pled with the observation of Weissgerber[7] that iodine was removed by dilute hydrochloric acid with the production of oxindole, led us to attempt the reaction of 3-iodoindole with silver acetate under mild acidic conditions. We find that in acetic acid solution at room temperature over extended periods of time indoxyl acetate is produced in fair yields. This novel preparation of this class of compounds is expected to open the way to derivatives unobtainable by other routes.

EXPERIMENTAL

3-Iodoindole. A solution of 11.7 g. of indole (0.1 mole) and 4.0 g. (0.1 mole) of sodium hydroxide in 400 ml. of methanol was treated with 101 ml. of iodine-potassium iodide solution containing 25.4 g. (0.2 mole) of iodine with vigorous stirring. No heat was evolved and it was found that the iodine solution could be added as rapidly as possible. Water was added with stirring and the precipitate was filtered and washed with water. This material is unstable and should be used immediately without purification.

Indoxyl acetate. The crude iodoindole was dissolved in 400 ml. of glacial acetic acid and 33.4 g. (0.2 mole) of silver acetate was added in one portion and the suspension was stirred for 20 hr. At the end of this period the mixture was filtered and the filtrate was evaporated to dryness under vacuum. The dark purple residue was recrystallized twice from a 40% solution of methanol in water. The product crystallized as fine white needles which melted at 126° (reported 126–127°).[1] A mixed melting point with an authentic sample of indoxyl acetate was not depressed. The overall yield was 5.4 g. or 28%.

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[7] R. Weissgerber, *Ber.*, **46**, 655 (1913).

Reaction of Carbon Suboxide with Nitro Alcohols

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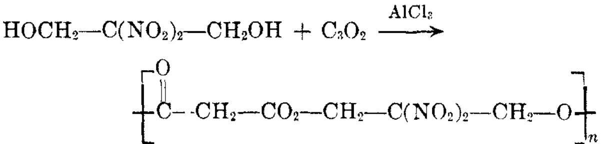
In view of the reactions of carbon suboxide (I) with alcohols,[2] amines, acids and related classes of compounds,[3] it was anticipated that I would also react with primary and secondary nitroparaffins to yield α,α'-dinitro diketones. Since α-nitro ketones possessing alpha hydrogen are unstable compounds, secondary nitro- and *gem*-dinitro compounds were chosen, so that the resulting products would not contain an alpha hydrogen. When 2-nitropropane or 1,1-dinitroethane was treated at room temperature with an ethereal solution of I in the absence of a catalyst or in the presence of such catalysts as sulfuric acid and triethylamine, no addition took place, and the nitro compounds were recovered unchanged. The sulfuric acid caused polymerization of I[2] and the triethylamine formed an addition compound with I which is probably similar to those resulting from the reaction of alkaloids and I.[4]

Since I did not react with nitroparaffins, reactions were initiated with primary, secondary, and tertiary 2-nitroalcohols in order to establish whether the presence of a nitro group adjacent to the reaction center would affect the esterification. It was found that the expected malonic esters formed readily at room temperature, but in small yields unless a catalyst was present. Thus the reaction of 2-nitro-2-methyl-1-propanol (II) with excess of I in ether at room temperature for 24 hours gave di(2-methyl-2-nitropropyl)malonate (III) in only a 39% yield. The yield of III increased to 53% in the presence of sulfuric acid, which, however, also caused extensive polymerization of I. This polymerization was minimized when the reaction was carried out in the presence of hydrogen chloride or aluminum chloride, affording III in yields of 87% and 100%, respectively.

The structure of ester III was established by elemental analysis, and by a mixed melting point determination with an authentic sample of III which was prepared from malonic acid and II and which in its turn analyzed correctly.

Besides compound II, 3-methyl-3-nitro-2-butanol, 2-nitro-1-butanol and 2-nitroethanol (IV) reacted smoothly with I. The ester (V) which was obtained with IV was an oil which could not be distilled even in high vacuum without causing decomposition. However, the structure of V was confirmed by the identity of its infrared spectrum with that of the ester, prepared from IV and malonic acid.

The reaction of I with 2,2-dinitropropanediol yielded a polymeric material.



$$HOCH_2{-}C(NO_2)_2{-}CH_2OH + C_3O_2 \xrightarrow{AlCl_3} \left[\overset{O}{\overset{\|}{C}}{-}CH_2{-}CO_2{-}CH_2{-}C(NO_2)_2{-}CH_2{-}O \right]_n$$

VI

It was soluble in hot methanol, and on addition of water was partially converted to a solid, the elemental analysis of which was in agreement with the unit structure of polyester VI. The remainder was an oil which could not be solidified.

EXPERIMENTAL

The carbon suboxide was produced by thermal degradation of diacetyltartaric anhydride. Essentially the method of Hurd and Pilgrim[5] was followed, with one variation. The

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[1] From the M.S. dissertation of Robert Miller, Purdue University, May, 1956.

[2] G. Hagelloch and E. Feess, *Ber.*, **84**, 730 (1951).

[3] L. H. Reyerson and Kenneth Kobe, *Chem. Revs.*, **7**, 479 (1930).

[4] O. Diels and K. Hansen, *Ber.*, **59**, 2555 (1926).

[5] C. D. Hurd and F. D. Pilgrim, *J. Am. Chem. Soc.*, **55**, 757 (1933).

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).