

carbon dioxide was evolved and oily layers formed which distilled with the water vapor. The products were dried over calcium chloride and distilled. The decreased yields found among the higher members of the series as indicated in the table below are probably the result of partial hydrolysis by water. Longer heating with water is necessary to steam distil these higher boiling substances than is necessary with the members of lower molecular weight.

With bromine the 1,1-dibromoolefins form tetrabromides which are colorless oils and which have an intense camphor-like odor. These products were not further investigated.

Summary

The decompositions of α,β -dibromo and α,α,β -tribromo aliphatic acids with alkaline reagents yield the corresponding 1-bromoolefins and α -bromoolefinic acids in the first case and 1,1-dibromoolefins in the second case.

The 1-bromo-1-olefins may serve as intermediates in the preparation of normal acetylenes in good yields. The 1-bromoolefins as well as the 1,1-dibromoolefins add one mole of bromine to yield oils having camphor-like odors.

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Phosphoric Acid in Organic Reactions

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Phosphoric acid is superior to sulfuric acid as a catalyst in certain organic reactions of hydrolysis,¹ dehydration and isomerization. Its chief advantages are disclosed in its lesser tendency to carbonize or otherwise to react with the organic materials, hence these processes can be made to deliver larger yields of desired products. Furthermore, the phosphoric acid can be recovered from the reaction mixtures practically pure for repeated use.

We have found that it is the ideal catalyst for ketonic hydrolyses of alkyl acetoacetates, having obtained 95% yields of the ketones and no fatty acids, whereas sulfuric acid and the alkalis give less than 70% yields of the ketones. The advantages here result from lesser carbonization, from lesser quantities of water used, and in the simple method of reprocessing fractions containing unchanged acetoacetates. Because either acids or alkalis hydrolyze the acetoacetates, the mechanism of reaction seems to be conditioned by the capacity of the reagent to add to the reactant before hydrolysis results.

(1) For the use of phosphoric acid to prepare olefins. see Newth, *J. Chem. Soc.*, **79**, 915 (1901); Adams, Kamm and Marvel, *THIS JOURNAL*, **40**, 1951 (1918); German Patent 66.866.

Cyclohexanol, menthol and certain hydroxylated terpene derivatives were practically quantitatively dehydrated by phosphoric acid. It isomerized pinene to dipentene and terpinene, and gave dipentene, terpinolene and terpinene as the chief products from terpin hydrate, terpineol² and cineol. Also it polymerized pinene and other terpenes. In all cases, the concentration of the acid and a high temperature were the important conditions to effect either dehydration or isomerization, otherwise quite different products were formed.

As a qualitative reagent, for example, in testing for cocaine and other benzoylated derivatives, the acid gave positive indications with minute quantities of material tested. The acid was found to be useful for the identification of carbohydrates³ and glucosides.

Experimental

In the following experiments phosphoric acid of 85% concentration was used. For recovery of the acid, the residual mixture was diluted with water and filtered. If too dark in color, this was concentrated by evaporating with a little nitric acid to sp. gr. 1.70.

Ketonic Hydrolysis of Ethyl *n*-Amylacetate.—A mixture of 200 g. of acid and 200 g. of the acetoacetate was placed in a one-liter round-bottomed flask which carried a dropping funnel and was attached to a condenser. Moderate heating in an oil-bath caused evolution of carbon dioxide and the distillation of an oil-water mixture. From time to time this distillate was placed in the dropping funnel and the lower aqueous layer was permitted to drop into the flask as the distillation continued. Later the oily layer was fractionated through a column and the oil boiling above 155° was returned to the flask for further hydrolysis. By repetition of these processes and with effective fractionation of the oils, 95% yields of methyl amyl ketone boiling at 150–150° were obtained. The alcohol fraction must be salted out with calcium chloride to obtain the maximum yield of the ketone.

Because ketones give high boiling chain condensation products by treatment with the acid at high temperatures, the above reaction should be carried on so as to avoid the evolution of white cloudy vapors.

