procedure requires that the fused anhydride at 150° be forced by displacement with mercury into a tube kept at 675°. A safer and more convenient method consisted of using sand instead of mercury.

Di(2-methyl-2-nitropropyl)malonate. (*a*) *With carbon suboxide.* To a Dry Ice trap, containing 35.7 g. (0.30 mole) of 2-nitro-2-methyl-1-propanol dissolved in 120 ml. of anhydrous ethyl ether and 0.5 g. of anhydrous aluminum chloride at −78°, was distilled 20 g. (0.29 mole) of carbon suboxide. The trap was then provided with a Dry Ice condenser and drying tube, and the reaction mixture was allowed to warm up to 25° and remain at that temperature for 24 hr. The solvent was then evaporated, the residue taken up in hot methanol and after filtration, small portions of water were added until no more material precipitated. The mixture was then filtered, yielding 45.9 g. (100%) of di(2-methyl-2-nitropropyl)malonate, m.p. 50–51° after recrystallization from hexane.

Anal. Calcd. for $C_{11}H_{18}N_2O_8$: C, 43.13; H, 5.88; N, 9.15. Found: C, 42.99; H, 5.98; N, 9.31.

(*b*) *With malonic acid.* To a flask equipped with a condenser were added 10.4 g. (0.1 mole) of malonic acid, 25.0 g. (0.21 mole) of 2-nitro-2-methyl-1-propanol, 85 ml. of ethylene chloride, and 4 ml. of conc. sulfuric acid. The mixture was refluxed for 30 hr. and the lower ethylene chloride layer was washed with water and a sodium bicarbonate solution. The solvent was removed *in vacuo,* the residue taken up in methanol, and reprecipitated by the addition of water. This gave a 35% yield of ester, m.p. 50–51° after recrystallization from hexane. A mixed melting point determination with the ester obtained from the procedure (*a*) showed no depression.

The following esters were prepared by procedure (a).

2-Di(3-methyl-3-nitrobutyl)malonate, m.p. 83–84° after recrystallization from hexane and then absolute ethanol (yield 85%).

Anal. Calcd. for $C_{13}H_{22}N_2O_8$: C, 46.70; H, 6.63; N, 8.38. Found: C, 46.69; H, 6.76; N, 8.44.

Di(2-nitrobutyl)malonate, $n_D^{19.5}$ 1.4587, was distilled at 1 micron at a bath temperature of 57° (yield 80%).

Anal. Calcd. for $C_{11}H_{18}N_2O_8$: C, 43.13; H, 5.88; N, 9.15. Found: C, 43.22; H, 5.81; N, 9.27.

Di(2-nitroethyl)malonate, $n_D^{19.5}$ 1.4670, decomposed on distillation at 5 microns at a bath temperature of 45°.

Preparation of a polyester (VI) *from carbon suboxide and 2,2-dinitropropanediol.* 2,2-Dinitropropanediol[6] (32.2 g., 0.2 mole), 0.5 g. of anhydrous aluminum chloride and 25 g. (0.37 mole) of carbon suboxide in ether were allowed to react as described in procedure (a). On cooling the reaction mixture, 0.52 g. of a solid, m.p. 95–110° precipitated. On evaporating the solvent from the filtrate, an oil remained which was taken up in hot methanol; after addition of water, 6.4 g. of solid precipitated. Evaporation of the filtrate left 32 g. of an oil which could not be crystallized. It solidified to a waxy solid on cooling, but melted before reaching room temperature. The above solid melted at 82–83° after recrystallization from absolute ethanol and analyzed correctly for VI.

Anal. Calcd. for $C_6H_6N_2O_8$: C, 30.78; H, 2.58; N, 11.97. Found: C, 31.06; H, 2.89; N, 11.99.

When the above diol and malonyl dichloride were refluxed[7] in dioxan for 23 hr., a polymer was obtained which softened at 115–123° but gave the same analysis as the polyester VI.

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(6) H. Feuer, G. B. Bachman, and J. P. Kispersky, *J. Am. Chem. Soc.,* **73,** 1360 (1951).

(7) Unpublished results from the Ph.D. thesis of J. P. Kispersky, Purdue University, August 1950.

