

placed in the inner chamber of the vapor bath and brought to temperature. Then weighed amounts of tri-*n*-butyl amine (when used) and diisocyanate were added in amounts sufficient to prepare 0.01*N* and 0.1*N* solutions respectively. The inner chamber of the bath was stoppered to prevent undue exposure of the reaction mixture to moisture.

Reaction rates were determined by following the disappearance of isocyanate by a modified Stagg method.⁷ Samples were removed periodically, and warmed with excess dibutyl amine to react completely the remaining diisocyanate in the sample. Unreacted dibutyl amine was titrated potentiometrically with 0.025*N* HCl, using a Beckman Model K Automatic Titrator. In catalyzed runs, titrations were corrected for the amount of tri-*n*-butyl amine in the sample.

Data were calculated and plotted according to the usual second-order reaction rate equation for reactants at equal initial concentration. Representative rate plots are given in Fig. 1. Rate constants were determined from the slope of

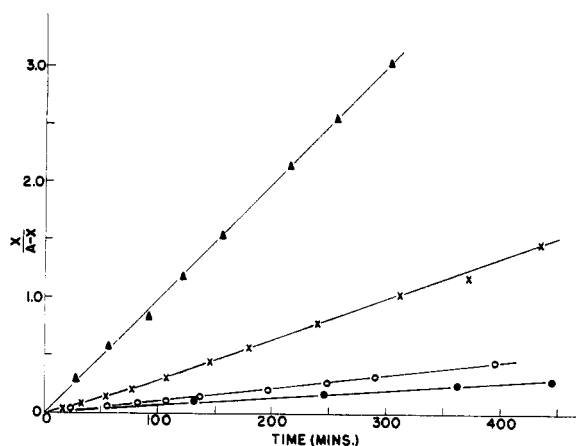


Fig. 1. Representative second-order rate plots for the reaction of 3,3'-dimethyl-4,4'-biphenylene diisocyanate with ▲ 1-octanol, catalyzed; × 2-octanol, catalyzed; ○ 1-octanol, uncatalyzed; ● 2-octanol, uncatalyzed. Additional points were obtained on the first and last curves which established the linearity of the plots at higher extents of reaction.

the best straight line drawn (by visual methods) through the points of the plot. Reproducibility of runs was quite good (*i.e.*, agreement of duplicate runs was $\pm 1.5\%$), and all sets of data fitted the second-order rate equation with two exceptions. For both catalyzed and uncatalyzed reactions of 1-octanol with 4,4'-methylenebis(phenyl isocyanate), the rate plots drifted upward slightly at high extents of reaction. No satisfactory explanation could be found for this, so rate constants for these reactions were determined from the best straight lines drawn through the first few points of the plots (up to about 30% reaction). Blank runs, in which the diisocyanates were heated alone, with or without the amine catalyst, resulted in negligible or no disappearance of the diisocyanate. No evidence was found for any reaction taking place other than urethane formation except for the above-mentioned reactions of 4,4'-methylenebis(phenyl isocyanate) and 1-octanol. Even in these cases, deviation of the rate plots from linearity corresponded to only a few percent of the total diisocyanate that had reacted. Consideration of data in the literature,⁸ as well as the experiments of this work, indicated that allophanate formation, or dimerization or trimerization of the diisocyanate, either would not occur at all under the experi-

mental conditions of this work, or would take place only slowly in comparison to the rate of urethane formation.

When two isocyanate groups are attached to the same benzene nucleus, as in *m*-phenylene diisocyanate and 2,4-tolylene diisocyanate, two separate rate constants are obtained for each diisocyanate.⁴⁻⁶ With *m*-phenylene diisocyanate, the two isocyanate groups have equal initial reactivity. Beyond 50% reaction, however, when one isocyanate group has been converted to a urethane group, the second isocyanate group exhibits a slightly lower reactivity, due to the lesser activating effect of a *m*-urethane group in comparison to that of a *m*-isocyanate group.⁴⁻⁶ With 2,4-tolylene diisocyanate, because of the presence of the methyl group on the benzene nucleus, the 4-isocyanate group has higher initial reactivity.⁴⁻⁶ When rate data for such diisocyanates are plotted, curvatures are obtained in the plots near 50% reaction. The best straight line was drawn through the first few points of the plot, and from this k_1 , the rate constant for the more reactive isocyanate group, was determined. Similarly, k_2 , the rate constant for the less reactive group, was determined from the last few points on the curve beyond 50% reaction.

