salt of a weaker acid, phosphoric acid, was tried and found to be singularly effective for the formation of hydrazides.

Other acids, *e.g.*, sulfuric, hydrochloric, benzenesulfonic, dichloroacetic, potassium bisulfate and sodium dihydrogen phosphate made up to hydrogen ion concentrations comparable to that of the phosphoric acid used, gave no yield of the phenylhydrazide in any case. Sodium benzenesulfonate and other phosphate salts were tried with negative results.

It appears that the reaction proceeds by a base–acid-catalyzed mechanism in which the phosphoric acid is the acid and the $H_2PO_4^-$ is the base in as much as the amount of acid required to catalyze the reaction lies within a minimum and maximum limit. The effect of minimum and or excess amounts of phenylhydrazine on the yield also seems to support this view.

Experimental

In a typical experiment to prepare the β-acetylphenylhydrazine, 8.8 g. (0.1 mole) of ethyl acetate, 43 g. (0.4 mole) of phenylhydrazine, 5.4 g. (0.3 mole) of water and 1.2 g. (0.01 mole) of sirupy phosphoric acid (85%) were placed in a 100-ml. round-bottom flask and refluxed gently for 1 hour. The water, unreacted ester, and excess phenylhydrazine were then removed by distillation at reduced pressure (*ca.* 20 mm.), the distillation being stopped when the temperature rose above 100° to prevent decomposition of the residue. The material remaining in the flask was then extracted with 100 ml. of hot benzene, from which on cooling, about 9 g. (60% yield) of the phenylhydrazide crystallized out. A single recrystallization from hot benzene produced the silvery platelets characteristic of the phenylhydrazides, m.p. 128° (uncor.), reported 129°.[5] The solubility of the phenylhydrazides in benzene is greatly increased by small amounts of ester or phenylhydrazine. Failure to obtain a solid product on extraction of the residue from the vacuum distillation was usually due to incomplete removal of these reactants.

The same general procedure was suitable for preparing other phenylhydrazides except for the length of time of refluxing. For formates, 0.5 hour was sufficient while for the higher aliphatic esters and benzoates, up to 3 hours were required. For esters of the higher dibasic acids such as ethyl adipate and for methyl salicylate, up to 5 hours of reflux time were needed. The reaction has been tried on all the aliphatic esters through the caprylates, giving yields from 60% for the lower members of the series to as low as 20% for the higher members. For esters of the dibasic acids the yields were about 20%.

When moderate amounts of phenylhydrazides of acids were desired as derivatives for identification purposes,[6] it was found that an adequate yield was produced by heating together under reflux for 1 hour a mixture containing 1 g. of an ester, *e.g.*, ethyl propionate, 4 g. of phenylhydrazine, 0.3 g. of water and 1 drop of phosphoric acid. The hot solution after refluxing was poured into about 75 ml. of 1.4 *N* hydrochloric acid at 30° and stirred until the phosphate salt of the unreacted phenylhydrazine and phenylhydrazine dissolved (*ca.* 5 min.). It was found necessary to maintain these conditions closely because an increase in the temperature or the concentration of the acid caused hydrolysis of the product while a decrease in the temperature or acid concentration extended unnecessarily the time required to dissolve the phenylhydrazine and its salts. After filtering, the crystals were washed free of the ester and other adsorbed impurities with cold cyclohexane or ligroin (b.p. 75–110°), and recrystallized from benzene.

The effect of varying the amount of phenylhydrazine used while holding the quantities of the other reactants and conditions constant was tried. The maximum yields were obtained using 4 equivalents of phenylhydrazine. When the amount of phenylhydrazine was reduced to 2.8 equivalents or increased to 5.6 equivalents the yield was about half of the maximum. If the amount of phenylhydrazine was increased to 8 equivalents or reduced to 1 equivalent, the yield dropped to 5–10%.

The effect of varying the amount of phosphoric acid used while holding the amounts of the other reactants and conditions constant was tried with similar results. The maximum yield was produced with 0.1 molar equivalent of phosphoric acid with little or no yield resulting if the amount of the acid was reduced to 0.025 or increased as high as 0.3 molar equivalent. Decreasing the amount of water to 1 molar equivalent or increasing to 8 molar equivalents cut the yield to about 10%. No yield was obtained in trials when no water was present or when the water was increased to 15 molar equivalents or more.

