Under similar conditions, the use of *m*-chlorophenyl isocyanate gave the dimer, m.p. 227–229° (ethanol), not depressing the melting point of dimer prepared by an authentic procedure.

N-(Carbanilido)-3-oxypyridyl betaines, IV. These compounds were obtained by heating an equimolar mixture of the aryl isocyanate and 3-hydroxypyridine in a bath maintained at 195° for 0.5 hr. When cool, the reaction product was recrystallized (acetonitrile).

The compounds were of analytical purity, and were obtained as follows: R (melting point) respectively: H (135–136°); *o*-CH_3 (81–84°); *m*-CH_3 (120–121°); *p*-CH_3 (153–155°); *o*-Cl (103–104°); *m*-Cl (159–160°); *p*-Cl (196–197°); *p*-Br (203–208°); *o*-CH_3O (83–84°); *p*-CH_3O (134–135°); bisbetaine from 4,4′-diisocyanate-3,3′-bitolyl (128–132°).

One gram of IV, R = H, was boiled in 20 ml. of ethanol, the ethanol removed to a residual volume of 5 ml., and upon addition of 5 ml. of water and 1.7 ml. of 3*N* hydrochloric acid, *N*-phenylurethane was isolated, m.p. 49–50° (hexane), not depressing the melting point of authentic *N*-phenylurethane, mixed m.p. 49–50°.

Acknowledgment. The authors wish to thank V. Parrino for the preparation of the betaines, Dr. G. Ungar and his staff for the pharmacological screening of the compounds, and M. Blitz and D. Farkas for the ultraviolet absorption spectra.

YONKERS 1, N. Y.

[CONTRIBUTION FROM THE ROHM & HAAS CO.]

The Vinylation of Glycerol

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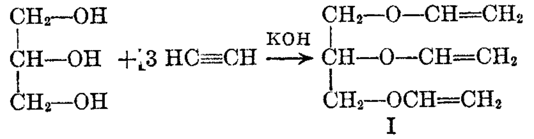
Received March 14, 1961

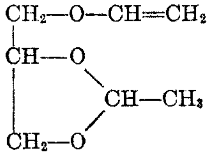
The base-catalyzed vinylation of glycerol in a batch process afforded predominantly 2-methyl-4-vinyloxymethyl-1,3-dioxolane (II) together with 5–12% of 1,2,3-trivinyloxypropane (I). When the reaction was stopped before completion, the precursor of II, 4-hydroxymethyl-2-methyl-1,3-dioxolane (III) was isolated in 30% yield. These results contradict earlier reports[1-3] concerning the course of the reaction. By means of a continuous condensed-phase coil reactor under pressures much above those generally employed in batch experiments, the conversion of glycerol to the trivinyl ether I was increased to 50%; the major by-product was the dioxolane II.

The trivinyl ether of glycerol, 1,2,3-trivinyloxypropane (I), was disclosed first by Favorskii and Shostakovskii in a general survey of the vinylation reaction.[1] Later publications by Shostakovskii and Gracheva[2,3] described the base-catalyzed vinylation of glycerol in greater detail. They reported that I was obtained in 90% yield by the treatment of glycerol with acetylene at 10–12 atmospheres initial pressure in the presence of powdered potassium hydroxide at 170–190°.

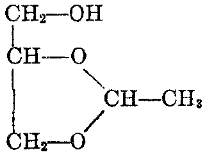


I

Our attempts to reproduce these results were consistently unsuccessful. It was observed that when glycerol was heated with acetylene under 13–35 atmospheres for seven to twenty-nine hours in the presence of a catalytic quantity of sodium glyceroxide or powdered potassium hydroxide, the major product, isolated in 33–66% yield, was 2-methyl-4-vinyloxymethyl-1,3-dioxolane (II). In addition, only small amounts (5–12%) of the trivinyl ether I were produced. The precursor of II, 4-hydroxymethyl-2-methyl-1,3-dioxolane (III), was



II



III

obtained in 30% yield by limiting the vinylation time to two hours.

The structure II was established by hydrogenation, followed by mild acid hydrolysis and periodate analysis for 1,2-glycol. Similarly, the structure III was confirmed by periodate analysis of the hydrolyzate of the methyl ether of III. The periodate analyses for vicinal hydroxyl functions eliminate the isomeric 1,3-dioxane structures as possible alternatives for II and III. The analytical and hydrogenation data left little doubt as to the structure of I. The infrared spectra of I, II, and III were entirely consistent with their assigned structures.

