zene, gave a colorless solid which, melting and mix-melting with an authentic sample at 147°, proved to be the oximino-hydroxylamino compound of Auwers and Muller.[10] 3,5-Diphenylisoxazoline shows strong absorption at 5.85 μ in 0.01 *M* solution in dioxane.

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The Synthesis of Dimethyl β-(Carboxymethoxy)-propionate

BY WARREN J. BREHM[1] AND THEODORE LEVENSON

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In connection with another problem we had need of the dimethyl ester of β-(carboxymethoxy)-propionic acid. While this material was known, the reported[2,3] syntheses were inconvenient for our purposes and an improved synthesis was sought.

Attempts to cyanoethylate glycolonitrile or to add methyl glycolate to methyl acrylate according to the procedures of Hansley[4] or Woodward and Eastman[5] were failures. The desired ester was obtained in small yield through the diazoketone rearrangement applied to the half methyl ester acid chloride of diglycolic acid. However, the reaction of methyl glycolate with β-propiolactone[6] is to be considered the preferred method of synthesis.

Experimental

α-(Carbomethoxymethoxy)-acetyl Chloride.—Following the procedure of Anschütz and Jaeger[7] diglycolic acid was converted into its half methyl ester and, with an excess of thionyl chloride, into the desired product, b.p. 104–108° (11 mm.) (78% yield based on diglycolic acid).

α-(Carbomethoxymethoxy)-α-diazoacetone.—A solution of 10 g. of α-(carbomethoxymethoxy)-acetyl chloride in 100 ml. of anhydrous ether was slowly dropped into a cold stirred solution of excess diazomethane in ether. After standing overnight at room temperature protected from atmospheric moisture the ether was removed from the reaction mixture *in vacuo*. The residual yellow oil crystallized on standing. A portion melted at 35° after recrystallization from carbon tetrachloride–petroleum ether.

Dimethyl β-(Carboxymethoxy)-propionate.—The main portion of the crude diazoketone was dissolved in 125 ml. of methanol and 2.0 g. of freshly prepared silver oxide was added. The suspension was stirred mechanically and heated under reflux for about one hour until evolution of nitrogen ceased. The gases evolved had a strong "acrylate" odor. Using charcoal and Hiflo Supercel the mixture was filtered and the filtrate fractionated *in vacuo*. After removing methanol the high boiling material was separated into two fractions. The first, b.p. under 30° (0.2 mm.), 1.2 g., was methyl glycolate and gave glycolamide, m.p. 117–119°, on treatment with ammonia. The second, b.p. 40–87° (1.5 mm.), 2.3 g., was redistilled to give 1.1 g. of product, b.p. 87° (1.5 mm.). With ammonia this gave a solid, m.p. 175.5–177.5°, identical with authentic diamide of β-(carboxymethoxy)-propionic acid, and is considered to be dimethyl β-(carboxymethoxy)-propionate.

β-(Carbomethoxymethoxy)-propionic Acid.—A mixture of 17.3 g. (0.24 mole) of β-propiolactone and 50.0 g. (0.55 mole) of methyl glycolate was kept at 80° for 72 hours. At this time, titration of an aliquot with standard thiosulfate indicated that 90% of the β-propiolactone had been consumed. Fractionation gave 35 g., b.p. 47° (9 mm.), of unreacted methyl glycolate. There was also isolated 16 g., b.p. 129–131° (0.6 mm.) (41% of theory), of material with a neutral equivalent of 174 (theory is 162 indicating 93% purity). Redistillation of the second fraction gave an analytical sample, b.p. 138° (1.5 mm.).

Anal. Calcd. for $C_6H_{10}O_5$: C, 44.4; H, 6.17. Found: C, 45.2, 45.5; H, 6.37, 6.53.

Dimethyl β-(Carboxymethoxy)-propionate.—Esterification of the half ester with diazomethane gave an 88% yield of material, b.p. 82–83° (0.8 mm.).

Anal. Calcd. for $C_7H_{12}O_5$: C, 47.7; H, 6.87. Found: C, 47.9; H, 6.89.

The **diamide**, prepared by saturating a methanol solution of the diester with ammonia, was a white solid, m.p. 174–176°. Baker[3] reports m.p. 174° for this compound.

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Cleavage of Hexaphenyldisilane by Sodium and Lithium

BY A. G. BROOK AND HENRY GILMAN

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The solvent for the preparation of triphenylsilylpotassium in this Laboratory has until recently been restricted to diethyl ether. In this medium, the triphenylsilylpotassium, derived by cleavage of hexaphenyldisilane with sodium–potassium alloy,[1] is an almost completely insoluble yellow-brown solid.

