

pared with myrcene, 1-pentene and styrene dibromide, the approximate speed and the intensity of the color formation were greatest in the case of the 1-phenyl-1,2-butadiene and decreased in the order named with the other compounds.

Since compounds possessing a cumulated system of double bonds respond to the Meinel tests, the method is not specific for the conjugated system.

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U. S. DEPARTMENT OF AGRICULTURE
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Preparation of Phenylacetone

BY J. PHILIP MASON AND LEWIS I. TERRY

Phenylacetone has been prepared by several methods.¹ We have obtained it in a 32% yield from benzene, chloroacetone and anhydrous aluminum chloride.

Experimental

Forty-one grams (0.31 mole) of anhydrous aluminum chloride and 100 ml. of anhydrous benzene (free from thiophene) were put in a 500-ml. three-necked flask which was equipped with a mercury-sealed stirrer, a reflux water condenser and a small addition funnel. The top of the condenser was connected to a sulfuric acid trap and this trap was connected to a gas absorption bottle. The mixture was stirred, heated to refluxing on a steam-bath and 13.9 g. (0.15 mole) of chloroacetone was allowed to drop in slowly during a period of thirty minutes. After refluxing for five hours, the mixture was practically black. After cooling to room temperature, the reaction mixture was decomposed by adding water slowly through the addition funnel, stirring during the addition. When no more hydrogen chloride was evolved, 20 ml. of water and 20 ml. of concentrated hydrochloric acid were added. The benzene layer was separated and the aqueous layer extracted with four 25-ml. portions of benzene. All of the benzene solutions were combined and filtered. The benzene was distilled and the remaining viscous oil was distilled under reduced pressure. Nine grams of liquid boiling below 123° (20–22 mm.) was obtained. Approximately 10 g. of high-boiling liquid was left in the distilling flask.

Phenylacetone was recovered from the distillate by making the sodium bisulfite addition product, filtering, decomposing the addition product with sodium carbonate solution and steam distilling as long as any oil distilled. The distillate was extracted with ether, the ether solution dried over anhydrous magnesium sulfate and the ether distilled on a steam-bath. The phenylacetone was distilled under reduced pressure, b. p. 108–114° at 20–22 mm.; yield, 6.5 g. or 32%. The semicarbazone melted at 188°.²

Several variations of this procedure were tried in an effort to increase the yield. The yield was decreased by

(a) decreasing the time of refluxing to one or two hours after the addition of the chloroacetone, (b) lowering the temperature of the reaction and allowing a longer time for its completion, (c) adding the aluminum chloride in small portions over a period of two hours to a boiling mixture of benzene and chloroacetone, and then refluxing for two hours. No change in the yield occurred when (a) the ratio of chloroacetone and aluminum chloride to benzene was increased, or (b) the ratio of aluminum chloride was increased from two equivalents to 2.5 equivalents.

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Vapor Pressures of Trimethylphosphine, Trimethylarsine and Trimethylstibine

BY E. J. ROSENBAUM AND C. ROGER SANDBERG

We prepared pure samples of the methyl derivatives of phosphorus, arsenic and antimony for an investigation of their Raman spectra. Because of the paucity of data on the physical constants of these compounds we have measured their vapor pressures. Phosphorus methyl and antimony methyl were prepared from methylmagnesium iodide and the corresponding trichloride.¹ The crude phosphorus methyl was purified by precipitation with silver iodide,² washing thoroughly and heating gently in a vacuum to regenerate the phosphorus methyl. Arsenic methyl was prepared by a modification of the method of Renshaw and Holm.³ A small amount of arsenic trichloride was condensed on zinc methyl cooled by a carbon dioxide-acetone bath, which was slowly removed until the reaction was complete. Then the bath was replaced and more arsenic trichloride was condensed. This procedure was repeated until all of the reagents were used up. The resulting double salt was decomposed with sodium hydroxide solution, forming arsenic methyl.

In all cases the products were dried over phosphorus pentoxide and fractionated many times, the final fractionation being in a vacuum. The vapor pressures of head and tail fractions agreed to within 1 part in 500. The Raman spectra of these compounds showed no lines which could not be attributed to the compounds themselves. This, of course, is not a very sensitive criterion of purity.

The vapor pressures were measured in the range –25 to +25° with a mercury manometer and a cathetometer. The temperatures were measured

(1) Herbst and Manske, "Organic Syntheses," Vol. XVI, 1936, p. 47. Additional references on p. 50.

(2) Pickard and Kenyon, *J. Chem. Soc.*, **105**, 1124 (1914).

(1) Hibbert, *Ber.*, **39**, 160 (1908).

(2) Mann, Wells and Purdie, *J. Chem. Soc.*, 1828 (1937).

