

ammonia itself, it can easily be seen that temperature variations cannot account for the difference from Ogg's result. To agree with his results the elevation of the meniscus would have had to be about ten times the values (3.0 and 0.5 mm.) we observed.

DEPARTMENT OF CHEMISTRY
IOWA STATE COLLEGE
AMES, IOWA

RECEIVED APRIL 7, 1948

The Preparation of Some Cyclic Acetals

BY M. SULZBACHER, E. BERGMANN AND E. R. PARISER

The present investigation of cyclic acetal derivatives of ethylene glycol (1,3-dioxolanes) was undertaken because of their possible convertibility, by hydrogenolysis, into ethylene glycol monoalkyl ethers,¹ not always available by the usual methods. It was known that aldehydes condense with ethylene glycol without catalyst² and that acidic substances accelerate the reaction.³ It was also known that ketones which cannot easily be acetalated by monohydric alcohols, are capable of such

zene in presence of the catalyst.^{4,5,6} The time required for the liberation of the theoretically expected quantity of water gives an at least qualitative indication of the reactivity of the carbonyl compounds. From Table I in which our results are briefly summarized, the following conclusions can be drawn: Benzaldehyde has approximately the same reactivity as heptaldehyde. As in many other instances,⁷ a 4-methoxy group decreases, while halogen, even in ortho-position, increases the activity of the carbonyl group. Among the ketones, those containing the $-\text{CH}_2-\text{CO}-\text{CH}_2-$ group, are most active, and in the case of cyclohexanone, even an ortho-methyl group does not affect the activity. Bulky radicals, as in the case of pinacolone, acetophenone and benzophenone deactivate the carbonyl group. Methyl isobutyl ketone shows an unexpectedly slow reaction, although it contains the group $-\text{CH}_2-\text{CO}-\text{CH}_2-$. This recalls the inactivity of that ketone in other instances, e.g. in the condensation with chloroform.⁸ Mesityl oxide behaves in a

TABLE I
CONDENSATION PRODUCTS WITH ETHYLENE GLYCOL

Carbonyl compound	Time required, hr.	Yield, %	B. p.		Formula	Carbon		Hydrogen		Dioxolanes		Mol. refraction Calcd.	Mol. refraction Found
			°C.	Mm.		Calcd.	Found	Calcd.	Found	d_{20}^{25}	n_D^{20}		
Heptaldehyde ¹	2.5	81.0	94	20	C ₇ H ₁₄ O ₂	0.9077 ^a	1.43080 ^a	44.85	44.70
Benzaldehyde ¹	2.5	82.7	101	10	C ₇ H ₆ O ₂	1.1156 ^a	1.52696 ^{a,b}	41.25	41.53
4-Methoxybenzaldehyde	3.25	84.4	158-60	17	C ₁₀ H ₁₀ O ₂	66.7	66.8	6.7	6.9	1.1776 ^a	1.53622 ^a	47.51	47.79
2-Chlorobenzaldehyde ¹⁰	1.00	83.5	150-52	16	C ₇ H ₅ O ₂ Cl	58.7	58.5	4.9	5.1 ^c	1.2639 ⁱ	1.2631 ⁱ	56.11 ⁱ	45.99 ⁱ
Methyl isobutyl ketone	4.0	84.0	48	10	C ₈ H ₁₆ O ₂	66.7	66.9	11.5	11.5	0.908	1.4180	40.23	40.00
Mesityl oxide ^{11,d}	5.5	66.9	156	760	C ₉ H ₁₀ O ₂	67.6	67.3	9.9	9.8	.9471 ^j	1.43963 ^j	39.76 ^j	39.52 ^j
Pinacolone ¹²	4.5	80.5	139	760	C ₈ H ₁₆ O ₂	66.7	66.9	11.1	11.4	.9239	1.42356	40.23	39.77
Cyclohexanone ¹³	1.5	84.5	65	10	C ₆ H ₁₀ O ₂	1.026 ^e	1.4580 ^{e,f}	38.07	37.67
2-Methylcyclohexanone	1.4	83.3	82	15	C ₈ H ₁₄ O ₂	69.2	69.3	10.3	10.1	1.0000 ^a	1.45579 ^a	42.65	42.41
Acetophenone	3.5	85.3	110	30	C ₁₀ H ₁₂ O ₂	73.2	73.5	7.3	7.6
Methyl benzyl ketone ¹⁴	1.5	78.5	133-34	40	C ₁₁ H ₁₄ O ₂	74.2	73.9	7.9	7.7	1.0520 ^a	1.51028 ^a	50.49	50.62
Dibenzyl ketone ¹⁵	1.15	85.8	200-202	18	C ₁₅ H ₁₆ O ₂	80.3	80.6	7.1	7.3
Benzophenone	5.0	81.4	168	10	C ₁₃ H ₁₂ O ₂	79.6	80.0	6.2	6.1	1.1794 ^a	1.59013 ^a	65.36	65.53