Recent studies of other organometallic systems[2] have indicated that ethylene glycol dimethyl ether is an excellent solvent for these reactions and consequently tests using this solvent as a medium were carried out with the triphenylsilylpotassium preparation.

We have found that hexaphenyldisilane is readily cleaved by sodium–potassium alloy in ethylene glycol dimethyl ether and further that the triphenylsilylpotassium formed is soluble in this solvent, a marked advantage over the suspensions obtained in diethyl ether. However not only is hexaphenyldisilane cleaved by sodium–potassium alloy in this ether, but it is also readily cleaved by sodium and by lithium. These cleavages are the first reported successful cleavages of the silicon–silicon bond by these metals.[3] Attempts to cleave hexaphenyldisilane with magnesium in this solvent have been made, but have not been successful as yet.

The cleavages of hexaphenyldisilane with sodium–potassium alloy and with lithium occur quite rapidly and are complete in a period of 2–4 hours, as indicated by the absence of any undissolved material. With sodium the reaction is much slower, due to the lumping of the metal. All the

$$\mathrm{(C_6H_5)_3Si{-}Si(C_6H_5)_3 \xrightarrow{Li} (C_6H_5)_3SiLi \xrightarrow{(CH_3)_3SiCl} (C_6H_5)_3Si{-}Si(CH_3)_3}$$

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triphenylsilylmetallic solutions give a positive Color Test I,[4] and can be titrated for the content of the organometallic reagent by the double titration method,[5] although these results do not appear to be entirely reliable. The reagents have been derivatized with trimethylchlorosilane to give yields of the known 1,1,1-triphenyl-2,2,2-trimethyldisilane (I) in excess of 70%.

Unfortunately the solutions of triphenylsilylmetallic reagent are not stable with time in ethylene glycol dimethyl ether. If the solution is stirred in contact with excess metal, the metal is slowly consumed, and the concentration of the triphenylsilylmetallic reagent decreases, as indicated by the yield of the derivative obtained. That this further reaction is probably due to reaction of the triphenylsilylmetallic reagent with the solvent is indicated by studies of Dr. K. M. Tai of this Laboratory who has found that solutions of the reagent, in absence of excess metal, likewise decrease in concentration, particularly if refluxed Such behavior is best explained on the basis of a reaction of the reagent with the solvent, probably resulting in the cleavage of the ether. These cleavage fragments must be such that they are capable of reacting with excess metal, if present, since several equivalents of the metal are consumed over a period of days if the reaction is permitted to proceed. It therefore appears highly advisable to use the triphenylsilylmetallic reagent as soon as prepared, in order to minimize further reaction.

Experimental[6]

Cleavage of Hexaphenyldisilane with Sodium–Potassium Alloy.—To a suspension of 5.0 g. (0.00965 mole) of hexaphenyldisilane in 10 ml. of sodium-dried, redistilled ethylene glycol dimethyl ether was added 2 ml. of 1:5 sodium–potassium alloy. A green color formed at the surface of the alloy and as the mixture was stirred, the color changed through yellow to brown; the material appeared to dissolve. After 15 minutes an additional 25 ml. of the ether was added. At the end of 2 hours all the material was in the dark brown solution with the excess alloy floating on top. A 5-ml. aliquot was removed and run into a solution of 0.5 ml. (0.0046 mole) of trimethylchlorosilane in 5 ml. of the ether. The color immediately was discharged, and a small amount of white precipitate was formed. After 5 minutes the reaction mixture was drowned in about 100 ml. of water, which was thrice extracted with ether. The extracts were dried over sodium sulfate. The ether was removed under reduced pressure and the resulting white solid was recrystallized from 95% ethanol to yield a total of 0.7 g. (77%) of 1,1,1-triphenyl-2,2,2-trimethyldisilane, m.p. 103–104°, identified by mixed melting point.

The main bulk of the solution gave a strong positive Color Test I and a 2-ml. aliquot, 1 hour after the reaction was apparently complete, indicated by the double titration method, that the concentration of the reagent was 59% of the theoretical. The main bulk of the solution was stirred at room temperature an additional 30 hours, by which time all the sodium–potassium alloy (originally present in excess) was consumed. A 5-ml. aliquot, derivatized as before with trimethylchlorosilane, gave only 0.35 g. (38%) of triphenyltrimethyldisilane.

