tion of an unconjugated isomer on protonation of such a species has many analogies.

EXPERIMENTAL[17]

N-Phenylpyridinium chloride was prepared according to the method of Grigor'eva *et al.*[18]

N-Phenyl-1,2-dihydropyridine (I). To a stirred solution containing 7.4 g. (0.041 mole) of *N*-phenylpyridinium chloride and 4.6 g. (0.082 mole) of potassium hydroxide dissolved in 1 l. of water, 0.584 g. (0.0155 mole) of sodium borohydride in 50 ml. of water was added all at once. The reaction mixture was stirred for 16 hr. under a nitrogen atmosphere and then filtered, yielding 6.4 g. of a yellow solid containing approximately 20% of the 1,4 isomer (crude m.p. 77–80°). The product was recrystallized three times from methanol (2.8 g., m.p. 81.5–82.5°). Another 1.3 g. was obtained from two recrystallizations of the combined mother liquor. The combined 1,4-free yellow plates, were sublimed at 60°/0.1 mm., yielding 3.9 g. (60%) of yellow crystals, melting at 82.5–83.5°.

Anal. Calcd. for $C_{11}H_{11}N$: C, 84.04; H, 7.05; N, 8.91. Found: C, 83.97; H, 7.30; N, 9.17.

N-Phenyl-1,4-dihydropyridine (II). A solution of 10.0 g. (0.0555 mole) of *N*-phenylpyridinium chloride in 1 l. of water was stirred with 400 g. (0.26 mole) of 3% sodium amalgam for 12 hr. under a nitrogen atmosphere. The reaction mixture was filtered, and the solid product was sublimed twice at 30°/0.1 mm., yielding 6.1 g. (70%) of white crystals, melting at 48–50° (lit.,[11,12] m.p. 48–50°).

Oxidation of N-phenyl-1,2-dihydropyridine. A. With iodine. To a stirred solution of 0.1 g. (0.637 mole) of *N*-phenyl-1,2-dihydropyridine dissolved in 10 ml. of chloroform, 0.161 g. (0.637 mole) of iodine, dissolved in 25 ml. of chloroform was added dropwise for 1 hr. The solution was extracted six times with 10-ml. portions of hot water. Evaporation of the water yielded 0.05 g. (29%) of a white crystalline solid melting at 190–200°. One recrystallization from ethanol raised the melting point to 210–211° (lit.,[11] m.p. 210°). A mixed melting point with an authentic sample of *N*-phenylpyridinium iodide was undepressed. Infrared, ultraviolet and NMR spectra were identical to those of the known iodide.

B. *With methyl iodide.* A 0.1-g. sample (0.637 mole) of *N*-phenyl-1,2-dihydropyridine was dissolved in 2 ml. of methyl iodide and allowed to react for 5 days. The well formed white plates that precipitated from the solution weighed 0.04 g. (22%) and melted at 209–210° without recrystallization. The compound was identical with the known *N*-phenylpyridinium iodide.

C. *With silver nitrate.* An ethanolic solution of silver nitrate turned black instantaneously in the cold, upon addition of a few milligrams of *N*-phenyl-1,2-dihydropyridine.

Oxidation of N-phenyl-1,4-dihydropyridine with methyl iodide. In a similar manner, from 0.1 g. of *N*-phenyl-1,4-dihydropyridine in 2 ml. of methyl iodide, *N*-phenylpyridinium iodide was obtained in 14% yield.

N-Phenylmaleimide adduct of N-phenyl-1,2-dihydropyridine (III). A 0.363-g. sample (2.1 moles) of *N*-phenylmaleimide was placed in a flask which was then evacuated to 10^{-5} mm. From a side arm, 0.300 g. (1.9 moles) of *N*-phenyl-1,2-dihyropyridine was sublimed into the flask. After sublimation was complete, 10 ml. of degassed ethyl ether was distilled into the mixture, giving a clear yellow solution. After a short time, a white solid began to form. The mixture was allowed to stand for 6 hr., after which the mixture was filtered and washed with ethyl ether, yielding 0.450 g. (71%) of the white adduct, melting at 212–215°. Recrystallization from a benzene–methylcyclohexane mixture raised the melting point to 215–216°.

