

ples⁵ which melted at 93–96° showed an ultraviolet absorption maximum at 2275 Å. ($\log \epsilon$ 4.07, cyclohexane). By brominating the combined intermediate fractions (0.5 g.) in cold acetic acid (5 cc.) there was obtained 0.20 g. of impure 1-cholestenone dibromide (effervesces at 85°). On allowing the filtrate to stand for a few minutes, hydrogen bromide was evolved and there separated 0.095 g. of needles, m. p. 152–156°. The dibromide liberated iodine on warming in an alcoholic sodium iodide solution but the needles did not. The latter on crystallization from methyl acetate melted at 169° and mixed with 2-bromocholestanone showed no depression. The crude dibromide was debrominated with sodium iodide or zinc dust in alcohol, or potassium iodide in 80% acetone, to give the corresponding unsaturated ketone, m. p. 102–104°. By repeating the purification through the dibromide, pure 1-cholestenone, crystallizing as a hydrate from 98% methanol or aqueous acetone, m. p. 107–108° ($[\alpha]^{24D} + 65^\circ$).

These observations indicate that the collidine treatment of 2-bromocholestanone, under the conditions specified, gives principally a mixture of 1-cholestenone and cholestanone. The formation of the latter compound is not surprising in view of

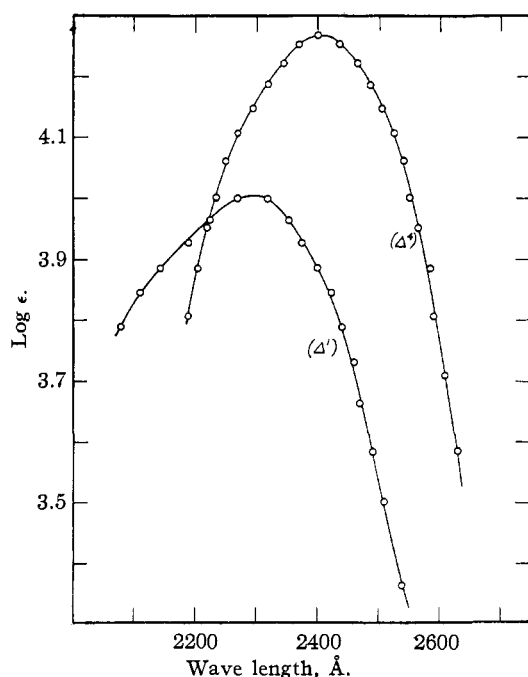


Fig. 1.

(5) These properties correspond closely to those of the product (m. p. 95°) of Butenandt, *et al.*, who reported a maximum at 230 $m\mu$ ($\log \epsilon$ 4.03).

the work of Schwenk and Whitman,⁶ who obtained cholestanone as the principal product of the treatment of 2-bromocholestanone with dimethylaniline.

The ultraviolet absorption in alcohol of 1-cholestenone hydrate (calculated on the anhydrous basis) in the region of the maximum is compared with that of the Δ^4 -isomer in Fig. 1.

The preparation of 1-cholestenone will be detailed later in connection with a report of photo-dehydrogenation studies now in progress.

(6) Schwenk and Whitman, *THIS JOURNAL*, **59**, 949 (1937).

WASHINGTON BIOPHYSICAL INSTITUTE

BETHESDA, MARYLAND

RECEIVED APRIL 27, 1940

The Behavior of Certain Substituted Allenes toward the Meinel Color Test¹

BY F. B. LAForge AND FRED ACREE, JR.

A method for the detection of conjugated double bonds has been proposed by Meinel^{1a} based upon the treatment of the compound to be tested with one molecular equivalent of bromine in methanol solution. The isolated reaction product is then treated with a suspension of silver thiocyanate containing ammonium ferric sulfate. The formation of a red color of variable intensity depending upon the compound is indicative of the presence of a conjugated system of double bonds.

Conant and Jackson² have reported the formation of dibromo compounds along with the methyl hypobromite addition products when bromine in methanol solution is allowed to react on an unsaturated compound. Thus, while Meinel indicated that the methyl hypobromite addition product is responsible for the reaction with silver thiocyanate, there also is the possibility that the dibromo addition product might be the influencing factor in the reaction.

Meinel subjected a number of compounds to the test but did not include any that possessed a cumulated system of double bonds.

In studying the reaction of halogens³ on compounds of this class it was of interest to determine whether or not they would also respond to the color test.

It was found that 1-phenyl-1,2-butadiene, 2,3-pentadiene, 1-cyclohexyl-2,3-pentadiene, and pyrethrene gave a positive reaction. When com-

(1) Not subject to copyright.

(1a) K. Meinel, *Ber.*, **70B**, 429 (1937).

(2) J. B. Conant and E. L. Jackson, *THIS JOURNAL*, **46**, 1727 (1924).

(3) Fred Acree, Jr., and F. B. LaForge, *J. Org. Chem.*, (in press).

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.

BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE
U. S. DEPARTMENT OF AGRICULTURE
WASHINGTON, D. C. RECEIVED APRIL 10, 1940

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.

CHEMISTRY LABORATORY
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BOSTON, MASSACHUSETTS RECEIVED MARCH 14, 1940

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).