^a Temperature, 19.5°. ^b Salmi and Louhenkurru (ref. 11) give d_{20}^{25} , 1.1116; n_D^{20} 1.52513. ^c Calcd.: Cl, 19.2. Found: Cl, 19.0. ^d The bromine addition product, b. p. 80-90° (30 mm.), was a purple-colored liquid which gradually split off hydrobromic acid, upon standing. ^e Temperature, 21°. ^f Salmi (ref. 4) gives d_{20}^{25} , 1.0280; n_D^{20} 1.45828. ^g The acetal crystallized and had, after recrystallization from alcohol, m. p. 60°. It was described recently by Salmi, Tamminen and Louhenkurru.¹⁶ ^h The acetal crystallized: m. p. 69° (from methanol). ⁱ Data by Salmi and Kyrki (ref. 4). ^j Data by Salmi and Rannikko, *Ber.*, 72, 600 (1939).

catalyzed condensation with glycols; *p*-toluenesulfonic acid has proved to be an efficient catalyst.⁴ Without catalyst, the reaction is extremely slow: in the same period in which cyclohexanone, e.g., reacts completely with glycol in presence of the above acid, the reaction proceeds only to an extent of 10% in its absence.

The most convenient method for the preparation of the acetals consists in the azeotropic distillation of the mixture of the components with ben-

manner similar to that of its hydrogenation product, methyl isobutyl ketone.

(5) Meerwein in Houben-Weyl, Vol. 3, 3rd edition, Leipzig, 1930, p. 191.

(6) Haworth and Lapworth, *J. Chem. Soc.*, 121, 81 (1922); see also Senkus, U. S. Patent 2,419,505 (C. A., 42, 616 (1948)).

(7) Compare, e. g., Petrenko-Kritschenko, *Ann.*, 341, 165 (1905).

(8) Ch. Weizmann, E. Bergmann and Sulzbacher, *THIS JOURNAL*, 70, 1189 (1948).

(9) Hibbert and Timm, *ibid.*, 46, 1283 (1924).

(10) Salmi and Kyrki (ref. 4).

(11) Salmi, *Ber.*, 72, 600 (1939). The normal acetal formation of unsaturated aldehydes has already been observed by Leopold and Michael, German Patent 434,989 (*Chem. Zentr.*, 97, II, 2846 (1926)); by Senkus, U. S. Patent 2,383,622 (C. A., 40, 898 (1946)), and by Fourneau and Chantalou (ref. 4). See also Salmi and Louhenkurru, C. A., 42, 537 (1948).

(12) Salmi and Rannikko (ref. 11).

(13) Salmi (ref. 4).

(14) Preparation by hydrolysis of phenylacetone nitrile, prepared according to "Organic Syntheses," Coll. Vol. II, p. 487.

(15) Salmi, Tamminen and Louhenkurru, C. A., 42, 537 (1948).

(1) Hydrogenolysis of 2-phenyl-1,3-dioxolane and of furfural diethylacetal: Adkins, Covert and Connor, *THIS JOURNAL*, 54, 1651 (1932), of ethylenimine derivatives: Karabinos and Serijan, *ibid.*, 67, 1856 (1945); Campbell, Sommers and Campbell, *ibid.*, 68, 140 (1946).

