

This apparent redistribution reaction is reminiscent of the work of Kipping and co-workers<sup>3</sup> with the chlorosilanes and sodium at high temperatures. Work is now in progress in this Laboratory to relate the action of sodium on  $\text{>Si-H}$  and  $\text{>Si-Cl}$  compounds at elevated temperatures.

#### Experimental

All yields represent the percentage of phenyl groups that were introduced into the reaction as triphenylsilane, diphenylsilane or phenylsilane.

**Triphenylsilane and Alloy.**—Thirteen grams (0.05 mole) of triphenylsilane and 7 g. of sodium-potassium alloy (1:5 by weight) were stirred vigorously for 12 hours at room temperature in 300 ml. of anhydrous ethyl ether under a nitrogen atmosphere. The reaction mixture was green-black in color by the end of the reaction. At this point 6 *N* hydrochloric acid was added to destroy the excess metal. There was suspended in the ether layer a small amount of insoluble material from which 0.6 g. of tetraphenylsilane (mixed m.p.) was obtained after recrystallization from xylene. Concentration of the ether layer was followed by distillation at reduced pressure. From the distillate there was obtained 5.6 g. (41%) of triphenylsilanol and 4.2 g. (32%) of triphenylsilane. From the pot residue there was obtained a trace amount of hexaphenyldisiloxane.

If instead of hydrolyzing with acid one adds trimethylchlorosilane a 43% yield of 1,1,1-trimethyl-2,2,2-triphenyldisilane<sup>2</sup> can be obtained.

**Diphenylsilane and Alloy.**—A mixture of 9.2 g. (0.05 mole) of diphenylsilane<sup>1</sup> and 7 g. of sodium-potassium alloy (1:5 by weight) was stirred in 350 ml. of anhydrous ethyl ether under nitrogen for 8 hours at room temperature. A yellow color developed immediately on mixing and the solution turned deep red by the end of the reaction. To the reaction flask immersed in an ice-bath was added sufficient 8 *N* hydrochloric acid to destroy the excess metal and completely decolorize the mixture. The two colorless layers were separated and the solid suspended in the ether layer was filtered off. The ether layer was dried and concentrated. The solid obtained from the ether concentrate, along with the ether insoluble material, was extracted with boiling xylene. From the xylene solution there was obtained 6.8 g. (80%) of tetraphenylsilane, 0.7 g. (8%) of triphenylsilane and 0.4 g. (4%) of triphenylsilanol. The xylene-insoluble material, 2.1 g., was amorphous in character, infusible, insoluble in organic solvents and contained 34% silicon. The material dissolved almost completely in hydrofluoric acid with the evolution of a gas.

**Phenylsilane and Alloy.**—A mixture of 10.8 g. (0.1 mole) of phenylsilane<sup>1</sup> and 6 g. of sodium-potassium alloy (1:5 by weight) in 250 ml. of anhydrous ethyl ether was stirred under nitrogen for 14 hours at room temperature. The solution became pink after two hours and gradually darkened with continued stirring. To the reaction flask immersed in an ice-bath was added sufficient 8 *N* hydrochloric acid to completely decolorize the mixture and destroy the excess metal. The solid suspended in the ether layer was filtered off and extracted with boiling xylene. Only a portion of this material was soluble in xylene. From the xylene extract there was obtained 4.7 g. of tetraphenylsilane (mixed m.p.). The ether layer was concentrated and distilled under reduced pressure. That portion boiling up to 175° (0.2 mm.) was collected and from the distillate was obtained 0.5 g. (6%) of triphenylsilanol, mixed melting point 157–159°, and 0.8 g. (9%) of triphenylsilane, mixed melting point 43–46°. From the pot residue there was obtained an additional 0.9 g. of tetraphenylsilane giving a total of 5.6 g. (68%) of this material. The insoluble material, 2.8 g., after washing repeatedly with hot organic solvents and water, contained 36% silicon. The material dissolved almost completely in hydrofluoric acid with the evolution of a gas.

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(3) See A. R. Steele and F. S. Kipping, *J. Chem. Soc.*, 1431 (1928). Also R. A. Thompson and F. S. Kipping, *ibid.*, 1176 (1929); F. S. Kipping, J. E. Blackburn and J. F. Short, *ibid.*, 1999 (1931).

