Experimental

Formation of Formic Ethylcarbonic Anhydride.—Formic acid (99+%) prepared using phthalic anhydride[10] (4.6 g., 0.1 mole) was dissolved in 200 ml. of anhydrous ether, and freshly distilled ethyl chlorocarbonate (10.9 g., 0.1 mole) was added and the mixture was cooled to −15°. Freshly distilled triethylamine (10.1 g., 0.1 mole) was added dropwise with stirring, preventing rise in temperature. At the end of 30 min., a portion of this mixture was quickly shaken with solid sodium bicarbonate, the mixture was filtered, and the infrared spectrum was taken in the ether solution; it revealed peaks at 1730 and 1793 cm.$^{-1}$, indicating the formation of the expected mixed anhydride, but attempts to isolate it ended in failure.

Evidence for the Existence of the Mixed Anhydride.—The preparation of the mixed anhydride was done exactly as outlined above except that 15 min. after the reaction mixture had been stirred at −15°, α-naphthylamine (14.3 g., 0.1 mole) in ether was added to the mixture and stirring continued for 1 hr. The mixture was then filtered and the pale pink ether solution was washed with dilute acid, saturated bicarbonate solution, and several times with water. The ether solution was evaporated to dryness, giving 6 g. of a crude product which after two or three recrystallizations from benzene melted at 142°. This product did not depress the melting point of the formyl-α-naphthylamide, m.p. 142°, prepared from formic acid and α-naphthylamine independently. The infrared spectra of both samples were identical.

Determination of Carbon Dioxide and Carbon Monoxide.—In a three-necked flask fitted with an addition flask, a gas inlet tube, and a Dry Ice condenser, were placed formic acid (4.6 g., 0.1 mole) and ethyl chlorocarbonate (10.9 g., 0.1 mole) in 200 ml. of anhydrous ether. A gentle stream of nitrogen was passed through an ascarite bulb into the flask. Two previously weighed ascarite bulbs followed by three weighed bulbs containing freshly prepared cuprous sulfate in sulfuric acid[8] were connected to the exit outlet of the Dry Ice condenser. While the ether was cooled at −15°, triethylamine (10.1 g., 0.1 mole) was added dropwise with stirring. Stirring was continued for 2 hr. at −15 to 0° and the temperature was allowed to rise to room temperature at the end of 4–6 hr. While the stream of nitrogen was continued care was taken to replenish the Dry Ice condenser with Dry Ice and acetone to condense any ether that might be carried by the nitrogen. The ascarite and cuprous sulfate bulbs were weighed at various time intervals and usually there was no increase in weight after 4–6 hr. The yields of CO_2 and CO are based on values obtained from about ten runs and were 80 ± 10% and 60 ± 15%, respectively.

Estimation of Ethanol and Ethyl Formate.[11,12]—In the above reaction after the completion of the evolution of the carbon dioxide and carbon monoxide, the mixture was filtered into a volumetric flask and the volume was made up to 250 ml. by washing the amine hydrochloride several times with dry ether. The ethanol was estimated by taking accurately 25 ml. of this solution and treating with acetic anhydride and pyridine on a steam bath for 2 hr. and titrating the excess acetic acid with standard alkali.[12] The ester in the mixture was determined by standard saponification procedures.[12] The average values of eight to ten runs ran parallel to the estimation of these components in the v.p.c. method.[11] Pure ethanol (0.1 μl.), ethyl formate, and ether were run through an Apiezon L column at 55° and also an Ucon Polar column at 75° in the Hy-Fi Aerograph which is equipped with an integrator and a hydrogen flame ionization detector. The areas were considered proportional to the integral values and thus calibrations were made for the pure substances. Several runs of the unknown mixture (0.1 μl.) were run through the columns and from the integral values the yield of ethanol was found to be 60 ± 5%, based on complete reaction between formic acid and ethyl chlorocarbonate, and that of ethyl formate was 35 ± 5% on the same basis.