(2) Lochert, *Ann.*, [6] 16, 26 (1889).

(3) Delépine, *Bull. Soc. Chim.*, [3] 23, 915 (1900); Verley, *ibid.*, 21, 275 (1899); Trillat and Cambier, *Compt. rend.*, 118, 1277 (1894).

(4) Salmi, *Ber.*, 71, 1803 (1938); Salmi and Kyrki, C. A., 41, 5480 (1947); see also Fourneau and Chantalou, *Bull. Soc. Chim.*, [5] 12, 845 (1945).

The acetals were purified by treatment of the reaction product with dilute sodium carbonate solution or solid magnesium carbonate, and subsequent fractionation in an efficient column. With few exceptions, they are colorless liquids; their molecular refraction is, within the limits of error, in accord with the theoretical values, as Table II shows. The same conclusion can be drawn from the data observed by Salmi and Kyrki.⁴

DANIEL SIEFF RESEARCH INSTITUTE
REHOVOTH, PALESTINE

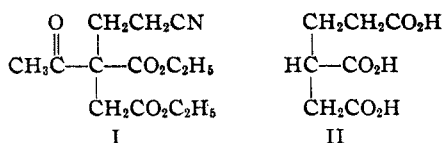
THE GROSVENOR LABORATORY
LONDON S. W. 1, ENGLAND RECEIVED JANUARY 13, 1948

A New Synthesis of Butane-1,2,4-tricarboxylic Acid

BY P. O. TAWNEY AND E. J. PRILL

Butane-1,2,4-tricarboxylic acid (II) has been prepared by various methods.¹ We report herein a new synthesis of this compound.

Diethyl acetosuccinate² was treated with acrylonitrile in the presence of a basic catalyst to give a monocynoethyl derivative (I). The structure of the adduct was demonstrated to be 1-cyano-3-acetyl-3,4-dicarboethoxybutane (I) through conversion to butane-1,2,4-tricarboxylic acid (II) and acetic acid by hydrolysis with concentrated, aqueous potassium hydroxide.



Experimental

1-Cyano-3-acetyl-3,4-dicarboethoxybutane (I).—Potassium hydroxide (1.5 ml. of 50% aqueous solution) was added to a stirred solution of diethyl acetosuccinate² (164.8 g., 0.3 mole) and acrylonitrile (18.0 g., 0.34 mole). The temperature of the slightly exothermic reaction was kept at 30–35° by occasional cooling using an ice-bath. After three days at room temperature, the mixture was diluted with 2 vols. of chloroform. The resulting solution was washed successively with saturated sodium bicarbonate solution, dilute sulfuric acid and water. The solvent was removed by distillation at atmospheric pressure and the residue was fractionated at 1 mm.

Fraction I, b. p. 85–120°, 13.0 g. was recovered acetosuccinic ester. Fraction III, b. p. 154–160°, 55.0 g., (87% yield), n_D^{20} 1.4556, d_4^{20} 1.1186 was the desired 1-cyano-3-acetyl-3,4-dicarboethoxybutane.

Anal. Calcd. for $\text{C}_{13}\text{H}_{19}\text{O}_5\text{N}$: C, 58.0; H, 7.07; N, 5.2. Found: C, 58.15; H, 7.05; N, 5.07.

Butane-1,2,4-tricarboxylic Acid (II).—The ester (I) (68.0 g., 0.25 mole) was added in forty-five minutes with stirring to 120 ml. of 58% potassium hydroxide kept at 75–80°. The mixture was stirred for one hour at 75° and one hour at 100°. At the latter temperature ethanol and ammonia was removed by distillation. The solution was then cooled and acidified using 250 ml. of 35% sul-

furic acid. The resulting mixture was subjected to continuous extraction with ether for forty-eight hours. After evaporation of the ether, acetic acid and water were removed from the residue by distillation under reduced pressure. The acetic acid was identified as *p*-phenylphenacyl acetate.³ The crude product (40.5 g.) was crystallized from ethyl acetate to give 29.5 g. (62%) of white crystals, m. p. 120–121°. The reported¹ melting points for butane-1,2,4-tricarboxylic acid vary from 114° to 123–123.5°.

