Alkylation of Benzene with Triphenylmethyl Chloride

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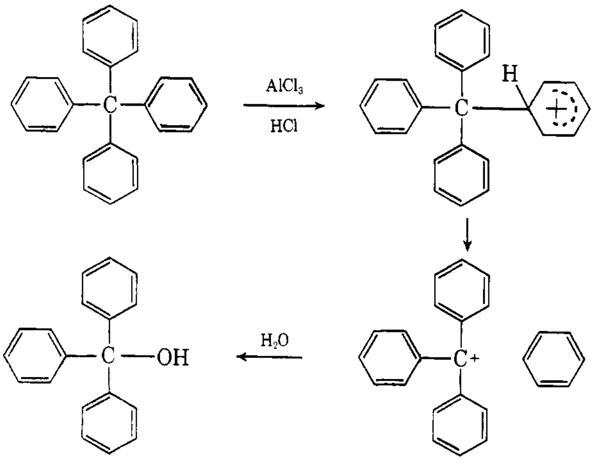
It is common knowledge that benzene and similar aromatic compounds may be readily alkylated with an alkyl halide under Friedel–Crafts conditions. It is, however, a curious fact that tetraphenylmethane cannot be prepared by such direct alkylation procedures.[1] Triphenylmethyl chloride fails to alkylate benzene as do similar systems which presumably involve an intermediate triphenylmethyl cation. Arguments have been presented[2] that this cannot be due to steric hindrance nor to instability of tetraphenylmethane for this substance is "thermally stable."

It appeared reasonable that the thermal stability of tetraphenylmethane should have little or no relationship to the failure of the Friedel–Crafts alkylation reaction but rather the product might well be unstable with respect to reactants under the alkylating conditions. The alkylation process is acknowledged as being in some measure reversible; hence one might anticipate fairly ready dealkylation of the substituted benzene to generate the relatively stable triphenylmethyl cation and benzene. Accordingly we allowed tetraphenylmethane to react with anhydrous aluminum chloride and hydrogen chloride in benzene solution. Hydrolysis of the reaction mixture gave an almost quantitative yield of triphenylcarbinol thus indicating facile dealkylation of the substituted benzene.



In contrast to its ready fragmentation in the presence of aluminum chloride, tetraphenylmethane appears to undergo very little change in concentrated sulfuric acid at room temperature. At higher temperatures the characteristic ultraviolet spectrum of the triphenylmethyl cation could be detected in the solution although the bulk of the tetraphenylmethane could be recovered unchanged from the solution.

The observance of similar behavior in related substances is to be anticipated.

One might now postulate that the triphenylmethyl cation will alkylate benzene but due to an unfavorable equilibrium one fails to obtain significant quantities of product. As a simple test of this hypothesis we allowed 4-methyltriphenylmethyl chloride[3] to react with benzene in the presence of aluminum chloride. If reversible alkylation and dealkylation occurs one would expect to generate a mixture of benzene, toluene, triphenylmethyl cation, and the cation derived from the original reactant. Such was evidently the case for hydrolysis of the reaction mixture afforded triphenylcarbinol, diphenyl-4-tolylcarbinol, and a liquid fraction containing largely benzene but in which toluene could be identified by vapor phase chromatography.

Experimental

Dealkylation of Tetraphenylmethane.—A solution of 1.60 g. (0.005 mole) of tetraphenylmethane in 20 ml. of anhydrous benzene was saturated with anhydrous hydrogen chloride. Upon addition of 2 g. of anhydrous aluminum chloride the colorless mixture turned deep red in color. The mixture was warmed briefly on a steam cone, poured into water, and extracted with ether. Evaporation of the ether extract left a yellow solid residue which, upon decolorization with charcoal and crystallization, afforded 1.25 g. of triphenylcarbinol, m.p. 162–163°. Admixture with authentic triphenylcarbinol gave no melting point depression. The infrared spectrum was identical with that of authentic material.

Attempted Alkylation of Benzene.—A solution of 5.8 (0.02 mole) of 4-methyltriphenylmethyl chloride and 4 g. of anhydrous aluminum chloride in 20 ml. of dry benzene was stirred for 6 hr. at room temperature and then warmed briefly on a steam cone and poured into ice–water. The organic material was extracted with ether and the extract was carefully fractionated by distillation to give an aromatic fraction which by vapor phase chromatography analysis contained a small but definite quantity of toluene. The distillation residue afforded 0.47 g. of authentic triphenylcarbinol after much tedious handling. Somewhat impure diphenyl-4-tolylcarbinol was also recovered and identified by its infrared spectrum.

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[1] C. A. Thomas, "Anhydrous Aluminum Chloride," Reinhold Publishing Co., New York, N. Y., 1941, p. 116.

[2] J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y.,1962, p. 357.

[3] A. Bistrzycki and J. Gyr, *Ber.*, **37**, 655 (1904).

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t-Butyl S-Methyl and S-Phenyl Thiolcarbonates[1]

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Since the first report[2] in 1956 describing the use of the carbo-*t*-butoxy protective group its numerous advantages over other protective groups have become clear. Sufficient effort has been expended regarding the introduction and removal of this function that it has become one of the most valuable of all amino-protecting groups.[3,4]

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[1] Supported by a grant (RG-9706) from the National Institutes of Health.

[2] L. A. Carpino, Abstracts of the 129th National Meeting of the American Chemical Society, Dallas, Tex., April, 1956, p. 59N.

[3] For references to earlier work, see L. A. Carpino, *J. Am. Chem. Soc.*, **82**, 2725 (1960).

[4] For recent examples of the advantageous utilization of the carbo-*t*-butoxy group in the synthesis of complex polypeptides and references to earlier work of the Swiss group, see R. Schwyzer and A. Tun-Kyi, *Helv. Chim. Acta*, **45**, 859 (1962).