(10) British Patent 308,731; *Chem. Zentr.*, **II**, 1215 (1929); *cf.* A. A. Pryanishnikov and Z. F. Shokhova, *J. Gen. Chem. USSR*, **2**, 84 (1932); *Chem. Abstr.*, **27**, 2672 (1933).

(11) A. I. M. Keulemans, "Gas Chromatography," Reinhold Publishing Corp., New York, N. Y., 1959.

(12) S. Siggia, "Quantitative Organic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1963, pp. 12, 138.

A Convenient Preparation of 1-Diazopropane

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A simple method for the preparation of 1-diazopropane was required. An examination of the literature revealed that 1-diazopropane has been prepared from N-nitroso-N-*n*-propylurethan (57%),[1] N-nitroso-β-*n*-propylaminoisobutyl methyl ketone (44%),[2] N,N′-dinitroso-N,N′-di-*n*-propyloxamide (50%),[3] and 1-*n*-propyl-1-nitroso-3-nitroguanidine (55%).[4] The preparation of a number of N-nitroso-N-alkylureas and their conversions into diazoalkanes has been reported.[5] This procedure has not been used for the preparation of N-nitroso-N-*n*-propylurea and its conversion into 1-diazopropane. As the latter procedure would appear to be shorter and less hazardous than the others, we undertook its investigation. The results supplement the existing methods.

N-Nitroso-N-*n*-propylurea was prepared in 30% yield by nitrosation of N-*n*-propylurea and in 28% over-all yield from butyramide through N-*n*-propyl-N′-*n*-butyrylurea. The product was stable at room temperature for at least a month and at refrigerator temperature for over 3 years as evidenced by the absence of any change in the melting point, infrared spectrum, or yield of 1-diazopropane obtained. The urea was converted in 52% yield to 1-diazopropane using the procedure[6] for the small-scale preparation of diazomethane from N-nitroso-N-methylurea. The product obtained from 1-diazopropane and benzoic acid was shown to be exclusively *n*-propyl benzoate by n.m.r. spectroscopy.

Nitrosation of N-isopropylurea, in an attempt to prepare N-nitroso-N-isopropylurea, and hence 2-diazopropane by this method, resulted even at −15° in a brisk evolution of colorless gases. This observation is in accord with the reported[7] instability of 2-diazopropane.

Experimental[8]

N-Nitroso-N-*n*-propylurea. A. From N-*n*-Propylurea.—A solution of 88.5 g. (1.50 moles) of *n*-propylamine in 250 ml. of water was cooled in an ice–acetone bath and neutralized (methyl red) by the addition of 127 ml. of concentrated hydrochloric acid. Urea (300 g., 5.0 moles) was added to the solution and the solution was boiled under reflux for 3 hr. Sodium nitrite (110 g., 1.60 moles) was dissolved in the solution, which was then cooled in an ice–acetone bath and siphoned, during 1 hr., under the surface of a stirred mixture of 100 g. of concentrated sulfuric acid and 600 g. of ice, which was also cooled by an ice–acetone

(1) A. L. Wilds and A. L. Meader, Jr., *J. Org. Chem.*, **13**, 763 (1948).

(2) D. W. Adamson and J. Kenner, *J. Chem. Soc.*, 286 (1935); 1551 (1937).

(3) H. Reimlinger, *Chem. Ber.*, **94**, 2547 (1961).

(4) A. F. McKay, W. L. Ott, G. W. Taylor, M. N. Buchanan, and J. F. Crooker, *Can. J. Res.* **28B**, 683 (1950).

(5) E. A. Werner, *J. Chem. Soc.*, 1093 (1919).

(6) F. Arndt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 165.

(7) D. E. Applequist and H. Babad, *J. Org. Chem.*, **27**, 288 (1962).