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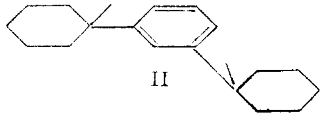
The Structure of Di-(methylcyclohexyl)-benzenes from the Cycloalkylation of 4-Methylcyclohexene with Benzene in the Presence of Hydrogen Fluoride[1]

BY V. N. IPATIEFF,[2] J. E. GERMAIN AND HERMAN PINES

RECEIVED JUNE 30, 1953

It was reported[3] that 4-methylcyclohexene reacts with benzene in the presence of hydrogen fluoride to form 1-methyl-1-phenylcyclohexane in about 75% yield. The remainder of the product consisted of dicycloalkylated benzene from which a solid was separated which melted at 70–71° and to which the structure of *p*-di-(methylcyclohexyl)-benzene (I) was assigned. In order to determine the composition of the dicycloalkylated benzene the higher boiling fractions from several experiments were combined and redistilled on a 30-plate, 26-mm. Oldershaw column.[4] The various cuts were further redistilled using a spinning band Piros–Glover column having an efficiency at a total reflux and at atmospheric pressure of about 60 theoretical plates. Two main fractions were separated: A and B.

I



II

A: b.p. 163.5° at 3.0 mm., n^{20}_{D} 1.5340, d^{20}_{4} 0.9688. *Anal.* Calcd. for $C_{20}H_{30}$: C, 88.82; H, 11.18; Mr_{D}, 86.56. Found: C, 89.32; H, 11.18; Mr_{D}, 86.75.

B: b.p. 181.5° at 3.7 mm., n^{60}_{D} 1.5238, m.p. 70–71° after crystallization from ethanol. *Anal.* Calcd. for $C_{20}H_{30}$: C, 88.82; H, 11.18. Found: C, 88.74; H, 11.17.

Based on spectrographic analyses and boiling point the polycycloalkylated benzene consisted of 23% compound II, most probably *m*-di-(1-methylcyclohexyl)-benzene, and 64% compound

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[1] This work was made possible in part through the financial assistance of the Universal Oil Products Company, Des Plaines, Illinois.

[2] Deceased, November 29, 1952.

[3] V. N. Ipatieff, E. E. Meisinger and H. Pines, THIS JOURNAL, **72**, 2772 (1950).

[4] F. C. Collins and V. Lantz, *Ind. Eng. Chem., Anal. Ed.*, **18**, 673 (1946).

I. The remainder was composed of higher boiling hydrocarbons most probably tri-(methylcyclohexyl)-benzene.

Proof of Structure. Fraction B.—Eighteen grams of B dissolved in 30 ml. of benzene was dehydrogenated by passing it over chromia–alumina catalyst[5] at 450°, according to the procedure described previously.[3] The solution was passed five times over the catalyst at an hourly liquid space velocity of 0.10, and the crystals removed between each pass. The gases, 8.3 liters, produced during the dehydrogenation consisted of 21% methane and 79% hydrogen. The crystalline material, amounting to 6.5 g., melted after crystallization from absolute ethanol at 202–205°.

Anal. Calcd. for $C_{10}H_{14}$: C, 93.87; H, 6.12. Found: C, 93.58; H, 6.56.

The melting point of a known sample of *p*-terphenyl, which was crystallized from ethanol, was 206–207.5°. The mixed melting point of the two samples was 204–205°. The infrared spectra showed that the sample obtained from dehydrogenation contained about 95% of *p*-terphenyl. Minor intensity bands at wave lengths of 12.3 μ which are characteristic of *m*-disubstituted aromatics were present.

Fraction A.—The product, 16.2 g., was dehydrogenated as indicated above. After four passes 12.0 g. of liquid and 7.7 liters of gas were recovered, the latter was composed of 86.6% hydrogen and 11.3% methane. From the liquid hydrocarbons 1.2 g. of solid separated on cooling, which after crystallization from ethanol melted at 83–85°. It did not depress the melting point of an authentic sample of *m*-terphenyl. The infrared spectra of the two compounds were identical.

