mole), the attack of the magnesium could not be maintained below −30°. The use of tetrahydrofuran instead of ether (470 ml. per mole) gave a 54% consumption of magnesium in 48 hours, and a yield of $C_3F_7CO_2H$ of 51%.

(c) **Condensation with Acetone.**—An equimolecular solution of 1/3 mole of C_3F_7I and 1/3 mole of acetone in 125 ml. of ether (370 ml. per mole) was stirred at −80° with an excess of magnesium for 58 hours, after initiation at room temperature. When allowed to warm up, the reaction mixture suddenly boiled over into the traps, from which it was returned. Working up gave a 10% yield of impure tertiary carbinol $C_3F_7C(OH)(CH_3)_2$, b.p. 100–110°, n^{20}D 1.3355, better characterized by dehydration to $C_3F_7C(CH_3)=CH_2$; see above. This reaction was then repeated at a progressively raised temperature: 18 hours at −40°, 19 hours at −25° and 5 hours at −15°. Even then, only 48% of the theoretical magnesium had been consumed. The working up of this reaction did not give any fluorinated tertiary carbinol, but only mesityl oxide in 31% yield, and high-boiling condensation products. Remembering the results obtained at room temperature, it was concluded that the carbonyl group of acetone interferes with Grignard formation, and that at intermediate temperatures the Grignard reagent causes ketolization instead of condensing with the keto group.

(d) **Condensation with Butyraldehyde.**—After initiating the attack of the magnesium at room temperature with a small amount of iodide, *n*-butyraldehyde (0.5 mole) was added at −40° to a stirred solution of C_3F_7I (0.4 mole) in 370 ml. of ethyl ether (923 ml. per mole of iodide) containing an equivalent quantity of magnesium. The mixture was stirred for 39 hours in the −50 to −40° range, then for .72 hours at about −30° and 17 hours at −20°. Much magnesium remained unconsumed, but was finally taken up during a 36-hour period of stirring at room temperature. In this time, 25.5 g. of low-boiling material was collected. After hydrolysis, working up gave first a mixture of recovered iodide and aldehyde, then a 16% yield of secondary alcohol, $C_3F_7CH(OH)C_3H_7$, b.p. 63.5° (45 mm.), n^{20}D 1.3391. Calcd.: C, 34.71; H, 3.72. Found: C, 34.18; N, 3.75. Dinitrobenzoate, m.p. 63.5–63.8°; Found: N, 6.91. Calcd.: N, 6.42. Analyses by Elek microanalytical laboratories, Los Angeles. The acidity and infrared characteristics of this alcohol are discussed in an accompanying paper.[8] The above conditions were an effort to avoid excessive interference with Grignard formation, and yet avoid aldolization at the expense of condensation.

(e) **Condensation with C_3F_7CHO.**—So little condensation occurred that only traces of the desired $C_3F_7CH(OH)C_3F_7$ were observed; this alcohol, prepared by reduction of $C_3F_7COC_3F_7$ is described in another paper.[8] Simultaneous Grignard formation and condensation was tried on 1/4 mole amounts of reagents in 313 ml. of ether (1250 ml. per mole) in the −50 to −40° temperature range. Even at that low temperature, C_3H_7CHO polymerized partly and, by coating, interfered with but did not prevent the progressive consumption of the magnesium in a 22-hour period. Working up recovered 86% of the aldehyde (48% as polymer and 38% as hydrate) and 6% of $C_3H_7CO_2H$, which accounted for 92% of the reagent. The failure to obtain much secondary alcohol can thus be attributed to the sluggishness of the perfluorinated aldehyde.

