anol there was obtained 20.5 g. (93%) of II which melted at 108°.[9]

Anal. Calcd. for $C_{11}H_{12}O_3N_2$: C, 60.0; H, 5.50. Found: C, 59.97; H, 5.42.

5-Amino-6-nitrohydrindene (III).—A mixture of 5-acetylamino-6-nitrohydrindene (11 g.) and 20% hydrochloric acid was refluxed for two hours. The cooled solution was stirred with activated charcoal (5 g.), filtered and made alkaline with sodium carbonate solution. The orange precipitate was filtered, dried and recrystallized from ligroin. There was obtained 7.8 g. (87%) of III which melted at 129–130°.[9]

Anal. Calcd. for $C_9H_{10}O_2N_2$: C, 60.6; H, 5.6; N, 15.7. Found: C, 60.5; H, 5.6; N, 15.8.

Deamination of III.—A solution of 5-amino-6-nitrohydrindene (1.0 g.) in ethanol (5 ml.) and concentrated sulfuric acid (0.7 ml.) was cooled to 10° and sodium nitrite (0.5 g.) dissolved in a minimum of water was added slowly with stirring. The mixture was then warmed on the steam-bath until the evolution of nitrogen was complete. The reaction mixture was diluted with water and the product extracted with ether. The residue remaining after evaporation of the ether was sublimed twice. The light yellow crystals which were obtained melted at 39.5–40°. A mixture of this substance and authentic 5-nitrohydrindene also melted at 39.5–40°. A mixture with authentic 4-nitrohydrindene liquefied at room temperature.

5-Chloro-6-nitrohydrindene.—5-Amino-6-nitrohydrindene (17.8 g.) was dissolved in concentrated hydrochloric acid (100 ml.) by heating to 90°. The solution was rapidly cooled to 0° by addition of chopped ice and then a cold solution of sodium nitrite (7.0 g.) was added during 15 minutes to the well-stirred suspension. A cold solution of cuprous chloride (prepared from 31.2 g. of copper sulfate) in concentrated hydrochloric acid (34 ml.) was added keeping the temperature at 0–5°. The reaction mixture was allowed to warm to room temperature and finally was heated at 60° for one hour. The product was separated by ether extraction. There was obtained 17 g. of crude product. A by-product (2 g., m.p. 193–194°) remained undissolved when this substance was treated with warm methanol. Recrystallization from methanol yielded 13 g. (66%) pure 5-chloro-6-nitrohydrindene which melted at 40.5–41.0°.

Anal. Calcd. for $C_9H_8O_2NCl$: C, 54.69; H, 4.08. Found: C, 54.30; H, 3.81.

5-Acetylamino-6-chlorohydrindene.—A mixture of iron powder (17 g.), acetic acid (10 ml.) and water (36 ml.) was stirred and heated on a water-bath until there was no further evolution of hydrogen. Ethanol (20 ml.) was added, followed by 5-nitro-6-chlorohydrindene (15.9 g.) in portions during 10 minutes. The mixture was heated and stirred at reflux temperature for four hours, then filtered and the filtrate diluted with water. The crude amine was extracted with ether and separated from any starting material by extracting with dilute hydrochloric acid. The amine (12.2 g., 90%) obtained by addition of 20% sodium hydroxide solution solidified in an ice-bath but melted again at room temperature. It reacted with acetic anhydride to yield an acetyl derivative which melted at 138–139° after recrystallization from ligroin.

Anal. Calcd. for $C_{11}H_{12}ONCl$: C, 62.99; H, 5.77. Found: C, 62.85; H, 5.85.

5-Iodo-6-chlorohydrindene.—The liquid 5-amino-6-chlorohydrindene (11.4 g.) obtained in the previous experiment was diazotized using concentrated sulfuric acid (20 ml.), water (61 ml.) and sodium nitrite (4.8 g.). Potassium iodide (11.3 g.) was added to the cold diazonium salt and the solution slowly warmed to 45–50°. The product was removed by ether extraction and obtained as a brown oil (11 g., 58%) which crystallized on cooling in ice. This product could be purified by recrystallization from aqueous methanol, m.p. 46–47°.

Anal. Calcd. for C_9H_8ClI: C, 38.82; H, 2.90. Found: C, 38.57; H, 3.01.

(9) W. Borsche and A. Bodenstein, ref. 2, report the melting point of their "5-acetylamino-4-nitrohydrindene" to be 107° and that of its hydrolysis product, "5-amino-4-nitrohydrindene" to be 128–129°.