## Preparation and Reactions of $\alpha$ -Phenylisobutyraldehyde and $\alpha$ -Phenylisobutyric Acid

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RECEIVED APRIL 2, 1952

$\alpha$ -Phenylisobutyraldehyde ( $\alpha$ -methylhydratropaldehyde) had been obtained previously in low yields by Tiffeneau and Dorlencourt<sup>1</sup> and again by Lévy<sup>2</sup> from the treatment of 1-phenyl-2-methylpropanediol-1,2 with dilute sulfuric acid. Lévy claimed that 60% of the product consisted of 2,2,5,5-tetramethyl-3,6-diphenyldioxane. Following the suggestion of Darzens and Levy<sup>3</sup> for similar reactions we have obtained this aldehyde in better than 90% yields using anhydrous formic acid as the dehydration-rearrangement media.

This aldehyde was readily oxidized with silver oxide to the known  $\alpha$ -phenylisobutyric acid<sup>4</sup> ( $\alpha$ -methylhydratropic acid) and gave the expected semicarbazone.<sup>1</sup>  $\alpha$ -Phenylisobutyryl chloride was prepared in fair yield by the action of thionyl chloride with the acid. This acid chloride was condensed with  $\beta$ -diethylaminoethanol to produce  $\beta'$ -diethylaminoethyl  $\alpha$ -phenylisobutyrate, isolated as the hydrochloride. This product has shown no outstanding pharmacological activity in various screening tests which have been performed with it.<sup>5</sup>

Although phenylacetaldehyde<sup>6</sup> and hydratropaldehyde ( $\alpha$ -phenylpropionaldehyde)<sup>7</sup> condense readily with malonic acid with the evolution of carbon dioxide to give  $\alpha,\beta$ -unsaturated acids,  $\alpha$ -phenylisobutyraldehyde gave only a very low yield of the expected  $\gamma,\gamma$ -dimethyl- $\gamma$ -phenylcrotonic acid. The carbonyl group in this aldehyde is apparently considerably more hindered than that of even pivaldehyde which condenses fairly well with malonic ester<sup>8</sup> and with acetone.<sup>9</sup>  $\alpha$ -Phenylisobutyraldehyde failed to give appreciable amounts of condensation products with either malonic ester or acetone when the usual conditions for such reactions were employed.

#### Experimental

**$\alpha$ -Phenylisobutyraldehyde.**—Thirty-seven grams of 1-phenyl-2-methylpropanediol-1,2<sup>10</sup> was heated under reflux for four hours with 60 g. of anhydrous formic acid. After cooling, the brown colored acid solution was carefully neutralized with a saturated solution of potassium bicarbonate.

(1) M. Tiffeneau and H. Dorlencourt, *Ann. chim. phys.*, [8] **16**, 248 (1909).

(2) J. Lévy, *Bull. soc. chim.*, [4] **29**, 820 (1921).

(3) G. Darzens and A. Levy, *Compt. rend.*, **196**, 185 (1933).

(4) O. Wallach, *Chem. Centr.*, **70**, **II**, 104 (1899).

(5) This compound has been found by the Smith, Kline and French Laboratories, Philadelphia, Pa., to be devoid of activity as a topical local anesthetic, as an anti-histaminic compound, and as an anti-hypnotic agent. The Sloan-Kettering Institute, New York, has found the compound to have no activity against mouse sarcoma 180. Its maximum tolerated dose intraperitoneally in mice or rats is about 300 mg./kg. L. Buchel, J. Lévy and B. Tchoubar, *Compt. rend. soc. biol.*, **144**, 175 (1950), have reported this compound to be about three times as active as papaverine as a spasmolytic drug on isolated rat duodenum, but apparently have not yet reported the details for the preparation of this ester.

(6) E. Strunck, *Ann.*, **345**, 244 (1906).

(7) A. Michael and J. Ross, *This Journal*, **53**, 1170 (1931).

(8) L. Foreman and S. M. McElvain, *ibid.*, **62**, 1438 (1940).

(9) K. N. Campbell, *ibid.*, **59**, 1980 (1937).

(10) This glycol was prepared by the method of Tiffeneau and Dorlencourt<sup>1</sup> from methyl mandelate which was prepared from mandelic acid according to the directions of B. Baer and M. Kates, *This Journal*, **67**, 1462 (1945).