(f) **Condensation with Ethyl Formate.**—The experiment was started by initiating the magnesium attack with 5 ml. of C_3F_7I in 25 ml. of tetrahydrofuran at room temperature, quickly cooling to −80° by immersion in a Dry Ice-bath, then rapidly adding the remainder of the iodide (0.17 mole total) in 200 ml. of solvent. Immediately following, a solution of 0.41 mole of formate in 275 ml. of tetrahydrofuran was dripped in over a 90-minute period. The concentration was thus 2850 ml. of solvent per mole of iodide. The mixture was stirred under nitrogen for 23 hours at −80°, then 20 hours at −30°, when it appeared chocolate brown and practically free of magnesium. After hydrolysis and treatment with ferrous sulfate to destroy peroxides, distillation up to 65° removed unreacted reagents and the solvent. The remaining aqueous solution was continuously extracted with ether. After removal of the ether by distillation, the aldehyde hydrate $C_3F_7CH(OH)_2$ distilled at 92–98° (9.2 g.), then the azeotrope of formic acid and water came over at 102–104° (7.0 g.); the residue distilled at 125–130° (20 mm.) (7 g. of wet material) and after drying proved to be 1,4-diiodobutane, b.p. 130° (20 mm.), n^{15}D 1.6201, % iodine 79.02, obtained at the expense of the solvent. The aldehyde hydrate was thus obtained in 24% yield; its 2,4-dinitrophenylhydrazone, m.p. 102–104°, was made in 6 *N* sulfuric acid, and its free aldehyde, b.p. 28°, in agreement with the literature,[12] was obtained by distillation from P_2O_5.

(g) **Condensation with $C_3F_7CO_2Et$.**—Pure ethyl perfluorobutyrate was prepared in 91% yield[13] by mixing one mole of acid and 2 moles of absolute alcohol in a flask equipped with a reflux condenser, pouring 1.5 moles of concentrated sulfuric acid in small portions through the condenser as fast as the exothermic reaction would permit, cooling, decanting the top layer of nearly pure ester and rectifying from a small amount of P_2O_5; observed b.p. 95°, n^{20}D 1.3011, literature values[12] b.p. 95°, n^{20}D 1.3032.

After initiation of the magnesium attack, a mixture of 0.3 mole of iodide and 0.3 mole of ester in 390 ml. of ether (1300 ml. of ether per mole of iodide) was stirred with magnesium for 18 hours at −50°, 24 hours at −40° and 12 hours at −30°, and practically all the magnesium was consumed. After hydrolysis, the mixture was continuously extracted with ether. The ether solution was dried, its ether removed by distillation, and most of the residue rapidly brought over at 27–40° (100 mm.) to a Dry Ice cooled receiver. Redistillation at one atmosphere gave a fraction of crude ketone contaminated with alcohol at 63–85°, then recovered ester at 93–95°. after which a residue was left in the flask. Rectification of the first fraction from P_2O_5 to destroy the alcohol gave the ketone at 74–78° and a small amount of ester at 94°. Rectification of the residue, diagnosed as mostly hemi-ketal was also done from P_2O_5 and gave a small additional amount of ketone. When an attempt was made to simplify the separation by distilling all of the first ether extract from P_2O_5, a considerable amount of ethyl iodide distilling as an azeotrope with the ketone at 54° complicated the procedure; this was due to the solubility of magnesium iodide in ether.

Final distillation from P_2O_5 gave, in 20% yield, pure $C_3F_7COC_3F_7$, b.p. 75° (740 mm.), d^{20}_4 1.6250, with a refractive index too low to be read on an Abbe refractometer. *Anal.* Calcd.: C, 22.9; F, 72.7. Found: C, 22.6; F (cor.), 72.5. The carbon microanalysis was obtained from Dr. Robert N. Haszeldine, of Cambridge University. This ketone is very hygroscopic, and is easily split by 5% aqueous alkali into $C_3F_7CO_2H$ characterized by its odor and its amide m.p. 105° (mixed m.p.), and C_3F_7H characterized by its infrared spectrum. Figure 1 shows the spectrum of the ketone $C_3F_7COC_3F_7$ with a strong absorption band (12% transmittance) at 5.8 μ characteristic of the carbonyl function, and with strong absorption for C–F stretching in the 7.1 to 10 μ region. Repeated attempts to prepare a 2,4-dinitrophenylhydrazone, a semicarbazone or an oxime were all unsuccessful. The ketone is insoluble in water or in concentrated sulfuric acid, which shows the non-basic character of its carbonyl oxygen atom.

(h) **Condensation with C_3F_7COCl.**—This is not recommended, as it has no advantage over a condensation with the ester in preparing a ketone. The condensation cannot be performed on nascent C_3H_7MgI, because the acyl chloride stops the reaction of the iodide on magnesium. In trying the condensation at −30° after completing the Grignard formation at low temperature, a 4% yield of ketone was obtained.

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[13] T. S. Reid, Minnesota Mining and Manufacturing Co., private communication.