Anal. Calcd. for $C_{21}H_{18}N_2O_2$: C, 76.34; H, 5.49; N, 8.48. Found: C, 76.45; H, 5.64; N, 8.78.

The infrared spectrum showed the imide carbonyl stretch at 1766 and 1701 cm.$^{-1}$, as well as the expected phenyl absorption. The NMR spectrum showed four main areas at 2.92 (10), 3.52 (2), 4.94 (1), and 6.77 (5) τ (parts per million referred to tetramethylsilane as 10.00).

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[17] All melting points are uncorrected. Infrared spectra were taken with a Perkin-Elmer Model 221 recording spectrophotometer. Ultraviolet spectra were taken with a Cary Model 11S recording spectrophotometer. NMR spectra were taken with a Varian Associates 60-mc. high resolution spectrometer. Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside 17, N. Y.

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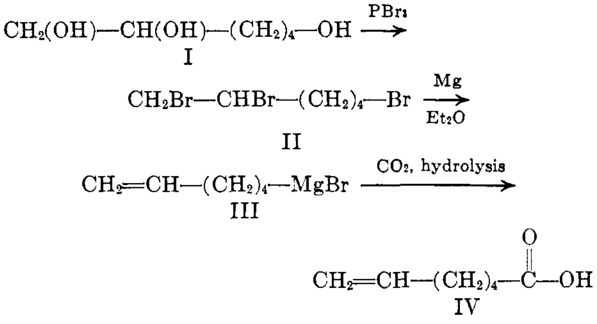
1,2,6-Tribromohexane, 5-Hexenylmagnesium Bromide, and 6-Heptenoic Acid[1]

Robert C. Lamb and P. Wayne Ayers

Recently we have used a new method (in the accompanying scheme) to prepare 6-heptenoic acid (IV). The procedure appears to be the simplest yet reported:



$$\underset{\mathrm{I}}{\mathrm{CH_2(OH){-}CH(OH){-}(CH_2)_4{-}OH}} \xrightarrow{\mathrm{PBr_3}} \underset{\mathrm{II}}{\mathrm{CH_2Br{-}CHBr{-}(CH_2)_4{-}Br}} \xrightarrow[\mathrm{Et_2O}]{\mathrm{Mg}} \underset{\mathrm{III}}{\mathrm{CH_2{=}CH{-}(CH_2)_4{-}MgBr}} \xrightarrow{\mathrm{CO_2,\ hydrolysis}} \underset{\mathrm{IV}}{\mathrm{CH_2{=}CH{-}(CH_2)_4{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH}}$$

Producing Grignard reagents from tribromides, where two bromine atoms are *vicinal*, was developed years ago by von Braun and co-workers.[2] However, application of this procedure to 1,2,6-tribromohexane appears to be new.

The more obvious precursors to III would be 6-bromo-1-hexene[3] and 6-chloro-1-hexene.[4] 6-Bromo-1-hexane has been obtained by the reduction of 6-

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[1] This work was supported by the National Science Foundation, NSF-G11277.

[2] Julius von Braun and G. Kirschbaum, *Ber.*, **52**, 1713 (1919); J. von Braun and Z. Koehler, *Ber.*, **51**, 79 (1913); J. von Braun, H. Deutsch, and A. Schmatloch, *Ber.*, **45**, 1246 (1912); J. von Braun and H. Deutsch, *Ber.*, **44**, 3699 (1911); J. von Braun and W. Sobecki, *Ber.*, **44**, 1938 (1911).