A brown oil separated which was extracted with ether. The product distilled at 93–97° (12–13 mm.), giving 30.1 g. (91.2% yield);  $n_D^{25}$  1.5114.<sup>2</sup>

*Anal.* Calcd. for  $C_{10}H_{12}O$ : C, 81.04; H, 8.17. Found: C, 81.26; H, 8.29.

This aldehyde gave positive tests with both Tollens and Schiff reagents. The semicarbazone was recrystallized from 50% water–ethanol, m.p. 178–179°.<sup>1</sup>

**$\alpha$ -Phenylisobutyric Acid.**—Forty-six grams of  $\alpha$ -phenylisobutyraldehyde was dissolved in 320 ml. of a 30% methanol–water solution containing 115 g. of silver nitrate. To this solution was added 50.6 g. of sodium hydroxide dissolved in 920 ml. of water. This slurry was boiled under reflux for 1.5 hours. The hot mixture was filtered and the cooled filtrate acidified with dilute nitric acid to produce a colorless, flocculent precipitate, wt. 27.8 g., m.p. 74–77°. An additional 10 g. of crude product was obtained by ether extraction of the filtrate. Recrystallization from aqueous methanol gave the pure product, m.p. 77–78°.<sup>4</sup>

**$\alpha$ -Phenylisobutyryl Chloride.**—Thirty grams of  $\alpha$ -phenylisobutyric acid was heated under reflux for 45 minutes with 30 g. of thionyl chloride. The colorless product was fractionally distilled under vacuum; b.p. 94–96° (10 mm.);<sup>4</sup> yield 17 g. (50%). A higher boiling fraction, b.p. 194–196° (7 mm.), which produced no acidic product on warming with sodium hydroxide followed by treatment with hydrochloric acid was not identified.

**$\beta'$ -Diethylaminoethyl- $\alpha$ -phenylisobutyrate Hydrochloride ( $\beta'$ -Diethylaminoethyl- $\alpha$ -methylhydatropate Hydrochloride).**—A 13.5-g. (0.074 mole) sample of  $\alpha$ -phenylisobutyryl chloride was added over a period of two minutes to 100 ml. of dry ether solution of 16.5 g. (0.148 mole) of  $\beta$ -diethylaminoethanol. After standing at room temperature for 17 hours the theoretical amount of  $\beta$ -diethylaminoethanol hydrochloride was removed from the reaction mixture by filtration. The ether solution, after washing with cold water, drying and treatment with dry hydrogen chloride gas, gave 15.0 g. of a colorless product, m.p. 134–136°.<sup>5</sup> The melting point was unchanged after recrystallization from a mixture of dry ether and absolute ethanol. This product is very soluble in water.

*Anal.* Calcd. for  $C_{18}H_{26}NO_2Cl$ : C, 63.94; H, 8.74. Found: C, 64.01; H, 8.47.

**$\gamma,\gamma$ -Dimethyl- $\gamma$ -phenylcrotonic Acid.**—A mixture of 14.8 g. (0.10 mole) of  $\alpha$ -phenylisobutyraldehyde, 11.4 g. (0.11 mole) of pure, dry malonic acid, 7.9 g. of dry pyridine and 0.5 ml. of piperidine was heated at 100° until the evolution of carbon dioxide had ceased (four hours). The cooled reaction mixture was diluted with 10 ml. of concd. ammonium hydroxide. The non-acidic layer was removed by ether extraction and distilled to return 12.2 g. of the starting aldehyde. Acidification of the basic solution with hydrochloric acid produced 0.45 g. (2.4% yield) of the crude acid, m.p. 84–86°. Recrystallization from aqueous ethanol or low boiling petroleum ether gave a colorless, crystalline product, m.p. 86.5–87.5°. This unsaturated acid readily reduced potassium permanganate in a 95% ethanol solution.

*Anal.* Calcd. for  $C_{12}H_{14}O_2$ : C, 75.76; H, 7.42; neut. equiv., 190. Found: C, 75.71; H, 7.53; neut. equiv., 191, 192.

The employment of excess amounts of malonic acid and longer reaction times did not improve the yield.

