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

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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

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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

$$(C_6H_5)_3Si\text{–}Si(C_6H_5)_3 \xrightarrow{Li} (C_6H_5)_3SiLi \xrightarrow{(CH_3)_3SiCl} (C_6H_5)_3Si\text{–}Si(CH_3)_3$$

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