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Silico-alkylation of Sodio Esters with Trimethylchlorosilane to Form Silyl Esters[1]

BY CHARLES R. HANCE AND CHARLES R. HAUSER

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It has previously been shown in this Laboratory that ethyl isobutyrate and certain other esters may

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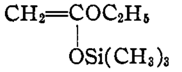
[1] Supported by the Office of Naval Research.

be alkylated with alkyl halides by means of sodium triphenylmethide.[2] We have now found that ethyl isobutyrate and even acetate, which underwent self-condensation instead of being alkylated by benzyl chloride, may be silico-alkylated by the more reactive trimethylchlorosilane.[3] The ester was first converted to its sodio derivative which was then condensed with the chlorosilane (equations 1 and 2).

$$CH_3COOC_2H_5 \xrightarrow[2,\ (CH_3)_3SiCl]{1,\ NaC(C_6H_5)_3} \underset{\text{I}}{(CH_3)_3SiCH_2COOC_2H_5} \quad (1)$$

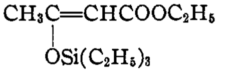
$$(CH_3)_2CHCOOC_2H_5 \xrightarrow[2,\ (CH_3)_3SiCl]{1,\ NaC(C_6H_5)_3} \underset{\text{II}}{(CH_3)_3SiC(CH_3)_2COOC_2H_5} \quad (2)$$

These reactions are assumed to produce the C-derivatives, I and II, rather than the O-derivative, for example, III. The related reaction of sodioacetoacetic ester with triethylchlorosilane has been assumed to form such an O-derivative (IV)[4] but this structure has been questioned.[5]



$$CH_2{=}\underset{OSi(CH_3)_3}{\underset{|}{C}}OC_2H_5$$

III



$$CH_3\underset{OSi(C_2H_5)_3}{\underset{|}{C}}{=}CHCOOC_2H_5$$

IV

Evidence that the reaction represented by equation 1 formed structure I is the fact that the product had physical properties practically identical with those reported previously[6] for the silyl ester obtained from the reaction represented by equation 3 which must produce structure I.

$$(CH_3)_3SiCH_2MgCl + ClCOOC_2H_5 \longrightarrow \underset{\text{I}}{(CH_3)_3SiCH_2COOC_2H_5} + MgCl_2 \quad (3)$$

Similar to earlier observations with silyl ester I,[6] silyl ester II was found to undergo cleavage, on refluxing with ethanol, to form ethyl isobutyrate and trimethylethoxysilane. It should be pointed out that the silyl esters obtained in the present work were isolated in the absence of water or acid. When the reaction mixture from sodio ethyl isobutyrate and trimethylchlorosilane was acidified as in the alkylations of esters,[2] only cleavage products, ethyl isobutyrate and hexamethyldisiloxane, were obtained.

Experimental

Trimethylchlorosilane, obtained from the General Electric Co., was used without further purification. Ethyl isobutyrate (Florasynth Laboratories) and ethyl acetate (Eastman Kodak Co.) were dried over Drierite and distilled prior to use.

Sodium triphenylmethide was prepared in ether solution from 3% sodium amalgam and triphenylchloromethane.[7] Triphenylchloromethane, obtained from Columbia Organic Chemicals Co., or prepared in this Laboratory,[8] was recrystallized from benzene; it then melted at 111–113°.

Ethyl Trimethylsilylacetate (I).—A solution of 0.16 mole of sodium triphenylmethide in 750 ml. of ether was transferred under nitrogen pressure[9] to a nitrogen flushed one-liter, three-necked, round-bottomed flask equipped with a sealed stirrer, a dropping funnel, and bulb-type reflux condenser topped with a drying tube. To the stirred dark red solution, cooled to 0° or below by means of an ice–salt-bath, was added rapidly 16.0 g. (0.18 mole) of ethyl acetate in 50 ml. of ether, followed immediately (red color being discharged) by the rapid addition of 20.2 g. (0.184 mole) of trimethylchlorosilane in 50 ml. of ether. After stirring 3 hours and standing 12 hours, the mixture was filtered and the gelatinous precipitate washed thoroughly with ether. The filtrate and washings were concentrated and the precipitate of triphenylmethane removed by filtration and washed with ether. The solvent was removed from the filtrate and washings and the residue distilled through a 15-cm. Vigreux column. The distillate was redistilled through a 21-cm. glass helices-packed column to give 8.2 g. (51%) of recovered ethyl acetate, b.p. 76–78° (n^{20}_D 1.3735) and 6.9 g. (27%, 48% based on unrecovered ethyl acetate) of ethyl trimethylsilylacetate, b.p. 74.5° (41 mm.), n^{20}_D 1.4150, d^{20}_4 0.8761 (reported b.p. 75.5° (42 mm.), n^{20}_D 1.4149, d^{20}_4 0.8762).[6]