[3] R. E. Lyle, E. J. Dewitt, and I. C. Pattison, *J. Org. Chem.*, **21**, 61 (1956).

chloro-1-hexyne.[4,5] 6-Heptenoic acid has also been prepared by the malonic ester synthesis,[6,7] by action of nitrous acid on 7-aminoheptanoic acid,[8] and by the dehydrohalogenation of 7-chloroheptanoic acid.[9]

EXPERIMENTAL

1,2,6-Tribromohexane. Practical grade 1,2,6-hexanetriol (230 g., 1.7 moles) was treated with phosphorus tribromide (500 g., 1.85 moles) according to the procedure which has been given by Schurink for the synthesis of pentaerythrityl bromide.[10] Two slight modifications were (a) the flask was not heated until all the phosphorus tribromide had been added, and (b) heating was discontinued shortly after the orange color appeared.

After adding the flask contents to 500 ml. of water, the bottom layer was separated, washed twice with cold 2% sodium hydroxide solution, once with water, and dried over anhydrous calcium chloride. The crude tribromide was distilled twice by simple vacuum distillation, b.p. 104° at 1.2 mm. (uncorr.). The yield of pure product, d^{20}_{4}: 1.959; n^{25}_{D}: 1.5507 was 318 g. (58 %).

Anal.[11] Calcd. for $C_6H_{11}Br_3$: C, 22.32; Br, 74.25. Found: C, 22.43; H, 3.32; Br, 74.19.

This previously unreported tribromide was found to lose hydrogen bromide slowly upon standing; hence it was used immediately after distillation.

5-Hexenylmagnesium bromide and 6-heptenoic acid. The Grignard reagent was prepared from 240 g. (0.74 mole) of 1,2,6-tribromohexane and 50 g. (2.06 g.-atoms) of magnesium turnings, and subsequently carbonated with Dry Ice by the usual procedure.[12] The crude 6-heptenoic acid was distilled under reduced pressure, b.p. 78° at 1.0 mm. The yield of pure acid, neut. equiv. 128.2, 128.7 (calcd. 128.2), was 63 g., or 66 % based on the tribromide.

The acid thus obtained gives an infrared spectrum which is identical to that of an authentic sample of 6-heptenoic acid which had been prepared by the method of Gaubert, Linstead, and Rydon.[6] Oxidation of a sample of the acid, prepared by the method described here, with an excess of hot concentrated nitric acid gave a white, crystalline substance in good yield, which by its m.p. 150–151° (rep. 151–153°),[13] and by its neut. equiv. 73.7 (calcd. 73.1), has been identified as adipic acid.

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Catalysis of Acetylation Reactions of Sugars with an Ion Exchange Resin

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Ion exchange resins have been widely used in many types of physical and chemical studies for many purposes. Resins have been used in many chemical reactions as catalysts and their application and properties as catalysts have been reviewed.[1] The resin used in the acetylation reactions reported herein, Amberlite IR-120,[2] bearing the sulfonic acid group, has been used to promote the hydrolysis of disaccharides, starch, and methylated polysaccharides,[3] the preparation of certain glycosides,[3,4] and to catalyze the inversion of sucrose,[5] and catalyze or promote many other chemical reactions.[6]

Acetylated sugars are usually prepared at precise temperatures using an excess of acetic anhydride plus catalytic amounts of pyridine,[7,8] sulfuric acid,[9] zinc chloride,[10,11] or sodium acetate.[12] The particular ring modification of the sugar derivative which is formed depends upon the type of catalyst and the reaction temperature,[11] but often a crystalline product is difficult to obtain because of unfavorable equilibria between these modifications even under carefully controlled conditions. In addition, crystallization is impeded in some cases by trace amounts of those catalysts which are difficult to separate from the product.

Crystalline acetyl derivatives of three sugars were prepared at specified temperatures using Amberlite IR-120 as a catalyst. The insoluble character of the cation exchange resin simplified the isolation and purification of the products and probably is a significant reason why crystalline products in relatively high yield were obtained.

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