In contrast to these findings, it has been reported[2,3] that partial vinylation afforded, in addition of I, the 1-mono and 1,3-divinyl ethers of glycerol; cyclic acetals were not observed as primary reaction products. A comparison of the published data for I[1,2] with the physical constants summarized in Table I suggests that the product

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(1) A. E. Favorskii and M. F. Shostakovskii, *J. Gen. Chem. U.S.S.R.*, **13**, 1 (1943).

(2) M. F. Shostakovskii and E. P. Gracheva, *J. Gen. Chem. U.S.S.R.*, **19**, 1250 (1949).

(3) M. F. Shostakovskii and E. P. Gracheva, *Akad. Nauk. S.S.S.R. Inst. Org. Khim. Sintezy Org. Soedinenii Sbornik*, I, 144 (1950); *Chem. Abstr.*, **47**, 8002 (1953).

TABLE I

PHYSICAL PROPERTIES FOUND FOR VINYLATION PRODUCTS

Compound	B.P./Mm.	n_D(T.)	d_4^{25}
I	178/760	1.4543 (20°)	0.965
	98/30		
	71/7		
II	98/83	1.4339 (20°)	1.016
	83/42		
	55/8		
III[a,b]	76/9.5	1.4372 (25°)	1.112
	62.5/3.5		

[a] H. S. Hill, A. C. Hill, and H. Hibbert, *J. Am. Chem. Soc.*, **50**, 2242 (1928), found that III had a b.p. of 68–70° (1 mm.), n_D^{17} 1.4413, d_4^{17} 1.1243. Owing to the discrepancy in the boiling point, the dioxolane III was synthesized from paraldehyde and glycerol exactly as described by the above authors. The compound (b.p. 63.5° (3.6 mm.)) was identical with the product obtained from the vinylation reaction; the infrared spectra were superimposable. [b] I. G. Nieuwland, R. R. Vogt, and W. L. Foohey, *J. Am. Chem. Soc.*, **52**, 1018 (1930).

designated I by Shostakovskii and Gracheva was largely III.[4]

In a batch reactor under moderate pressure (10–30 atm.) the concentration of acetylene is generally much less than that of the reacting alcohol throughout most of the reaction. Accordingly, opportunity is afforded under these conditions for the slower concurrent intramolecular cyclization to occur. The importance of this side reaction would be decreased by an increase in acetylene concentration. This was accomplished by the use of a continuous condensed-phase coil reactor under pressures (100–135 atm.) much above those employed in the batch reactions. These experiments were conducted in the highly polar solvent, *N*-methylpyrrolidone, which, although sensitive to base on prolonged contact at the high reaction temperature, was not affected perceptibly during the short reaction times employed. By means of this technique, a 50% conversion of glycerol to the trivinyl ether I was achieved; the major by-product was the dioxolane II.

EXPERIMENTAL

Batch vinylations of glycerol. (a) To a solution of sodium *n*-butoxide in 1-butanol, prepared from 75 g. (3.3 g.-atoms) of sodium and 1500 g. (20.3 moles) of 1-butanol, was added 1457 g. (15.8 moles) of glycerol. Most of the 1-butanol was removed from the mixture by distillation under reduced pressure (51 g. remaining). The solution was heated at 140–160° in a 3-l. mechanically stirred autoclave for 11.6 hr., during which time acetylene (1017 g.; 39.1 moles) was introduced at a pressure of 27–35 atm. The raw product mixture afforded 1777 g. of a colorless distillate by flash distillation. The products, I and II, were separated by fractional distillation under reduced pressure and purified by redistillation.

The major product, 2-methyl-4-vinyloxymethyl-1,3-dioxolane (II), boiled at 98° (83 mm.) and 55° (8 mm.), n_D^{20} 1.4339, d_4^{25} 1.016, yield 1168 g. (51%); reported b.p. 56° (9 mm.).[5]

Anal. Calcd. for $C_7H_{12}O_3$: C, 58.31; H, 8.39; hydrolyzable aldehyde, 13.9 meq./g.; vinyl ether, 6.94 meq./g. Found: C, 58.51; H, 8.50; hydrolyzable aldehyde,[6] 13.5 meq./g.; vinyl ether,[7] 6.34 meq./g.