Ethyl Trimethylsilylisobutyrate (II).—This ester was prepared in a manner similar to that described for silyl ester I. To a stirred solution of 0.32 mole of sodium triphenylmethide in 700 ml. of ether at room temperature was added 43.8 g. (0.378 mole) of ethyl isobutyrate in 50 ml. of ether and, after 15 minutes, 40.8 g. (0.376 mole) of trimethylchlorosilane in 50 ml. of ether was added. After stirring one hour and standing 12 hours, the gelatinous precipitate was removed by centrifuging and washed thoroughly with ether. The ether solution was concentrated, the triphenylmethane removed, and the solvent distilled. The residue was distilled through a 30-cm. Vigreux column to give 23.0 g. (52%) of recovered ethyl isobutyrate, b.p. 100–110°, and 22.0 g. (38%, 65% based on unrecovered ethyl isobutyrate) of ethyl trimethylsilylisobutyrate, b.p. 50° (9 mm.), n^{20}_D 1.4168, d^{20}_4 0.8553; *MR*D calcd.[10] 55.20, found 55.32.

Anal.[11] Calcd. for $C_9H_{20}SiO_2$: C, 57.40; H, 10.70. Found: C, 57.20; H. 10.31.

Treatment of 7.3 g. (0.0388 mole) of silyl ester II with 50 ml. of absolute ethanol, refluxing 4 hours, gave 2.1 g. of material, b.p. 67–70°, which appeared to be an azeotrope of trimethylethoxysilane and ethanol (reported b.p. 66.4°)[12] and 1.2 g. of impure ethyl isobutyrate. None of the original silyl ester was recovered.

Silyl ester II decolorized bromine in carbon tetrachloride within a few minutes. The products were not determined.

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(2) B. E. Hudson and C. R. Hauser, THIS JOURNAL, **62**, 2457 (1940).

(3) Trimethylchlorosilane is the silicon analog of *t*-butyl chloride but, unlike this alkyl halide which exhibits β-elimination with bases such as ester anions, the chlorosilane undergoes the displacement reaction.

(4) H. Gilman and R. N. Clark, THIS JOURNAL, **69**, 967 (1947).

(5) F. C. Whitmore, L. H. Sommer, J. Gold and R. E. Van Strien, *ibid.*, **69**, 1551 (1947).

(6) J. R. Gold, L. H. Sommer and F. C. Whitmore, *ibid.*, **70**, 2874 (1948).

(7) W. B. Renfrow and C. R. Hauser, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 607.

(8) C. R. Hauser and B. E. Hudson, *Org. Syn.*, **23**, 102 (1947).

(9) E. Baumgarten and C. R. Hauser, THIS JOURNAL, **66**, 1039 (1944).

(10) E. L. Warrick, *ibid.*, **68**, 2455 (1946).

(11) Analysis by Clark Microanalytical Laboratory, Urbana, Ill.

(12) R. O. Sauer, THIS JOURNAL, **66**, 1707 (1944).

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The Reaction of Diphenyldichlorosilane with Ammonia and Amines

BY ERIK LARSSON AND LARS BJELLERUP

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As part of the investigation of the synthesis and the reactions of aminosilanes[1-7] the reactions of

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(1) E. Larsson and O. Mjörne, *Trans. Chalmers Univ. Technol., Gothenburg*, **87**, 29 (1949).

(2) E. Larsson, *Svensk Kem. Tid.*, **61**, 59 (1949).

(3) E. Larsson and B. Smith, *Acta Chem. Scand.*, **3**, 487 (1949).

(4) E. Larsson, *ibid.*, **4**, 45 (1950).

(5) E. Larsson and B. Smith, *Svensk Kem. Tid.*, **62**, 141 (1950).

(6) O. Mjörne, *ibid.*, **62**, 120 (1950).

(7) E. Larsson and R. Mårin, *Acta Chem. Scand.*, **5**, 1173 (1951).