(8) Melting points were observed using a Köfler hot stage and are corrected. Infrared spectra were obtained using a Perkin-Elmer Model 137 Infracord instrument. Analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

bath. During the addition, the temperature of the acid solution was not allowed to rise above −2°. The frothy precipitate that rose to the surface was collected by filtration and sucked dry; it was then slurried with 100 ml. of ice–water, filtered, and washed with three 100-ml. portions of ice-cold water. The product was dried in air to constant weight; the yield of off-white, fluffy powder was 59.4 g. (30%), m.p. 75–77°. There was no change in the melting point on storage at 0° for 3 years. For analysis, a sample was crystallized twice from aqueous methanol, m.p. 76.0–76.5°. The infrared spectrum of this material (1% solution in carbon tetrachloride) showed absorptions at 5.74 (C=O) and 6.64 μ (N—N=O). The spectrum of N-nitroso-N-methylurea (1% solution in carbon tetrachloride) showed corresponding absorptions at 5.70 and 6.68 μ.

Anal. Calcd. for $C_4H_9N_3O_2$: C, 36.63; H, 6.92; N, 32.05. Found: C, 36.65; H, 6.93; N, 31.81.

B. From N-*n*-Propyl-N′-*n*-butyrylurea.—N-*n*-Propyl-N′-*n*-butyrylurea was prepared in 61% yield from butyramide and 0.5 equiv. of bromine, m.p. 102.5–103.5° (lit.[9] m.p. 99–102°). A mixture of 72.0 g. (0.42 mole) of N-*n*-propyl-N′-butyrylurea and 265 ml. of concentrated hydrochloric acid was heated on a steam bath for 10 min. The solution was then cooled to 5°, diluted with 265 ml. of water, and a solution of 36.9 g. (0.53 mole) of sodium nitrite in 250 ml. of water was added during 15 min. The product was collected by filtration, washed with ice-cold water, and air-dried. The yield was 25.0 g. (46%). Recrystallization from aqueous methanol gave a sample that had m.p. 76.0–76.5°.

1-Diazopropane.—N-Nitroso-N-*n*-propylurea (1.0114 g.) was added during 2 min. to a mixture of 10 ml. of ether and 3 ml. of 40% potassium hydroxide at 0°. The mixture was allowed to stand at 0° for 30 min. and the ether layer was decanted onto potassium hydroxide pellets. After drying 2 hr. at 0°, the ether solution was filtered into an ethereal benzoic acid solution. Titration[6] indicated the presence of 0.28 g. (52%) of 1-diazopropane. The titration solution was diluted with water and extracted with ether. The ether solution was dried and evaporated. The n.m.r. spectrum[10] of the residue in carbon tetrachloride solution was superimposable on that of *n*-propyl benzoate.

The yield of 1-diazopropane was slightly less (43–47%) if the drying period or the time of addition was extended.

(9) M. Montagne, *Bull. soc. chim. France*, 125 (1947).

(10) A Varian A-60 instrument was used; tetramethylsilane served as internal reference.

Formation of 1,3-Dioxanes in Water

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Although Skrabal[1] showed by kinetic studies that 1,3-dioxanes are highly resistant to acid hydrolysis, few workers have investigated their preparation in water, a practical, but unappreciated solvent for the synthesis of derivatives of 1,3-dioxane. Conrad and co-workers[2] prepared 1,3-dioxanes by condensing water-soluble aldehydes with 2,2-dimethylpropanediol-1,3 and 2-hydroxymethylpropanediol-1,3; water-insoluble aldehydes underwent the same reaction in 1:1 dioxane–water. Read[3] formed spiro-1,3-dioxanes by condensing pentaerythritol in sulfuric acid (30–50%) at room temperature with aliphatic and aromatic, unhydroxylated aldehydes. Read also used crotonaldehyde to give a

(1) A. Skrabal and M. Zlatewa, *Z. Physik. Chem.* (Leipzig), **119**, 305 (1926).

(2) W. E. Conrad, B. D. Gesner, L. A. Levasseur, R. F. Murphy, and H. M. Conrad, *J. Org. Chem.*, **26**, 3571 (1961).

(3) J. Read, *J. Chem. Soc.*, **101**, 2090 (1912).