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## Acyl Migrations in Partially Acylated, Polyhydroxylic Systems<sup>1</sup>

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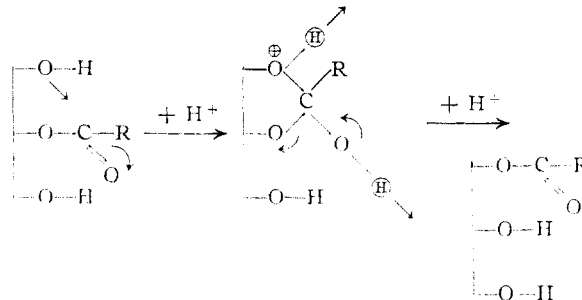
RECEIVED MARCH 21, 1952

Rearrangements involving acyl migrations under mild conditions are well known in a variety of par-

(1) This work was supported in part by a grant from the Nutrition Foundation, Inc.

(2) Lederle Laboratories Division, American Cyanamid Company, Pearl River, New York.

tially acylated hydroxyamino systems and polyhydroxylic systems possessing the proper spatial relationships.<sup>3</sup> The rearrangement of 1,2-diglycerides to 1,3-diglycerides has been used extensively in synthetic work.<sup>4</sup> A mechanism proceeding through a cyclic orthoester intermediate has been suggested<sup>5</sup> and a transition-state mechanism of the type:



is consistent with the facts that the benzoyl group does not migrate as readily as aliphatic acyl groups and that systems possessing R's that are strongly electron-attracting exist as cyclic orthoesters.<sup>6–8</sup> The acyl group transfer in the rearrangement is postulated as intramolecular, in contrast to the intermolecular acyl group transfers observed in the catalyzed, directed, glyceride interesterification reactions.<sup>9</sup>

We have carried out the rearrangement of 2-monopalmitin<sup>10</sup> in the presence of glycerol-1- $C^{14}$  and have observed no incorporation of  $C^{14}$  into the 1-monopalmitin product. The counting tube sensitivity, geometry and background, the sample size and character, and the specific radioactivity relationships during the experiments were such that an incorporation of glycerol-1- $C^{14}$  into the 1-monopalmitin on the part of 1% of the molecular rearrangements could have been measured and on the part of 0.3% easily detected. The results show that mechanisms involving hydrolysis and re-esterification play no part of consequence in this type rearrangement and suggest that the rearrangement reaction path is entirely intramolecular.

### Experimental

331 mg. (1 mM.) of 2-monopalmitin<sup>11</sup> was added to 381 mg. (4.1 mM.) of glycerol-1- $C^{14}$ , prepared from tartaric acid by oxidation to dihydroxymaleic acid, decarboxylation to hydroxyacetaldehyde, addition of  $HC^{14}N$ , hydrolysis, esterification, acetylation and reduction with lithium aluminum hydride<sup>12</sup> and containing a total radioactivity of  $1.30 \times 10^8$  c.p.m. The mixture was dissolved in a minimum of warm ethanol containing 0.6 N HCl, allowed to remain for 36 hours at room temperature, and then cooled to  $-18^\circ$ . The resulting crystals were dissolved in ethyl ether and the solution washed with water. The washed product after

(3) E. van Tamelen, *THIS JOURNAL*, **73**, 5773 (1951).

(4) F. L. Jackson, B. F. Daubert, C. G. King and H. E. Longenecker, *ibid.*, **66**, 289 (1944).

(5) E. Fischer, *Ber.*, **53**, 1621 (1920).

(6) D. T. Jackson and C. G. King, *THIS JOURNAL*, **55**, 678 (1933).

(7) H. Meerwein and H. Sonke, *Ber.*, **64B**, 2375 (1931).

(8) H. Hibbert, *ibid.*, **65B**, 199 (1932).

(9) F. J. Baur and W. Lange, *THIS JOURNAL*, **73**, 3926 (1951).

(10) B. F. Stimmel and C. G. King, *ibid.*, **56**, 1724 (1934).

(11) The author wishes to express his appreciation to Prof. B. F. Daubert, Department of Chemistry, The University of Pittsburgh, for his generous gift of crystalline 2-mono-palmitin (m.p. 68.5°).<sup>13</sup>

(12) L. J. Filer, Jr., S. S. Sidhu, B. F. Daubert and H. E. Longenecker, *THIS JOURNAL*, **66**, 1333 (1944).

(13) A. P. Doerschuk, *THIS JOURNAL*, **73**, 821 (1951).