

Anal. Calcd. for $C_8H_{18}O_3$: C, 62.94; H, 10.41. Found: C, 62.55; H, 11.09.

Sodium *n*-Hexylate.—The same general procedure was followed. From 20.4 g. (0.2 mole) of *n*-hexyl alcohol, 5.0 g. (0.21 mole) of sodium hydride and 13.0 g. (0.1 mole) of acetone cyanohydrin nitrate there was obtained, after following the same purification procedure outlined above, 3.3 g. (22%) of *n*-hexyl nitrate, b.p. 68–70° (13 mm.), n_D^{20} 1.4176 [lit.⁷ b.p. 46° (1 mm.), n_D^{20} 1.4180], and 6.3 g. (33%) of *n*-hexyl α -hydroxyisobutyrate, b.p. 78° (0.3 mm.), n_D^{20} 1.4248.

Anal. Calcd. for $C_{10}H_{20}O_3$: C, 63.79; H, 10.71. Found: C, 63.61; H, 11.31.

Sodium *n*-Octylate.—Following the general procedure described, from 26.0 g. (0.2 mole) of *n*-octyl alcohol, 5.0 g. (0.21 mole) of sodium hydride and 13.0 g. (0.1 mole) of acetone cyanohydrin nitrate there was obtained, after purification, 5.2 g. (26%) of *n*-octyl nitrate, b.p. 55–56° (0.3 mm.), n_D^{20} 1.4280 [lit.⁸ b.p. 110–112° (20 mm.)], and 7.8 g. (36%) *n*-octyl α -hydroxyisobutyrate, b.p. 62–64° (0.05 mm.), n_D^{20} 1.4310.

Anal. Calcd. for $C_{12}H_{24}O_3$: C, 66.62; H, 11.18. Found: C, 66.07; H, 11.31.

Alkaline Hydrolysis of Acetone Cyanohydrin Nitrate.—A solution of 13.0 g. (0.1 mole) of acetone cyanohydrin nitrate in 25 ml. of ethanol was added slowly to a solution of 11.2 g. (0.2 mole) of potassium hydroxide dissolved in 100 ml. of ethanol. The reaction was noticeably exothermic. The mixture was heated under reflux for two hours and then poured on ice. The water solution was extracted with ether to remove any unreacted nitrate ester (only a trace was found), then acidified with dilute sulfuric acid and subjected to continuous ether extraction for 18 hours. Upon drying the extracts and evaporating the ether, 7.2 g. (69%) of α -hydroxyisobutyric acid, m.p. 79–82°, was obtained. Its infrared spectrum was identical to that of an authentic sample.

(7) L. M. Soffer, E. W. Parrotta and J. DiDomenico, *THIS JOURNAL*, **74**, 5301 (1952).

(8) L. Bouveault and C. Wahl, *Bull. soc. chim. France*, [3] **29**, 937 (1903).

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Phosphorus Acids in Organic Systems. II. "Polyphosphoric Acid" as a Catalyst in the Fries Rearrangement

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RECEIVED MARCH 2, 1955

In the course of a study of the "polyphosphoric acid" (PPA) catalyzed acylation reaction, certain anomalies were noted in the case of phenols and their esters¹ which are accountable for in terms of a Fries-type of rearrangement. The Experimental section of the present report describes these results only in so far as they supplement a more recent paper.²

Phenyl acetate, for example, gave 35–50% yields of 4-hydroxyacetophenone when treated with PPA at moderate temperatures. Phenyl benzoate under similar conditions afforded a mixture of 4-hydroxybenzophenone and its benzoate. Resorcylic diacetate was converted to 4,6-diacetylresorcinol. In no case was the yield of rearranged product sufficiently high to recommend the method over the classical aluminum chloride catalyzed reaction. The reaction is of interest, however, in that (a) in the case of phenyl benzoate the phenolic ketone

was accompanied by its benzoate and (b) exclusively *para* rearrangement products were observed.³ Some of these observations are consistent with the finding that phosphorus pentoxide in nitrobenzene is effective in the rearrangement⁴ with resultant formation of keto esters. These authors also report *para* rearrangement.

When phenyl acetate was allowed to react with benzoic acid, in the catalyst as a medium, the major product was 4-acetylphenylbenzoate accompanied by some of the expected product, 4-benzoylphenyl acetate. This suggests that phenyl acetate is not receptive to attack by benzoyl ion under these conditions and that the observed ratio of products probably represents the result of competitive attack of the phenol moiety by acetyl and benzoyl ions. The acetylation of phenyl benzoate proceeded normally to give a poor yield of 4-acetylphenyl benzoate as the only isolable product. Acetylation of phenyl acetate (or phenol) afforded fair yields of 4-acetylphenyl acetate.

