazine in 6 ml. of pyridine was cooled and shaken while 0.25 g. (0.0025 mole) of liquid phosgene was added. After a few minutes, 10 ml. of water was added to the reaction mixture; then it was concentrated under reduced pressure. The residue was made alkaline and the precipitate was removed by filtration. After recrystallization from aqueous methanol it melted at 94–95° and was shown to be identical with the compound isolated in the preceding experiment.

Hydrogenation of a Mixture of *n*-Heptaldehyde and 1-Heptyl-2-carbomethoxyhydrazine.—A mixture of 2.85 g. (0.025 mole) of *n*-heptaldehyde, 4.7 g. (0.025 mole) of 1-heptyl-2-carbomethoxyhyrazine, 17 ml. of methanol, and 0.15 g. of prereduced platinum oxide catalyst was shaken for about 12 hr. with hydrogen at an initial pressure of 50 p.s.i. After removal of the catalyst and solvent, 7 g. of a solid residue was obtained. Recrystallization of this material from petroleum ether (b.p. 60–68°) afforded 4.5 g. (63%) of I which melted at 70–72°. There was obtained 2.5 g. of material from the mother liquors which remained oily at room temperature and was not investigated.

The Application of the Henkel Process to *o*-Phenylbenzoic and *o*-Toluic Acids

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As an extension of our investigation[1] on the mechanism of the Henkel process,[2,3] by which potassium benzoate or dipotassium phthalate is converted into dipotassium terephthalate, the reaction was applied to potassium *o*-phenylbenzoate and potassium *o*-toluate under similar conditions.

Although the reaction with potassium *o*-toluate gave a considerable amount of toluene, it is of interest to note that 2-methylterephthalic acid was also isolated from the reaction mixture. It is probably formed in the same way as the disproportionation of potassium benzoate.

Potassium *o*-phenylbenzoate gave appreciable amounts of both *m*- and *p*-phenylbenzoate together with diphenyl. A small amount of 4,4′-diphenyldicarboxylic acid was also found in this reaction.

Experimental

The Reaction of Potassium *o*-Toluate.—A mixture of finely powdered potassium *o*-toluate (3 g.) and cadmium carbonate (0.24 g.) in a test tube having a rubber stopper fitted with a constricted glass tube was heated for 1.5 hr. at 410° in a metal bath. While heating continuous evolution of toluene was observed. The toluene was collected by cooling and confirmed as 2,4-dinitrotoluene, m.p. and mixture m.p. 69.7°.[4] The solid product was dissolved in boiling water. Colloidal black material was removed by filtration with the aid of zinc sulfate,[1a] the filtrate being acidified with hydrochloric acid and then extracted with ether. On evaporation of ether there was obtained white solid. The petroleum ether-soluble portion of this material consisted of pure starting material, while the insoluble portion (0.13 g.) was shown to be 2-methylterephthalic acid by converting it into the dimethyl ester, m.p. and mixture m.p. 75.5°, lit.,[5] m.p. 76°.

Reactions carried out in ampoules showed similar results. Better yields were obtained using cadmium iodide instead of cadmium carbonate or in the presence of a small amount of water.

Reaction of Potassium *o*-Phenylbenzoate.—*o*-Phenylbenzoic acid was prepared by heating fluorenone with potassium hydroxide, its m.p. being 114°.[6] A mixture of dry potassium *o*-phenylbenzoate (5 g.) and cadmium iodide (1.5 g.) in a sealed tube was heated in an autoclave at 410° for 2 hr. The product was dissolved in 100 ml. of water and extracted with ether. On evaporation the extract gave 2.26 g. of diphenyl, m.p. and mixture m.p. 70°.[7]

The aqueous layer was acidified and then extracted with ether. After evaporation of the ether the residue was separated into two portions, a benzene-soluble one (1.35 g.) and a benzene-insoluble one (200 mg.). The soluble portion was dissolved in concentrated sulfuric acid, poured into water, made alkaline, and then extracted with ether. This process was effective to remove the unchanged *ortho* isomer as fluorenone (620 mg.). From this alkaline solution there was obtained 410 mg. of white crystalline material, which gave, on recrystallization from dry methanol, 50 mg. of *p*-phenylbenzoic acid, m.p. 225°, lit,.[8] m.p. 224°, and mixture m.p. with an authentic material which was prepared by the Gomberg reaction of diazotized *p*-toluidine and benzene followed by potassium permanganate oxidation, 225°. From the mother liquor of the recrystallization, there was obtained 35 mg. of *m*-phenylbenzoic acid by repeated recrystallizations using aqueous methanol as solvent, its m.p. being 160°, lit.,[9] m.p. 160°. The mixture m.p. was 160°, the authentic sample was prepared *via* the same way as the *p*-isomer. The benzene-insoluble portion gave, after conversion into its dimethyl ester and repeated recrystallizations from aqueous methanol, 4,4′-dicarbomethoxydiphenyl (less than 1 mg.), m.p. 224°, lit.,[10] m.p. 225°, and mixture m.p. with an authentic material prepared from diazotized *p*-aminobenzoic acid, 224°.

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