For all such reactions, the two rate constants so obtained were of the same order of magnitude. Hence, there was probably some overlapping and interfering reaction of both isocyanate groups throughout the entire course of each reaction. It was felt, however, that because of the reasonably good linearity obtained in the early and late stages of each such rate plot, there was sufficient justification for determining the two rate constants independently of each other by simple graphical means. All such rate constants in this work probably do contain some degree of approximation, however.

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Some 2,2-Disubstituted-3,5-morpholinediones

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These compounds were synthesized for comparison with the previously reported 2,2-disubstituted-3,5-thiomorpholinediones.³ In general, the 3,5-morpholinediones were prepared from the suitably substituted esters of glycolic acid by converting them to diesters of diglycolic acid, then to the diamides or ammonium salts which were pyrolyzed to the substituted 3,5-morpholinediones. Preliminary pharmacological screening tests indicate that compounds with like substituents possess similar activities as hypnotics and anticonvulsants.

(1) Work done at University of Delaware, Newark, Del.
(2) Work done at Merck, Sharp and Dohme Laboratories, West Point, Pa.

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EXPERIMENTAL

*α,α -Dimethyldiglycolamide.*² To a refluxing suspension of 19.5 g. (0.5 mole) of sodium amide in 300 cc. of ether was added dropwise ethyl α -hydroxyisobutyrate (66.0 g., 0.5 mole). After refluxing 45 min. longer to expel the ammonia ethyl bromoacetate (83.5 g., 0.5 mole) was added dropwise during 30 min. The stirred mixture was refluxed 2 hr. Water was added and the dried ether layer was distilled to yield 23.0 g. of product, b.p. 125–128° (13 mm.). This was dissolved in a solution of 25 cc. of liquid ammonia in 175 cc. of ethanol. The solution was heated in a pressure bottle 5 days at 70–80°. The solution was concentrated to 100 cc. and chilled to give 15.4 g. of crude amide, m.p. 160–162°. One crystallization from ethanol gave the pure product, m.p. 162–163°.

Anal. Calcd. for $C_6H_{12}N_2O_3$: N, 17.48. Found: N, 17.51.

*2,2-Dimethyl-3,5-morpholinedione.*³ The above amide (14.3 g., 0.09 mole) was heated at 200° (60 mm.) for 30 min. The temperature of the bath was raised to 260° whereupon the imide distilled at 20 mm. pressure and solidified in the receiver. The product was triturated with sodium bicarbonate solution to give 6.3 g., m.p. 73–76°. One recrystallization from benzene-ligroin yielded 5.0 g. of pure product, m.p. 74–76°.

Anal. Calcd. for $C_8H_{10}NO_3$: N, 9.79. Found: N, 9.75.

*α,α -Diethyldiglycolic acid.*² To a stirred suspension of 2.4 g. of sodium hydride in 100 cc. of dry benzene was added during 25 minutes 16.0 g. (0.10 mole) of ethyl α -ethyl- α -hydroxybutyrate and the stirring continued 40 min. until a clear yellow solution resulted. Ethyl bromoacetate (18.4 g., 0.11 mole) was added dropwise and the mixture was refluxed for 2 hr. Water was added. The organic layer was dried and distilled to give 9.2 g. of colorless oil, b.p. 152–157° (22 mm.). A total of 90.7 g. of this oil was dissolved in 340 cc. of hot hydrochloric acid (Sp. gr. 1.18) and the solution was heated 16 hr. in a steam bath. The solution was concentrated to 200 cc. and chilled. The crystalline product (41.5 g.) had m.p. 140–147° and was suitable for preparation of the ammonium salt. A small sample was crystallized twice from ethyl acetate to give the pure acid, m.p. 146–148°.

Anal. Calcd. for $C_8H_{14}O_5$: C, 50.52; H, 7.42. Found: C, 50.58; H, 7.50.