TABLE I

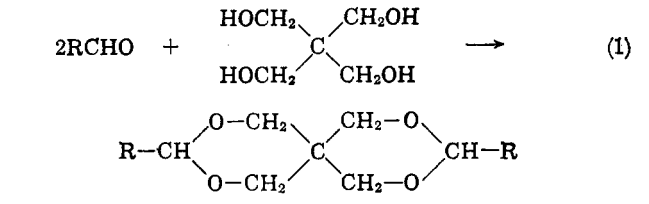
EFFECT OF REACTION CONDITIONS ON THE PREPARATION OF β,β,β′,β′-TETRAMETHYL-2,4-8,10-TETRAOXASPIRO[5,5]-UNDECANE-3,9-DIETHANOL (Ia)

Concn. of aldehyde, M[a]	Time, hr.	Temp., °C.	% yield of Ia	M.p.,[b] °C.
0.7	4.5	73 ± 3	19	203–205
1.3	4.5	73 ± 3	34	199–202
2.7	4.5	73 ± 3	70	201–202[c]
3.6	4.5	75 ± 3	75	201–202
2.7	4.5	53 ± 3	40	194–195
2.7	4.5	90	43	188–193
2.7	2.0	73 ± 3	23	199–202
1.3	6.0	25	7	193–194

[a] Pentaerythritol was added in stoichiometric amounts. [b] Determined on a Fisher-Johns melting point apparatus; J. R. Caldwell, R. Gilkey, and B. S. Meeks, Jr., U. S. Patent 2,945,008 (1960), give m.p. 197°. All melting points are uncorrected. [c] *Anal.* Calcd. for $C_{15}H_{28}O_6$: C, 59.29; H, 9.27. Found: C, 59.47; H, 9.25.

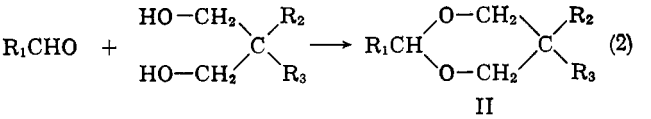
spiro-1,3-dioxane. Recently, Cohen and Lavin[4] described the condensation of water-soluble dialdehydes with pentaerythritol to polymeric 1,3-dioxanes.

Our work, which is summarized in eq. 1–3, features the use of water alone as the medium in which aliphatic aldehydes and 1,3-diols are converted to 1,3-dioxanes. *n*-Butyraldehyde and 2,2-dimethyl-3-hydroxypropionaldehyde, both only sparingly soluble in water, give high yields of products; dioxane is not required. Furthermore, the water-soluble products IIIa and IIIb are obtained in more than 90% yield; therefore, product insolubility is not a driving force for the reaction. The drastic conditions employed by Read are not necessary for the preparation of acetals from aliphatic saturated aldehydes but may be needed for reaction of α,β-unsaturated aldehydes. Crotonaldehyde would not condense with pentaerythritol under



(1)

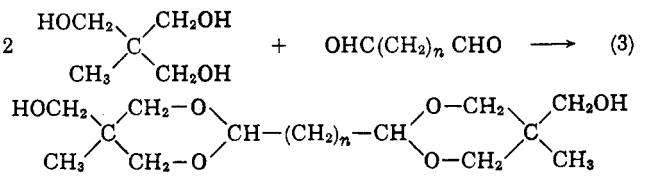
Ia, R = $HOCH_2C(CH_3)_2$
b, R = $CH_3CH_2CH_2$



(2)

II

IIa, R_1 = $HOCH_2C(CH_3)_2$; R_2 = $HOCH_2$; R_3 = CH_3
b, R_1 = $HOCH_2C(CH_3)_2$; R_2 = R_3 = CH_3
c, R_1 = H; R_2 = $HOCH_2$; R_3 = CH_3
d, R_1 = $HOCH_2C(CH_3)_2$; R_2 = $HOCH_2$; R_3 = CH_3CH_2



(3)

IIIa, n = 2
b, n = 3

(4) S. M. Cohen and E. Lavin, *J. Appl. Polymer Sci.*, **6**, 503 (1962).