tion of the carbon released during solution is effected by the catalytic properties of the metal component.

If the essential idea of the postulated reaction mechanism is correct we should find, for example, a compound such as magnesium silicide reacting with common sources of both halogen ions and protons to form silanes even in non-aqueous media. The preparation of monosilane by treating magnesium silicide with ammonium bromide in liquid ammonia is one example of this reaction.[16] Other examples have been found by experiment

1. The addition of magnesium silicide to molten ethylamine hydrochloride at 110° resulted in a vigorous reaction and the evolution of spontaneously inflammable silanes.

2. When powdered magnesium silicide was dropped into anhydrous trimethylamine hydrochloride at its melting point (ca. 300°) a violent reaction ensued and polymeric silane products were obtained as well as spontaneously inflammable silanes.

3. Heating magnesium silicide with dry ammonium bromide to a high temperature likewise gave evidence of the formation of polymeric silanes.

(16) W. C. Johnson and T. R. Hogness, THIS JOURNAL, 56, 1252 (1934).

Summary

An examination of the literature on hydride formation has indicated that the formation of volatile covalent hydrides by the hydrolysis of metal-non-metal binary compounds is a general reaction and is essentially an ionic reaction.

The ionic mechanism of reactions resulting in the formation of volatile hydrides is believed to be as follows: the removal of positively charged metal ions from the crystal lattice leaves the non-metal atoms in a more or less ionic condition, a condition in which they must have been to some extent even before reaction. These negatively charged non-metal atoms are in a highly reactive condition and will combine with protons, if protons are available under the conditions of the reaction, to form hydrides, provided that the non-metal to hydrogen bonds are stable. The nature of the volatile hydride products subsequently isolated will depend upon: (1) whether the non-metal atoms were initially present in the crystal structure in combination as complex ion units or present as discrete atoms, and (2) whether the particular hydrolysis medium, or the metal component of the binary compound, exerts any chemical effects on the hydrides thus formed.

[CONTRIBUTION FROM THE CENTRAL RESEARCH DEPARTMENT, MONSANTO CHEMICAL COMPANY]

Intermolecular Dehydrations by Means of Phosphorus Pentoxide. I. Preparation of Substituted Acetophenones

BY G. M. KOSOLAPOFF

The present investigation is an extension of previous work on intramolecular dehydrations by means of phosphorus pentoxide,[1] with application of the technique of effective utilization of phosphorus pentoxide developed at that time.

It appeared feasible to effect an intermolecular dehydration between aromatic nuclei and aliphatic acid under the influence of a powerful desiccant, such as phosphorus pentoxide, to give a method of synthesis of various substituted acetophenones. It was felt that such a method might be a valuable competitor for the usual Friedel–Crafts type of synthesis in that acids rather than the more expensive acid halides would be used.

The above expectations have been fulfilled in that a number of aromatic compounds have been successfully condensed with acetic acid to yield the corresponding acetophenones in satisfactory yields. In addition, it has been found that further condensation yields by-products in the form of polyacylated materials and other condensation products. The present paper is restricted to the

(1) G. M. Kosolapoff, Doctoral dissertation, University of Michigan, 1936.

description of syntheses of the first class of compounds.

The procedure used for the syntheses was extremely simple. A mixture of the aromatic compound, glacial acetic acid and phosphorus pentoxide, dispersed by filter-aid, was stirred at reflux for thirty to ninety minutes to complete the reaction. The mixture was treated with water and the organic layer was separated and distilled under reduced pressure. The variation of the ratio of the aromatic substance to acetic acid was found to be effective to a certain extent in controlling the extent of polyacetylation. Usually the use of two to three molar amounts of the aromatic constituent vs. one mole of acetic acid was satisfactory. The amount of phosphorus pentoxide necessary for effective condensation was found to be about half of a mole for each mole of acetic acid used.

The above acetylation method varies in its effectiveness with the reactivity of the aromatic substance used as the starting material. In this respect there is a definite analogy with the chloromethylation reaction, in that reactive substances

like phenolic ethers, xylenes and mesitylene gave very good yields of the acetyl derivatives, while alkylated benzenes, toluene and benzene gave considerably lowered yields, respectively. The most reactive compounds like phenol ethers were most successfully acetylated in a relatively inert solvent like benzene.

Experimental

m-Xylene.—1. *m*-Xylene (106 g., 1.0 mole) and glacial acetic acid (60 g., 1.0 mole) were mixed in a three-necked flask equipped with a Hershberg wire stirrer and a reflux condenser protected by a calcium chloride tube. With stirrer in operation, 3 g. of celite filter aid was added to the mixture, followed by 71 g. of phosphorus pentoxide (0.5 mole). The mixture was stirred vigorously with heating at gentle rate of reflux for two hours. The mixture rapidly assumed a dark color and within five to ten minutes of the initiation of the reaction the suspended pentoxide and the Celite coagulated temporarily to a viscous mass which was kept in motion by increasing the motor torque. Within five minutes the mass began to liquefy, after which it remained quite fluid and was readily stirred into the organic mixture. On cooling, the organic layer was decanted from the semisolid inorganic matter, which was mixed with 200 cc. of water and 100 cc. of benzene, stirred until solution occurred, filtered and the benzene extract combined with the original organic layer. Distillation of this under reduced pressure gave 52 g. of 2,4-dimethylacetophenone as a colorless liquid, b. p. 120–125° at 20 mm., and 10 g. of dimethyldiacetylbenzene, as a rapidly crystallizing oil, b. p. 100–150° at 5 mm. No attempt was made to recover the unused xylene from the forerun.