(3) Renshaw and Holm, *THIS JOURNAL*, **42**, 1468 (1920).

with a type K potentiometer and a copper-constantan thermocouple calibrated against a thermometer which had been calibrated by the Bureau of Standards. The molecular weights were determined by the vapor density method.

The measured vapor pressures could all be represented by an equation of the conventional form: $\log p = A/T + B$. The values of the constants, the average deviation of the observed from the calculated vapor pressures and the values of certain derived quantities and of the molecular weights are given in the table.

Compd.	P(CH ₃) ₃	As(CH ₃) ₃	Sb(CH ₃) ₃
A	-1518	-1456	-1697
B	7.7627	7.3936	7.7068
Av. dev., %	1	1.5	<1
B. p., °C.	37.8 ^a	49.5 ^b	78.5 ^c
ΔH_{vap} , cal.	6943	6660	7760
Trouton's constant, cal./T	22.3	20.6	22.1
Mol. wt.	Obsd.	75.5	119.0
	Calcd.	76.10	120.03

^a Previous recorded value, 40–42° (Cahours and Hofmann, *Ann.*, **104**, 29 (1857)). ^b Previous recorded values, 51.9° (Renshaw and Holm, *THIS JOURNAL*, **42**, 1468 (1920)); 51–53° (Dyke and Jones, *J. Chem. Soc.*, 2426 (1930)); 68–73° (G. Natta, *Chem. Zentr.*, **98**, I, 416 (1927)); 74° (Paneth and Loleit, *J. Chem. Soc.*, 366 (1935)). ^c Previous recorded values, 82° (Paneth and Loleit, *ibid.*, 366 (1935)); 80.6° (Landolt, *J. prakt. Chem.*, **84**, 329 (1861)).

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Hydrogen Fluoride as a Condensing Agent. XI. The Reaction of Alcohols and Ethers with Benzene¹

BY J. H. SIMONS AND S. ARCHER

Hydrogen fluoride has been found² to be an effective catalyst for alkylations in which aliphatic alcohols and ethers are used. We have now made additional studies of this reaction using primary, secondary, and tertiary alcohols and their ethers. Good yields were obtained with secondary and tertiary compounds at room temperature; but with primary compounds except benzyl alcohol and ether, 100° was necessary to obtain appreciable yields. *n*-Butyl alcohol and *n*-butyl ether both gave *s*-butylbenzene in about 20% yield. Benzyl alcohol and benzyl ether

(1) For the previous paper see Simons, Archer and Randall, *THIS JOURNAL*, **62**, 485 (1940).

(2) (a) Calcott, Tinker and Weigmayr, *ibid.*, **61**, 1010 (1939); (b) Simons, Archer and Passino, *ibid.*, **60**, 2956 (1938).

both gave a 65–70% yield of diphenylmethane at room temperature. From the reaction of isopropyl alcohol with benzene in a mole ratio of about one to seven, four compounds were isolated: isopropylbenzene, 1,4-diisopropylbenzene, 1,2,4-triisopropylbenzene, and 1,2,4,5-tetraisopropylbenzene, in yields of 22.4, 14, 26, and 28%, respectively. The ether gave the same products in yields of 26, 24, 25, and 8%. *t*-Butyl alcohol and *t*-amyl alcohol reacted with benzene, when the mole ratios were about one to seven, to give about 40% monoalkylated and 50% dialkylated products.

Several items of interest are noted from the above experimental results. Alcohols react more readily, *i. e.*, give a good yield at lower temperature, than the corresponding chlorides. For example, secondary chlorides reacted very slowly to give low yields in a twenty-four hour reaction time at room temperature, whereas secondary alcohols or ethers gave high yields at the same temperature. Although the mechanism of the reaction is unknown, one fact is obvious and may be a contributing factor when it is known. When the chlorides are used, hydrogen chloride is evolved; and for reactions at atmospheric pressure its thermodynamic activity in the reaction mixture must equal that for the gas at one atmosphere. When alcohols or ethers are used, water is a product of the reaction; and it remains in solution in the hydrogen fluoride. Its activity in this solution is very much lower than liquid water at the same temperature. For certain mechanisms this difference would contribute to the driving force of the reaction.

The other point of interest lies in the fact that when aluminum chloride is used as the condensing agent, the chlorides react more readily than the alcohols. Reasoning from this and also from the fact that chlorides can be made from the alcohols by treatment with aluminum chloride, the formation of the chloride may be postulated as the first step in the reaction. As the ease of reaction is in the opposite order when hydrogen fluoride is used, the reaction in this case may proceed through a different mechanism.

The ease of reaction of benzyl alcohol is a strong argument against the hypothesis that an olefin is an intermediate in the reaction. Such a mechanism has been postulated by McKenna and Sowa³ for reactions between alcohols and benzene

(3) McKenna and Sowa, *ibid.*, **59**, 470 (1937).