*2,2-Diethyl-3,5-morpholinedione.*³ A solution of 28.5 g. (0.15 mole) of α,α -diethyldiglycolic acid in 90 cc. ammonia water (Sp. gr. 0.90) was evaporated to dryness. The resulting salt was heated at 190° for 25 minutes at a pressure of 50 mm. The bath temperature was raised to 210° and the pressure was lowered to 14 mm., whereupon the product distilled and crystallized. It was triturated with sodium bicarbonate solution and recrystallized from a mixture of isopropyl alcohol and water to give 10.4 g. of the imide, m.p. 62–63°.

Anal. Calcd. for $C_8H_{14}NO_3$: N, 8.18. Found: N, 8.18.

*Methyl ethylphenylhydroxyacetate.*¹ Ethylphenylhydroxyacetic acid⁴ (11.4 g., 0.063 mole) was refluxed for 2.5 hr. with 60 cc. of methanol containing 0.3 cc. of sulfuric acid. The mixture was treated with 50 cc. of water and 50 cc. of saturated sodium bicarbonate solution. The solution was saturated with salt and extracted with ether. From the aqueous layer there was obtained unchanged acid (0.48 g.) and from the ether extract 11.11 g. of the ester, b.p. 86–88° (0.9 mm.), n_D^{25} 1.5080.

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 68.02; H, 7.27. Found: C, 67.98; H, 7.37.

*Methyl α -ethyl- α -phenyl- α -carbethoxymethoxyacetate.*¹ In a nitrogen atmosphere methyl ethylphenylhydroxyacetate (18.8 g., 0.097 mole) was added dropwise during 2 hr. to a rapidly stirred suspension of sodium hydride (1.9 g., 0.08 mole) in 200 cc. of dry benzene at room temperature. Nearly all of the sodium hydride dissolved after stirring 6.5

hr. Complete solution was then effected by refluxing for 1.5 hr. To the stirred solution at room temperature was added dropwise ethyl bromoacetate (13.4 g., 0.08 mole). After stirring overnight the reaction mixture was refluxed for 1 hr., cooled and treated with 100 cc. of cold water. Less than 0.002 mole of hydrogen ions was required for neutrality. The benzene layer was washed with sodium bicarbonate solution, dried, and distilled, yield 14.7 g. (65.6%), b.p. 133–135.5° (0.7 mm.), n_D^{25} 1.4945.

Anal. Calcd. for $C_{15}H_{20}O_6$: C, 64.27; H, 7.19. Found: C, 64.09; H, 7.11.

*α -Ethyl- α -phenyldiglycolamide.*¹ A solution of the above ester (4.2 g., 0.015 mole) in 100 cc. of anhydrous methanol contained in a pressure bottle was saturated at –5° with dry ammonia gas. The bottle was capped and allowed to stand for a week at 45–55°. Removal of the solvent afforded a quantitative yield of crude diamide, m.p. 169–173°. Recrystallization from methanol-ether gave the pure product, m.p. 175° (dec.).

Anal. Calcd. for $C_{12}H_{16}N_2O_3$: C, 60.99; H, 6.82; N, 11.86. Found: C, 60.90; H, 6.87; N, 11.86.

*2-Ethyl-2-phenyl-3,5-morpholinedione.*¹ The above amide was pyrolyzed at 210–220° to yield an amber oil which was dissolved in hot methanol and treated with boneblack to remove color. Hot water was added to the filtrate to the point of incipient precipitation. The crude imide (0.7 g., m.p. 115–125°) separated from the cold solution. This was crystallized from methanol-water to give 0.67 g. (73%) of the pure product, m.p. 124–125°.

Anal. Calcd. for $C_{12}H_{13}NO_3$: C, 65.75; H, 5.97; N, 6.39. Found: C, 65.87; H, 5.97; N, 6.41.

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Scission of the Silicon-Silicon Bond in Halogenated Polysilanes by Organometallic Reagents

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Cleavage of the silicon-silicon bond by organometallic reagents has been long known. First reports of cleavages of this nature were by Friedel and Ladenburg,^{1–3} who demonstrated that treatment of hexaiododisilane with diethylzinc gave a mixture of tetraethylsilane and hexaethylidisilane. Shortly thereafter it was reported⁴ that tetraphenyldisilane was the sole product from the reaction of hexachlorodisilane, chlorobenzene, and sodium. No yields or experimental details were mentioned. From the reaction of hexachlorodisilane with methyl magnesium iodide, Martin⁵ obtained oils which he postulated were mixtures of monosilanes containing methyl and chloro groups. From hexachlorodisilane

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