2. This run was like 1, but with a thirty-minute reaction period. The yield was 53 g. of dimethylacetophenone and 12 g. of dimethyldiacetylbenzene.

3. Carried out as in 1, using 53 g. (0.5 mole) of *m*-xylene, 60 g. (1 mole) of acetic acid and 71 g. (0.5 mole) of phosphorus pentoxide. The yield was 20 g. of dimethylacetophenone, 30 g. of dimethyldiacetylbenzene and 20 g. of undistillable dark semicrystalline residue.

The dimethylacetophenone fractions were combined and redistilled through a packed fractionating column to yield, after a minute forerun, pure 2,4-dimethylacetophenone, b. p. 117–118° at 18 mm., n^{25}D 1.5315. The structure was confirmed by hypochlorite oxidation, in 95% yield, to 2,4-dimethylbenzoic acid, m. p. 125.2–125.5° (from hot water).

The dimethyldiacetylbenzene fractions were combined and recrystallized from alcohol to yield the compound as colorless needles, m. p. 123.5–124°. Hypochlorite oxidation gave an acid which sublimed without melting at 300°; this indicates either 1,2,4,5 or 1,2,3,4, structures. (Confirmation of structure of this and other polyacetyl derivatives will appear in a subsequent paper.)

Toluene.—Toluene (92 g., 1.0 mole), glacial acetic acid (60 g., 1.0 mole), 71 g. (0.5 mole) of phosphorus pentoxide and 3 g. of Celite treated as above for two hours yielded only 15 g. of methylacetophenone, b. p. 115–120° at 20 mm. No diacetyl derivative was obtained.

Cyclohexylbenzene.—An experiment run analogously to that with toluene gave but 3 g. of high-boiling oil, pre-

sumably cyclohexylacetophenone, b. p. 150–160° at 10 mm.

t-Butylbenzene.—An experiment run as above gave 8 g. of *t*-butylacetophenone, b. p. 150–160° at 20 mm.

Anisole.—1. Anisole (108 g., 1.0 mole), 5 g. of Celite and 71 g. (0.5 mole) of phosphorus pentoxide were stirred vigorously with gentle reflux and treated with 60 g. of (1.0 mole) glacial acetic acid added over thirty-five minutes. After further stirring at reflux for ten minutes the mixture was cooled and worked up as above to yield 30 g. of unreacted anisole, 15 g. of methoxyacetophenone, b. p. 157–170° at 30 mm., 30 g. of diacetylanisole and 70 g. of dark residue.

2. Anisole (324.4 g., 3.0 moles), 90 g. (1.5 moles) of glacial acetic acid, 107 g. (0.75 mole) of phosphorus pentoxide, 200 cc. of benzene and 10 g. of Celite were subjected to stirring at reflux for ninety minutes to yield 106.5 g. of methoxyacetophenone, b. p. 90–110° at 1–2 mm., 36.7 g. of diacetylanisole, b. p. 110–260° at 1 mm. and 15.7 g. of undistillable residue. No attempt was made to recover anisole.

The monoacetyl fraction was redistilled through a fractionating column to yield after a minute forerun, pure *p*-methoxyacetophenone, b. p. 118–119° at 3 mm., f. p. 32°.

Phenetole.—1. The first run was made analogously to run 1 under anisole, using 122 g. (1.0 mole) of phenetole. There was obtained 50 g. of ethoxyacetophenone, b. p. 100–105° at 5 mm., and 35 g. of diacetylphenetole, b. p. 170–240° at 5 mm., as well as much undistillable residue.

2. Phenetole (244 g., 2.0 moles), glacial acetic acid (60 g., 1.0 mole), 200 cc. of benzene, phosphorus pentoxide (71 g., 0.5 mole) and 5 g. of Celite were treated as above for seventy-five minutes to yield 152 g. of unreacted phenetole, 95 g. of ethoxyacetophenone, b. p. 145–150° at 20 mm. for a 77% yield, and 20 g. of crude diacetyl derivative.

Redistillation of the monoketone fraction gave pure *p*-ethoxyacetophenone, b. p. 131° at 6 mm., 147° at 16 mm., f. p. 35°, n^{25}D 1.5429 (on supercooled sample). The structure was confirmed by hypochlorite oxidation, in 93% yield, to *p*-ethoxybenzoic acid, m. p. 194.5–195.5° (from ethanol).

The diacetyl compound on recrystallization from alcohol formed shiny pale yellow plates, m. p. 141.5–142°.

The fraction following the diacetyl derivative was a highly colored viscous liquid which appeared to be a dypnone derivative and was not investigated further at this time.

Mesitylene.—Mesitylene (100 g.), glacial acetic acid (120 g.), phosphorus pentoxide (71 g.) and 5 g. of Celite gave, after a ninety minute reaction, 20 g. of recovered mesitylene, 90 g. of acetomesitylene (b. p. 100–102° at 1 mm.) for an 82.5% yield, and 20 g. of semi-crystalline undistillable residue.

Summary

A method for acetylation of selected aromatic compounds is described in which intermolecular dehydration is effected with acetic acid by means of phosphorus pentoxide.