Preparation of 3-Triethoxysilylpropylamine and 1,3-Bis(3-aminopropyl)tetramethyldisiloxane

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Primary and secondary amines with silicon hydrides in the presence of chloroplatinic acid form hydrogen and unidentified products, presumably aminosilanes.[1] With allylamine triethoxysilane and chloroplatinic acid led to complex products along with hydrogen. However, despite the presence of an amino hydrogen, allylaminotrimethylsilane (I) reacted with triethoxysilane in the presence of chloroplatinic acid to give a small amount of tetraethoxysilane and silane with a product assumed to be 3-triethoxysilylpropylaminotrimethylsilane. *sym*-Tetramethyldisiloxane and I presumably gave 1,3-bis(3-trimethylsilylaminopropyl)tetramethyldisiloxane. These adducts were not isolated, but ethanol converted them in good yield to the free amines II and III, which were isolated and identified.

$$CH_2{=}CH{-}CH_2NHSi(CH_3)_3$$
I

$$(C_2H_5O)_3SiCH_2CH_2CH_2NH_2$$
II

$$[NH_2CH_2CH_2CH_2Si(CH_3)_2]_2O$$
III

$$C_2H_5O(CH_3)_2SiCH_2CH_2CH_2Cl$$
IV

$$C_2H_5O(CH_3)_2SiCH_2CH_2CH_2NH_2$$
V

The physical properties of II differed slightly from those previously reported,[2] but the infrared spectrum was identical with that of an authentic sample. The structure of III was established by an independent synthesis. The reaction of 3-chloropropyldimethylethoxysilane (IV) with liquid ammonia formed 3-ethoxydimethylsilylpropylamine (V). The hydrolyzate from V had the same infrared spectrum and yielded the same dihydrochloride as that of III.

EXPERIMENTAL

Allylaminotrimethylsilane was prepared in 70% yield.[3] Boiling point 111–112°, n_D^{25} 1.4130, d_4^{25} 7675.

3-Triethoxysilylpropylamine (II). A mixture of 115 g. of triethoxysilane, 94.5 g. of allylaminotrimethylsilane and

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(1) Unpublished results of this laboratory.

(2) V. B. Jex and D. L. Bailey, French Patent **1,140,301** (1957).

(3) J. L. Speier, R. Zimmerman, and J. Webster, *J. Am. Chem. Soc.,* **78,** 2280 (1956).

0.25 ml. of 0.2 molar chloroplatinic acid in ethanol was refluxed for 4 hr. A slow stream of an inflammable gas presumed to be silane was observed. Absolute ethanol (50 ml.) was then added, and the mixture was distilled to give 26.7 g. of tetraethoxysilane, b.p. 80–90° at 29 mm., n_{D}^{25} 1.3850, and 94 g. of II (61% yield), b.p. 119–122° at 29 mm., n_{D}^{25} 1.4220, D_4^{25} 0.9477, R_D calcd. 0.2670, R_D found 0.2676. Jex and Bailey[2] reported b.p. 123° at 30 mm., n_{D}^{25} 1.4195, D^{25} 0.942.

Anal. Calcd. for $C_9H_{23}NO_3Si$: Si, 12.61; neut. equiv. 221. Found: Si, 12.39; neut. equiv. 221.

1,3-Bis(3-aminopropyl)tetramethyldisiloxane (III). *sym*-Tetramethyldisiloxane (134 g.) was added slowly to refluxing allylaminotrimethylsilane (294 g.) which contained 0.2 ml. of 0.22 molar chloroplatidic acid in ethanol. After the reaction was initiated, the temperature of the mixture was maintained at 110° to 125° by regulating the rate of addition of the siloxane. After the reaction was complete, 100 ml. of absolute ethanol was added and the lower boiling components were distilled from the mixture. The residue was distilled at reduced pressure to give 191 g. (78% yield) of III, b.p. 96–104° at 2.5 mm., b.p. 134–142° at 11.5 mm., n_{D}^{25} 1.4475–1.4485, D_4^{25} 0.8956–0.8971. R_D calcd. 0.2995, R_D found 0.2989–0.2987.

Anal. Calcd. for $C_{10}H_{28}ON_2Si_2$: Si, 22.60; neut. equiv., 124. Found: Si, 22.38; neut. equiv., 124.5.

A solution of 4.5 g. of III in 200 ml. of anhydrous ether was saturated with dry hydrogen chloride to form the dihydrochloride. Recrystallized twice from ethyl acetate, 1,3-bis(3-aminopropyl)tetramethyldisiloxane dihydrochloride had a m.p. of 250–253°.

Anal. Calcd. for $C_{10}H_{30}ON_2Cl_2Si_2$: Si, 17.45. Found: Si, 17.69.

3-Chloropropyldimethylethoxysilane (IV). To a stirred solution of 252 g. of 3-chloropropyldimethylchlorosilane in 750 ml. of hexane was added 138 g. of absolute ethanol through a tube extending beneath the surface of the liquid. The mixture was refluxed for 2.5 hr., saturated with anhydrous ammonia, and filtered. The precipitate was washed with hexane, and the solvent was removed from the combined filtrates by distillation. The residue was distilled at reduced pressure to give 188.1 g. (69%) of IV. Boiling point 87° at 30 mm., n_{D}^{25} 1.4270, D_4^{25} 0.9319, R_D calcd. 0.2759, found 0.2755.