The aluminum chloride catalyzed reaction generally favors 4-substitution at low temperatures and 2-substitution at high temperatures, the 4-substituted product undergoing further rearrangement to the 2-isomer when the temperature is raised.⁵ A reasonable explanation of this has been proposed.⁶ To determine whether such a relationship exists in the PPA-catalyzed reaction one run (phenyl acetate) was made at 27° for 24 hours. Most of the starting material was recovered along with a very small amount of the 4-isomer. Temperatures higher than 100° did not permit the isolation of any of the 2-isomer but markedly increased the amount of resin formed. Further, to determine whether the 2-isomer might serve as an intermediate in one path to the 4-isomer, a sample of 2-hydroxyacetophenone was treated with the reagent. From a series of experiments of varying times and temperatures, only starting material and ether-insoluble resins could be isolated. The rate of resinification of this substance appeared to be much faster than that of rearrangement of phenyl acetate. Since some resinification occurs in all of these rearrangements, it can be concluded only that the 4-isomer is the more stable one in PPA and none of it is formed *via* the 2-isomer.

Experimental

Rearrangement of Phenyl Acetate.—Under conditions essentially the same as those reported by Snyder and Elston² 50% yields of 4-hydroxyacetophenone were obtained. A temperature of 90° for 1.5 hr. reduced the yield to 35%. A mixture of 28.0 g. of phenyl acetate and 250 g. of PPA was allowed to stand at 27° for 24 hr., decomposed with ice and water and the product separated by extraction with ether. Distillation of the liquid thus obtained through a 10-in. helices-packed column afforded 11.5 g. of starting material, b.p. 97–100° (20 mm.), 1.2 g. of intermediate fraction and 3.5 g. of 4-hydroxyacetophenone, b.p. 170–194° (20 mm.), m.p. and mixture m.p. 107–109°. The intermediate fraction yielded only phenyl acetate and 4-hydroxyacetophenone upon separation with aqueous base.

4-Acetylphenyl Acetate. (a) **From Phenol.**—A solution of 47.0 g. of phenol and 60.0 g. of acetic anhydride in 450 g.

(3) One example² of *ortho* rearrangement has been reported.

(4) A. Schönberg and A. Mustafa, *J. Chem. Soc.*, 79 (1943).

(5) A. H. Blatt in "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 342.

(6) G. W. Wheland, "Advanced Organic Chemistry," Second Edition, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 565.

(1) P. D. Gardner, *THIS JOURNAL*, **76**, 4550 (1954).

(2) H. R. Snyder and C. T. Elston, *ibid.*, **77**, 364 (1955).

of PPA was stirred at 75° for 1.5 hr. and treated as above. Distillation yielded 12.1 g. of phenyl acetate and 46.5 g. (51%) of 4-acetylphenyl acetate, b.p. 165–170° (19 mm.), m.p. 48–51°. Crystallization from ethyl acetate–petroleum ether (50–60°) raised the m.p. to 52–54°. A mixture with authentic material had the same m.p.

(b) **From Phenyl Acetate.**—A solution of 45.0 g. of phenyl acetate, 30.0 g. of acetic acid and 250 g. of PPA was stirred at 75° for 1.5 hr. and treated as above to give 9.02 g. of recovered starting material and 30.1 g. (50%) of 4-acetylphenyl acetate, m.p. 51–53°.

Rearrangement of Phenyl Benzoate.—A mixture of 30.0 g. of phenyl benzoate and 220 g. of PPA was stirred at 80° for 2.5 hr. Hydrolysis with ice and water followed by extraction with a benzene–ether solution afforded a heterogeneous organic mixture. Extraction of this with 10% sodium hydroxide solution followed by acidification of the aqueous phase gave 7.5 g. (25%) of 4-hydroxybenzophenone, m.p. 132–134°. When a sample of this was mixed with authentic material the m.p. was unchanged. The organic phase from the extraction was evaporated to dryness under reduced pressure and the residue crystallized twice from methanol–water to give 4.0 g. (13%) of 4-benzoylphenyl benzoate, m.p. and mixture m.p. 111–113°.

Rearrangement of Resorcylic Diacetate.—A mixture of 100 g. of resorcylic diacetate and 400 g. of PPA was stirred at 70° for 2 hr. and worked up as in the previous examples. There was obtained 19.1 g. (19.1%) of 4,6-diacetylresorcinol, m.p. 179–180°. One crystallization from ethyl acetate–cyclohexane raised the m.p. to 181–182° (lit.⁷ 182°).

Attempted Rearrangement of 2-Hydroxyacetophenone.—Forty grams of freshly distilled 2-hydroxyacetophenone⁸ (b.p. 110–112° at 19 mm.) was heated with 200 g. of PPA for 15 min. at 95°. Isolation in the usual manner afforded 28.1 g. of starting material, b.p. 110° (19 mm.). No fore-run or pot residue was obtained. A similar experiment in which the time was extended to 1.5 hr. gave no distillable product.