The liquid product obtained from dehydrogenation distilled at 204–230° at 12 mm., $n^{20}\text{D}$ 1.6070. Since the original product appears, according to infrared spectra and physical constants to consist of a pure compound, it is possible that during dehydrogenation a migration of a methyl group occurred.

Spectroscopic Data.—The wave lengths of the absorption bands of I (fraction B), II (fraction A), *p*-terphenyl and *m*-terphenyl are listed below in order of decreasing band intensity, expressed in microns.

I—*p*-di-(1-methylcyclohexyl)-benzene—6.88, 12.04, 6.60, 9.82, 7.27, 9.03, 10.37, 7.40, 7.66, 9.04, 7.14, 10.78 and 11.64.

II—*m*-di-(1-methylcyclohexyl)-benzene(?)—14.10, 12.58, 7.24, 7.02, 6.21, 6.69, 11.12, 10.32, 7.36, 9.00, 7.68, 8.33, 11.56, 11.66, 13.07, 10.75, 9.75, 8.12, 8.65, 9.60 and 12.07.

***p*-Terphenyl**—13.32, 14.39, 11.90, 12.97, 13.81, 9.89, 9.28, 10.95 and 8.96.

***m*-Terphenyl**—13.33, 14.33, 14.29, 13.07, 12.48, 11.16, 9.26, 9.67 and 9.83.

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Spectral Absorption of Solutions of Iodine in Liquid Hydrogen Fluoride

BY L. I. KATZIN AND J. J. KATZ

RECEIVED AUGUST 3, 1953

It is generally accepted that the colors of solutions of iodine reflect specific solvation interactions, the "violet" solutions in solvents like carbon tetrachloride, carbon disulfide or aliphatic hydrocarbons displaying no effect of solvent on the vapor-like absorption of the iodine, and the various red through brown solutions in the benzenoid hydrocarbons and oxygenated solvents showing shifts of the peak of the absorption toward the ultraviolet in relation to the strength of the specific interaction between the iodine and the solvent.[1-7] Mass action constants for formation of monosolvates have been determined for many of these systems, and similar relations have been shown for solutions of bromine in benzenoid hydrocarbons.[8]

Water as a solvent shifts the iodine spectrum in the same sense as do the oxygenated organic compounds. A recent publication[9] on another oxygenated inorganic solvent, 96% sulfuric acid, reports that iodine shows a red color (absorption at 502 mμ instead of the 517 mμ of carbon tetrachloride or 450 mμ of water), while in the oxygenated organic solvent, trifluoroacetic acid, iodine shows an absorption maximum at 515 mμ. We have hereby been stimulated to publish our observations on the absorption of iodine in liquid hydrogen fluoride, for which we find a broad absorption maximum centering at about 514 mμ. The solution is violet colored. Tracing the absorption with a Cary recording spectrophotometer, we can find no second absorption peak down to the limit of the instrument (and the cell system) at 220 mμ. This is therefore apparently not analogous to the case of iodine in *cis*-dichloroethylene, trichloroethylene and tetrachloroethylene, in which optically "violet" solutions show an intense absorption in the ultraviolet, in the vicinity of 270–280 mμ, which gives evidence of complex formation.[10,11]

If the color of the iodine solution in hydrogen fluoride is due to minimal solvent–solute interaction, addition of a strong-base solvent, such as diethyl ether, should affect the absorption. If iodine is dissolved in a mixture of one part by weight diethyl ether to 10 parts hydrogen fluoride, the solution is a red-orange, and the absorption peak is shifted down to about 508 mμ. With 33% ether, the orange color is more marked, and the absorption peak is at about 500 mμ. With a solution composed of 75% ether and only 25% hydrogen fluoride, a yellow-brown solution is found, with a principal absorption at about 360 mμ (it was followed only down to 340 mμ) and a lesser shoulder or peak with its maximum at about 460 mμ. The latter corresponds presumably to the iodine absorption in ether, and the intense 360 mμ peak is undoubtedly the long-wave length peak of the triiodide ion doublet, the second member falling below 300 mμ.

Qualitatively similar color changes could be seen for methanol–hydrogen fluoride mixtures as solvent, but spectral observations were impractical because of apparently accelerated reaction between the iodine and the nickel of the observation cell in this system. All of the colors seemed further

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