Cleavage of Hexaphenyldisilane with Sodium.—To 5.0 g. (0.00965 mole) of hexaphenyldisilane in 5 ml. of ethylene glycol dimethyl ether was added 1.0 g. (0.043 g. atom) of sodium. After stirring for about 15 minutes the reaction started, as evidenced by the formation of a green color on the surface of the sodium. After 1 hour an additional 30 ml. of the ether was added. The time required for completion of the reaction, as evidenced by complete solution of the white solid, was considerably greater than when sodium–potassium alloy was employed, because the sodium agglomerated together into a large lump; almost 36 hours of stirring was required before all the hexaphenyldisilane had reacted. Titration of an aliquot indicated a 71% yield of reagent. A 10-ml. aliquot was added to 2.0 ml. of trimethylchlorosilane in 5 ml. of ethylene glycol dimethyl ether, and after 5 minutes this was drowned in water and worked up as before to give 1.25 g. (68%) of 1,1,1-triphenyl-2,2,2-trimethyldisilane, m.p. 101–103°. The main bulk of the solution gave a positive Color Test I.

Cleavage of Hexaphenyldisilane with Lithium.—To 5.0 g. (0.00965 mole) of hexaphenyldisilane in 5 ml. of ethylene glycol dimethyl ether was added 1.0 g. (0.144 g. atom) of lithium wire, cut into 2–3 mm. lengths. At the end of 30 minutes, the reaction definitely had started, for the suspension was dark brown, and the lithium was shiny. An additional 35 ml. of the ether was added. The supernatant liquid gave a strong positive Color Test I. After 4 hours of stirring, the dark brown reaction mixture was homogeneous, except for the excess unreacted lithium. A 20-ml. aliquot was added to 1.5 ml. of trimethylchlorosilane in 5 ml. of the ether. The color of the reagent disappeared immediately and the reaction mixture became warm. A white solid was precipitated. After 5 minutes, the reaction mixture was drowned in 200 ml. of water, which was thrice extracted with ether. The ether extracts were dried over sodium sulfate, the ether was removed under reduced pressure, and the residual solid was recrystallized from 95% ethanol to yield a total of 2.8 g. (72%) of 1,1,1-triphenyl-2,2,2-trimethyldisilane, m.p. 102–104°, identified by mixed melting point with an authentic sample.[3]

Attempted Cleavage of Hexaphenyldisilane with Magnesium.—To 5.0 g. (0.00965 mole) of hexaphenyldisilane in 10 ml. of ethylene glycol dimethyl ether was added 1.0 g (0.042 g. atom) of powdered magnesium. The grey suspension was stirred at room temperature for 3 days, during which time no change occurred, even when a trace (0.5 ml.) of methyl iodide was added, or when additional magnesium powder, decanted from a Grignard preparation of phenylmagnesium bromide, was introduced. The reaction mixture at the end of the 3 days was derivatized with trimethylchlorosilane, and then acidified. A white insoluble residue weighing 4.65 g. (93%) was filtered off, and identified as hexaphenyldisilane by its melting point of 360–362°, which was not depressed when the material was admixed with an authentic sample. No other product was isolated.

A repetition of this reaction was carried out with 1.0 g. (0.041 g. atom) of magnesium turnings, and 1.0 g. (0.00193 mole) of hexaphenyldisilane in 2 ml. of ethylene glycol dimethyl ether. The reaction was catalyzed with a trace of triphenylsilylpotassium, so that a positive Color Test I was obtained shortly after stirring was started, but the magnesium did not appear to be consumed after 1 day of stirring. An additional 10 ml. of solvent was added. The reaction mixture was refluxed for 24 hours, and then stirred at room temperature an additional 48 hours. It was then derivatized with trimethylchlorosilane and worked up as before. Only hexaphenyldisilane, m.p. 361–363°, was recovered in 97% yield.

A third attempt, identical to the above, except that the reaction mixture was treated several times over the first 24 hours with small amounts of triphenylsilylsodium in ethylene glycol dimethyl ether, and was then stirred at room temperature for an additional 48 hours, gave similar results to those above.

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[5] H. Gilman and A. H. Haubein, *ibid.*, **66**, 1515 (1944).

[6] Melting points are uncorrected. Organometallic reactions were carried out in a dry, oxygen-free nitrogen atmosphere.

Reaction of Cycloheptene Oxide with Formic Acid

BY ARTHUR C. COPE AND WARREN N. BAXTER

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Since the solvolysis of cycloöctene oxide with formic acid followed by saponification has been observed to form 1,4-cycloöctanediol by a "trans-