Acetylation of Phenyl Benzoate.—A mixture of 30.0 g. of phenyl benzoate, 10.5 g. of acetic acid and 220 g. of PPA was stirred at 90° for 1 hr. The usual isolation technique gave 7.7 g. (21%) of 4-acetylphenyl benzoate, m.p. 132–134°. Crystallization from methanol–water raised the m.p. to 135–136°, not depressed on admixture with an authentic sample. Except for starting material no other product could be isolated.

Benzoylation of Phenyl Acetate.—A mixture consisting of 20.0 g. of phenyl acetate, 20.7 g. of benzoic acid and 220 g. of PPA was stirred at 85–90° for 1 hr. and submitted to the normal isolation technique. There was obtained, after one crystallization of the crude product from ethyl acetate–petroleum ether (50–60°), 7.5 g. (21%) of 4-acetylphenyl benzoate, m.p. 134–135°. A mixture m.p. with authentic material was not depressed. Chromatography of the mother liquor (after dilution with petroleum ether) on acid-washed alumina gave an additional 0.4 g. of the above benzoate melting at the same temperature and 1.1 g. (3%) of 4-benzoylphenyl acetate, m.p. and mixed m.p. 79–80°.

(7) K. W. Rosenmund and W. Schnurr, *Ann.*, **460**, 56 (1928).

(8) E. Klarman, *This Journal*, **48**, 2358 (1926).

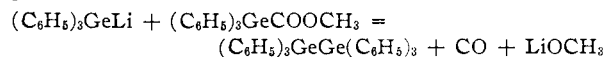
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The Formation of Hexaphenyldigermene and Carbon Monoxide from the Reaction of Triphenylgermyllithium with Some Esters

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RECEIVED MAY 2, 1955

In the course of investigations in this Laboratory an attempt was made to prepare alcohols and ketones containing the triphenylgermyl grouping attached to the carbinol or carbonyl carbon atom. Thus the reaction of triphenylgermyllithium with methyl triphenylgermanecarboxylate was investigated relative to the possibility of preparing bis-

(triphenylgermyl) ketone or tris-(triphenylgermyl)-carbinol. However, instead of obtaining these products, carbon monoxide was vigorously evolved and hexaphenyldigermene was the only other product isolated.



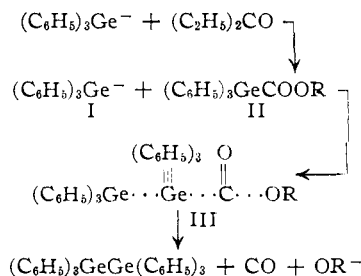
Since the triphenylgermyllithium had been prepared from the cleavage of tetraphenyldigermene,¹ the hexaphenyldigermene must have been a product of the reaction rather than unreacted starting material. Also, hexaphenyldigermene has never been isolated from the hydrolysis of triphenylgermyllithium, thus eliminating this reaction as a possible source of the hexaphenyldigermene.

An attempt to prepare the bis-(triphenylgermyl) ketone by the reaction of triphenylgermyllithium with diethyl carbonate again resulted in the evolution of carbon monoxide and the isolation of hexaphenyldigermene as the sole product.

Due to the symmetry of hexaphenyldigermene it was unclear where each germanium atom originated in the reaction of methyl triphenylgermanecarboxylate with triphenylgermyllithium. Accordingly the reaction of triphenylsilyllithium with methyl triphenylgermanecarboxylate was examined. In this reaction carbon monoxide was again vigorously evolved and the only other product isolated was triphenylsilyltriphenylgermane, thus indicating that in the analogous reaction of triphenylgermyllithium with methyl triphenylgermanecarboxylate, one atom of germanium in hexaphenyldigermene came from the ester and one atom from the triphenylgermyllithium reagent.

The nature of this reaction indicates that it may be of value in synthesizing other compounds of germanium containing silicon, tin or lead bound directly to the germanium atom. Studies with this view in mind are now in progress as well as reactions concerned with the mechanism of this decarbonylation.²

A possible mechanism would be the attack of the triphenylgermyl cation (I) on the germanium atom of the triphenylgermanecarboxylic acid ester (II) with the formation of a pentacovalent intermediate (III). In the case of the reaction of triphenylgermyllithium with diethyl carbonate, it is assumed that ethyl triphenylgermanecarboxylate is the initial product formed.



(1) It has been found in this Laboratory that triphenylgermyllithium may be prepared from the cleavage of hexaphenyldigermene, tetraphenyldigermene or triphenylchlorogermene by lithium in ethylene glycol dimethyl ether.

(2) The mechanism of similar base-catalyzed eliminations of carbon monoxide from triphenylsilanecarboxylic acid and its esters is discussed by A. G. Brook and H. Gilman, *This Journal*, in press.