It was thought that if the concentration of the hydroxyl ions was kept low, large yields of the ketone could be obtained with alkalies. Employing essentially the method of Johnson and Hager⁴ barium and calcium hydroxides were tried. With 0.2–1.0 mole of barium hydroxide, all added at once or aliquot parts added during four hour periods the yields were 40–60%. With 1.3–2.7 moles of calcium hydroxide, all added at once, the yields were 60–70%. Thus though the yields with calcium hydroxide were better, in no case of nine experiments could the yields be raised above 70%. Owing to the large quantities of water used, and otherwise, this method is laborious and is greatly inferior to the phosphoric acid method.

Cyclohexene from Cyclohexanol.⁵—A one-liter round-bottomed flask, containing 100 g. of acid and carrying both a dropping funnel and a distilling column attached to a condenser, was heated in an oil-bath at 160–170°. Through the funnel 500 g. of pure cyclohexanol was dropped in at such a rate as was convenient to collect the distillate, whose receiver was surrounded by ice water. During the distillation, a thermometer in

(2) Wallace [*J. Am. Chem. Soc.*, **27**, 106 (1893)] reports that 20% acid only slowly yields terpinene, terpinolene and cineol.

(3) Dehn, Jackson and Ballard, *Ind. Eng. Chem., Anal. Ed.*, **4**, 413 (1932).

(4) "Organic Syntheses," Coll. Vol. I, 1932, p. 343.

(5) For comparative methods, see "Organic Syntheses," Coll. Vol. I, 1932, p. 177.

the column registered temperatures below 100°. The distillate separated into oily and aqueous layers. The upper layer was dried with calcium chloride and then fractionated through an efficient column, taking only that which came over below 88°. The residual oil and the original aqueous layer were returned to the reaction flask for further dehydration and distillation. By repetition of these processes, ultimately 393 g. of oil boiling below 88°, or 96% of cyclohexene, was obtained. The residual oil (19 g.) yielded unchanged cyclohexanol and a higher boiling oil (200–230°) which will be investigated.

Menthene from Menthol.—A mixture of 100 g. of menthol and 50 g. of phosphoric acid was heated in a round-bottomed flask under a reflux condenser for four hours, and then the contents were distilled up to 200°. The oily layer was separated, dried with calcium chloride and distilled. The fraction boiling at 166–170° weighed 82 g., which is equal to a 94% yield of menthene.

Dehydration of Terpin Hydrate.—The reactions here are dehydration, isomerization and polymerization. A mixture of 100 g. of acid and about 200 g. of terpin hydrate was distilled from a flask heated to 200° in an oil-bath, then other similar portions of 970 g. of the hydrate were added and distilled. Finally the water of the distillate was dropped in as long as oily distillate passed over. The theoretical yield⁶ of dehydrated oil was 694 g.; found 685 g. Its repeated fractionation⁷ gave 65% boiling at 172–777° (dipentene); 18% boiling at 177–181° (terpinene); 2% boiling at 181–190° (terpinoline) and 11% boiling at 315–325° (colophene). A dehydration of 500 g. of terpinene hydrate at 150–160° gave 98% of oil, 50% of which boiled within the range of terpinene and only 2–3% was colophene.

Isomerization of Turpentine.—When turpentine was dropped into 40–60% acid at 200° only 10–20% was isomerized or polymerized. When 436 g. was dropped into 98–100% acid at 200° more than 95% was transformed, 430 g. being separated and fractionated as follows; 3% boiling below 170°; 72% boiling at 170–177°; 3% boiling at 177–190°; 16% boiling to 325°, mostly colophene.

Terbene.—Medicinal terbene, which fractionated 75% below 165°, was reprocessed as with turpentine and then gave 90% boiling above 170°.

Dehydration of Terpeneol.—When 100 g. of practical terpeneol and 50 g. of acid were refluxed for four hours, the oil was separated and fractionated as follows: 8% boiling up to 173°; 54% boiling at 173–177°; 15% boiling at 177–183°; 2% boiling at 183–187°; 16% above 187°.

Dehydration of Cineol.—When 100 g. of cineol and 50 g. of acid were mixed, heat developed and a white solid⁸ separated. This solid dissolves on heating. After refluxing for four hours, the oil gave the following fractions: 8% below 173°; 54%, 173–177°; 19%, 177–183°; 15% above 183°.