Anal. Calcd. for $C_7H_{17}OClSi$: Si, 15.50. Found: Si, 15.54.

3-(Ethoxydimethylsilyl)propylamine (V). A mixture of 90 g. of 3-chloropropyldimethylethoxysilane (IV) and 204 g. of anhydrous ammonia was heated at 95° for 2 hr. in a 1-l. stainless steel bomb. After the bomb was cooled the organic layer was separated from the ammonia-ammonium chloride layer; and a 52.5 g. portion of the product was distilled at reduced pressure to give 25.7 g. of 3-ethoxydimethylsilylpropylamine. Boiling point 79–78° at 24 mm., n_{D}^{25} 1.4276, D_4^{25} 0.8570. R_D calcd. 0.3004, found R_D 0.2999.

Anal. Calcd. for $C_7H_{19}ONSi$: Si, 17.39; neut. equiv., 161. Found: Si, 17.17; neut. equiv., 160.2.

A mixture of 16 g. of 3-ethoxydimethylsilylpropylamine, 20 ml. of water and 5 g. of potassium hydroxide was extracted with two 20-ml. portions of ether. The ether solution was dried over potassium hydroxide. A 10-ml. portion saturated with dry hydrogen chloride gave 4.15 g. of 1,3-bis(3-aminopropyl)tetramethyldisiloxane dihydrochloride, m.p. 249.5–251.5° from ethanol–ethyl acetate.

Anal. Calcd. for $C_{10}H_{30}ON_2Cl_2Si_2$: Si, 17.45. Found: Si, 17.39.

The remainder of the ether solution was evaporated to yield 10 g. of 1,3-bis(3-aminopropyl)tetramethyldisiloxane, n_{D}^{25} 1.4480, D_4^{25} 0.8960, R_D calcd. 0.2995, R_D found 0.2988.

Anal. Calcd. for $C_{10}H_{28}ON_2Si_2$: neut. equiv. 124. Found: neut. equiv. 124.6.

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2,5-Dibenzylidene-3-cyclopentenone

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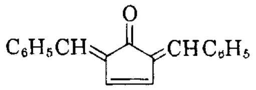
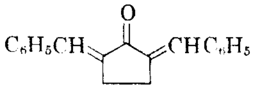
In an investigation of the photochemical properties of 2,5-dibenzylidene-3-cyclopentenone (I), we have encountered unambiguous evidence that I as previously prepared[1] is contaminated with 2,5-dibenzylidenecyclopentanone (II). This impurity was not removed by repeated recrystallization from a variety of solvents. Furthermore, the mixture of I and II gave satisfactory carbon, hydrogen analyses for I. General interest in the unique structure of 2,5-dibenzylidene-3-cyclopentenone has prompted us to relate this evidence together with a novel procedure for the elimination of the contaminant.


I


II

The unexpected presence of II was first detected in an attempt to prepare the uranyl chloride complex of I. Treatment of a hot, saturated solution of supposedly pure I[2] with uranyl chloride gave in low yield an orange-red, crystalline complex. This complex had an infrared spectrum identical to that of an authentic sample of the uranyl chloride-2,5-dibenzylidenecyclopentanone complex.[3] The complex on dissolution in ethanol precipitated a yellow ketone which was shown by mixed melting point and infrared and ultraviolet spectral identity to be 2,5-dibenzylidenecyclopentanone thus confirming the identity of the contaminant. Cooling of the filtrate, after removal of the highly insoluble complex, gave I, m.p. 156–157° (reported previously,[1] m.p. 150°). A second treatment of I with uranyl chloride gave no complex, and the 2,5-dibenzylidene-3-cyclopentenone recovered had melting point, infrared and ultraviolet absorption identical to those of I after a single treatment with uranyl chloride. 2,5-Dibenzylidene-3-cyclopentenone thus purified showed $\lambda_{\max}^{\text{EtOH}}$ 316 mμ (38,900) and 232–234 mμ (11,700).

The failure of I to form a uranyl chloride complex strongly supports the geometric configuration suggested for I by Wanzlick.[1] The structure of the uranyl chloride-2,5-dibenzylidene cycloalkanone complexes will be discussed in a forthcoming report of their photochemical transformations.

EXPERIMENTAL

2,5-Dibenzylidene-3-cyclopentenone (I) (*after Wanzlick*[1]). A solution of 2,5-dibenzylidenecyclopentanone (26 g., 0.1 mole)

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[1] H. Wanzlick, *Chem. Ber.*, **86**, 41 (1953).

[2] This material (m.p. 150°) had been recrystallized seven times from trichloroethylene.

[3] P. Pretorius and F. Korn, *Ber.*, **43**, 2744 (1910).