SCHOOL OF CHEMISTRY
RUTGERS UNIVERSITY
NEW BRUNSWICK, NEW JERSEY

The Reaction of Organosilanes with Sodium–Potassium Alloy

BY ROBERT A. BENKESER AND DONALD J. FOSTER

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In a previous publication[1] from this Laboratory it was suggested that the formation of tetraphenylsilane from the reactions of diphenylsilane and phenylsilane with sodium–potassium alloy proceeded by a different mechanism than that of triphenylsilane with alloy. This is now confirmed since it has been shown that both diphenylsilane and phenylsilane when treated with sodium–potassium alloy form tetraphenylsilane *without* the subsequent addition of bromobenzene. On the other hand tetraphenylsilane is formed in only negligible yields from triphenylsilane and alloy, *unless* bromobenzene is added to the reaction mixture. In the latter case, triphenylsilylpotassium is the reactive intermediate which couples with bromobenzene to form tetraphenylsilane.[1]

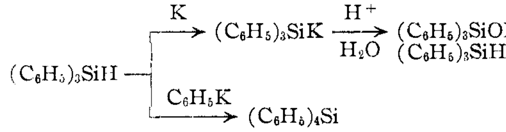
$$(C_6H_5)_3SiH \xrightarrow[\text{ether}]{\text{Na/K}} (C_6H_5)_3SiK + KH \xrightarrow{C_6H_5Br} (C_6H_5)_4Si + KBr$$

The formation of triphenylsilylpotassium can be further confirmed by coupling it with trimethylchlorosilane to form 1,1,1-trimethyl-2,2,2-triphenyldisilane.[2]

One can account for the formation of tetraphenylsilane in the case of diphenylsilane and phenylsilane by assuming the intermediate formation of phenylsodium or phenylpotassium. These compounds probably arise from a cleavage of the phenyl groups by the alkali metal. On this basis diphenylsilane reacts as

$$(1)\quad (C_6H_5)_2SiH_2 + 2K \longrightarrow C_6H_5K + C_6H_5SiKH_2$$

$$(2)\quad (C_6H_5)_2SiH_2 + C_6H_5K \longrightarrow$$



$$(C_6H_5)_3SiH \begin{cases} \xrightarrow{K} (C_6H_5)_3SiK \xrightarrow[H_2O]{H^+} \begin{matrix} (C_6H_5)_3SiOH \\ (C_6H_5)_3SiH \end{matrix} \\ \xrightarrow{C_6H_5K} (C_6H_5)_4Si \end{cases}$$

The presence of triphenylsilane and triphenylsilanol in these reaction products is interesting since it clearly supports the previous observation that when three phenyl groups are attached to the silane molecule, triphenylsilylpotassium forms, and relatively few phenyl groups are lost by cleavage. When only one or two phenyl groups are attached, however, they are readily cleaved by the alkali metal. The low yields of triphenylsilane and triphenylsilanol can be attributed to the greater speed of the reaction of phenylpotassium with triphenylsilane as compared to the reaction of triphenylsilane with potassium.

The infusible products obtained in these reactions appear to be largely SiO_2, silicic acid or partially dehydrated silicic acid, with or without some Si–C and Si–H compound copolymerized with it. Such materials could arise easily if the $C_6H_5SiKH_2$ postulated in Equation 1 above were stripped of another phenyl group by alkali metal and the product then hydrolyzed.

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[1] R. A. Benkeser, H. Landesman and D. J. Foster, THIS JOURNAL, **74**, 648 (1952).

[2] R. A. Benkeser and R. G. Severson, *ibid.*, **73**, 1424 (1951).

This apparent redistribution reaction is reminiscent of the work of Kipping and co-workers[3] with the chlorosilanes and sodium at high temperatures. Work is now in progress in this Laboratory to relate the action of sodium on $\equiv$Si-H and $\equiv$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[2] can be obtained.

Diphenylsilane and Alloy.—A mixture of 9.2 g. (0.05 mole) of diphenylsilane[1] 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[1] 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.

DEPARTMENT OF CHEMISTRY
PURDUE UNIVERSITY
LAFAYETTE, INDIANA

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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. C. Blackburn and J. F. Short, *ibid.*, 1290 (1931).

Preparation and Reactions of α-Phenylisobutyraldehyde and α-Phenylisobutyric Acid

BY NORMAN H. CROMWELL AND HAROLD H. EBY

RECEIVED APRIL 2, 1952

α-Phenylisobutyraldehyde (α-methylhydratropaldehyde) had been obtained previously in low yields by Tiffeneau and Dorlencourt[1] and again by Lévy[2] 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[3] 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 α-phenylisobutyric acid[4] (α-methylhydratropic acid) and gave the expected semicarbazone.[1] α-Phenylisobutyryl chloride was prepared in fair yield by the action of thionyl chloride with the acid. This acid chloride was condensed with β-diethylaminoethanol to produce β′-diethylaminoethyl α-phenylisobutyrate, isolated as the hydrochloride. This product has shown no outstanding pharmacological activity in various screening tests which have been performed with it.[5]

Although phenylacetaldehyde[6] and hydratropaldehyde (α-phenylpropionaldehyde)[7] condense readily with malonic acid with the evolution of carbon dioxide to give α,β-unsaturated acids, α-phenylisobutyraldehyde gave only a very low yield of the expected γ,γ-dimethyl-γ-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[8] and with acetone.[9] α-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

α-Phenylisobutylaldehyde.—Thirty-seven grams of 1-phenyl-2-methylpropanediol-1,2[10] 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.

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[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[1] from methyl mandelate which was prepared from mandelic acid according to the directions of E. Baer and M. Kates, THIS JOURNAL, **67**, 1482 (1945).