Pinacol Hydrate.—When 100 g. of pinacol hydrate and 50 g. of acid were refluxed for four hours and then distilled to 180°, refractionation gave: 3.8% below 80° (2,3-dimethylbutadiene); 7.8%, 80–90°; 5.7%, 90–100°; 70%, 100–110° (pinacolone); 10% 110–150° (dimethylisopropenylcarbinol).

Condensation of Acetone.—When equal weights of phosphoric acid and acetone are mixed, heat is developed; on distilling, fractions boiling up to 200° are obtained. When the lower fractions were dropped into the residue of phosphoric acid heated to high temperatures, heavy white smoke was evolved and the distillate yielded fluorescent

(6) In this paper the percentages of fractions obtained were calculated on the basis of the theoretical yields.

(7) Waletzky acted on terpine hydrate at 50–80° with anhydrous phosphoric acid and reported the formation of terpinene, *Compt. rend.*, **94**, 90 (1882).

(8) Baeyer and Villiger, *Ber.*, **35**, 1206 (1902). Terpinene, terpinolene, dipentene and dicinene [Hell and Stürche, *ibid.*, **17**, 197 (1884)] have been reported as dehydration products.

oils boiling all the way up to 350° and a residue of carbon was found in the acid. These chain condensation products will be studied.

Qualitative Tests.—Numerous compounds have been identified by the use of sulfuric acid, which may give colors, liberate odorous components or yield sublimates. Since it may sulfonate, oxidize or char various compounds, it was thought that substitution of it by phosphoric acid would give better tests for certain compounds. This substitution has been made before for a few color reactions⁹ and odors.¹⁰

Whereas cocaine has been identified¹¹ through its hydrolysis by sulfuric acid to benzoic acid, the following test is more convenient. In a clean, dry vial is placed some of the material, suspected to contain cocaine, to this is added 2–3 cc. of 85% phosphoric acid and the mixture is slowly heated on a hot-plate. If cocaine is present, needles of benzoic acid are sublimed to the upper part of the vial.

When material for melting point determinations is desired, longer heating is necessary. The bottom of a small crucible, covered with a thin layer of the solid, or 1–2 cc. of the liquid, to be examined, is treated with 2–3 cc. of phosphoric acid. The crucible, covered with a watch glass, is heated and, if a volatile acid is a product of the hydrolysis, it is obtained as a sublimate and its melting point can be taken. In case the substance under examination is a liquid requiring heating for a longer time, as is the case with methyl salicylate, a few cubic centimeters of water can be placed in the concave surface of the watch glass, to facilitate the collection of the sublimate.

The following substances easily gave benzoic acid with approximately correct melting point: alypin, benzaminoacetic acid, benzyl benzoate, butyl benzoate, cocaine, ethyl benzoate, ethyl hippurate, beta-eucaine, methyl benzoate, stovaine, tropacocaine.

The following substances easily gave salicylic acid with approximately correct melting point: aspirin, *o*-hydroxybenzoic acid, methyl salicylate, salol.

Summary

As a hydrolyzing agent, phosphoric acid gives superior yields of ketones from acetoacetates. As a dehydrating agent, it gives nearly quantitative yields of hydrocarbons from certain oxygenated terpenes, and pinacol hydrate. It isomerizes pinene to mixtures of monocyclic terpenes. It condenses terpenes to colophene and acetone to high boiling chain compounds. It is a convenient qualitative reagent to liberate benzoic and salicylic acids from their derivatives.

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(9) Alkaloids: Arnold, *Z. anal. Chem.*, **23**, 229 (1874); Palet, *J. pharm. chim.*, **19**, 295 (1919); Gallic acid: Drechsel, *J. prakt. Chem.*, **24**, 44 (1881); **27**, 424 (1883); Digitalin: Fluckiger, *Jahresber. Pharm.*, [3] **24**, 459.

(10) Atropine: Nowak and Kratschmer, *Med. chim.*, 276 (1895).

(11) Biel, *Pharm. Z.*, **31**, 132; Aurelj, *Giorn. farm. chim.*, **53**, 385; Scharges, *Z. anal. Chem.*, **36**, 541.