Anal. Calcd. for $\text{C}_7\text{H}_{10}\text{O}_6$: neut. equiv., 63.3. Found: neut. equiv., 63.5.

(3) Kamm, "Qualitative Organic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1932, p. 181.

GENERAL LABORATORIES
UNITED STATES RUBBER COMPANY
PASSAIC, NEW JERSEY RECEIVED APRIL 29, 1948

The Preparation of Fluoroacetyl Chloride

BY WILLIAM E. TRUCE

The synthesis of fluoroacetyl chloride was undertaken because of its potential value for directly introducing the group, $-\text{COCH}_2\text{F}$, into organic molecules. Such applications are being studied at this laboratory.

Experimental

Fluoroacetyl Chloride.—(Caution! Fluoroacetic acid, sodium fluoroacetate and fluoroacetyl chloride are potent poisons. The following reactions should be carried out under a hood.) Two hundred twenty grams (2.27 moles) of sodium fluoroacetate (Monsanto Chemical Co., 90% min. purity) and 530 g. (2.49 moles) of phosphorus pentachloride are mixed in a two-liter, round-bottom flask. The flask is immediately connected to a condenser arranged for downward distillation. The receiver is open to the atmosphere through a drying tube. When the initial reaction subsides, the flask is heated on a steam-bath until no further distillate comes over. The weight of distillate is 154 g. (1.60 moles). This material is redistilled through a 120-cm. helix-packed column. The fraction boiling at 70–71° (755 mm.) is collected. The colorless liquid weighs 123 g. and has n_D^{20} 1.3835.

Anal. Calcd. for $\text{C}_2\text{H}_2\text{ClFO}$: Cl, 36.7; neut. eq., 48.2. Found: Cl, 36.5; neut. eq., 47.9.

After standing for three weeks at room temperature, the compound was redistilled through the 120-cm. helix-packed column. Eighty-three per cent. of the material was recovered as a fraction boiling at 70–71° (755 mm.), signifying that fluorine-chlorine interchange was not great. A forerun, amounting to 6–7%, boiled at 62–70° (755 mm.). Since the column had a large hold-up, the rest of the material was accounted for in this way.

Fluoroacetamide.—This compound was prepared from fluoroacetyl chloride by the procedure used to make trifluoroacetamide.¹ The yield of crude fluoroacetamide is 73%. The product on recrystallization from chloroform melts at 107–108°. Fluoroacetamide has been prepared by other methods and the melting points reported are 104°,² 108°³ and 108°.⁴ This material gave no depression in melting point when mixed with an authentic sample of fluoroacetamide.²

Anal. Calcd. for $\text{C}_2\text{H}_4\text{FNO}$: N, 18.18. Found: N, 18.16.

DEPARTMENT OF CHEMISTRY
PURDUE UNIVERSITY
LAFAYETTE, INDIANA

RECEIVED JANUARY 27, 1948

(1) (a) "Beilstein," Vol. II, p. 819; 1st. Supp., p. 322; 2nd. Supp., p. 683; (b) Kiliani, *Ber.*, **62B**, 640–1 (1929); (c) Ruzicka, Borges de Almeida and Brack, *Helv. Chim. Acta*, **17**, 183–200 (1934); (d) Hardegger, *ibid.*, **39**, 1195–1198 (1946).

(2) Adkins, Isbell and Wojcik, "Organic Syntheses," **14**, 38 (1934).

(1) Simons and Ramler, *This Journal*, **65**, 389 (1943).

(2) Swarts, *Bull. soc. chim.*, [3] **15**, 1134 (1896).

(3) U. S. Patent 2,403,576 (1946) [C. A., **40**, 6498 (1946)].

(4) U. S. Patent 2,416,607 (1947).