The infrared spectrum of II (liquid) showed absorption ascribable to vinyl ether (1635, 1615, 1197, and 1078 cm.$^{-1}$) and acetal (1145 and 1109 cm.$^{-1}$) functions.

A sample of II (5.27 g.; 0.0366 mole) in 10 ml. of ethanol absorbed 905 ml. (0.0368 mole) of hydrogen at 27° over a platinum oxide catalyst at atmospheric pressure. The catalyst was removed by filtration and the filtrate was quantitatively transferred with ethanol to a flask equipped with a thermometer, a condenser and a magnetic stirrer. To the solution was added 25 ml. of 5% aqueous hydrochloric acid. The mixture was heated at 60–70° with stirring for 2 hr., cooled and analyzed quantitatively for vicinal hydroxyl groups by the periodate method.[8] The solution (108 ml.) contained 0.307 meq./ml. or a total of 0.0331 equivalent (90%) of vicinal hydroxyl functions.

The trivinyl ether I had a b.p. of 71–72° (7 mm.), n_D^{20} 1.4543, d_4^{25} 0.965, yield 271.6 g. (10%). On contact with boron trifluoride-etherate it reacted violently to give a hard solid polymer.

Anal. Calcd. for $C_9H_{14}O_3$: C, 63.51; H, 8.29; hydrolyzable aldehyde, 17.6 meq./g. Found: C, 63.80; H, 7.99; hydrolyzable aldehyde, 17.2 meq./g.

The infrared spectrum of I (liquid) exhibited intense vinyl ether absorption (1630, 1610, 1197, and 1075 cm.$^{-1}$) and did not contain any hydroxyl bands.

A sample of I (1.62 g.; 0.0095 mole) absorbed 675 ml. (0.027 mole) of hydrogen at atmospheric pressure and 27° over a platinum oxide catalyst.

(b) A solution of 7.3 g. (0.13 mole) of powdered potassium hydroxide in 89.8 g. (0.98 mole) of glycerol was heated at 180–190° in a magnetically stirred autoclave for a period of 2 hr. while acetylene was introduced at a pressure of 13–20 atm. The products were isolated as described in the previous experiment and purified by distillation. In addition to II (31 g.; 22%) and a trace of I (< 2% detected by means of vapor phase chromatography), 4-hydroxymethyl-2-methyl 1,3-dioxolane (III) was obtained; b.p. 76° (9.5 mm.), n_D^{25} 1.4372 yield 34 g. (30%). III was a colorless liquid which did not polymerize in the presence of boron trifluoride etherate.

Anal. Calcd. for $C_5H_{10}O_3$: C, 50.83; H, 8.53; hydrolyzable aldehyde, 8.47 meq./g.; hydroxyl number, 474. Found: C, 51.32; H, 8.63; hydrolyzable aldehyde, 9.11 meq./g.; hydroxyl number, 452.

The infrared spectrum of III (liquid) exhibited significant absorption bands at 3470 and 1040 cm.$^{-1}$ (hydroxyl function), and at 1145 and 1110 cm.$^{-1}$ (acetal function). The absence of absorption in the range 1500–1700 cm.$^{-1}$ showed that the compound did not contain a vinyl ether group.

The colorless liquid benzoate of III, prepared from benzoyl chloride (8.4 g.) and III (6.7 g.) in anhydrous pyri-

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(4) The physical constants given for I in reference 2 are b.p. 164–165°/760 mm. and 58°/7 mm., n_D^{20} 1.4381, d_4^{20} 1.0335. The experimental section of ref. 2 also contains the following analytical data for I: "11.55 mg. substance: 8.88 mg. H_2O; 20.71 mg. CO_2; 11.52 mg. substance: 8.32 mg. H_2O; 18.85 mg. CO_2. Found %: C, 63.42, 63.12; H, 8.86, 8.60. $C_9H_{14}O_3$. Calculated %: C, 63.53; H, 8.23." A recalculation of these fortunately complete analytical data showed a serious error. Recalculated. Found: C, 48.93, 49.00; H, 8.60, 8.85. $C_5H_{10}O_3$ (III). Calcd.: C, 50.83; H, 8.53.

(5) J. W. Copenhaver and M. H. Bigelow, *Acetylene and Carbon Monoxide Chemistry*, Reinhold, New York, 1949, p. 87.

(6) S. Siggia, *Quantitative Organic Analysis via Functional Groups*, Wiley, New York, 1949, p. 63.

(7) S. Siggia, *Quantitative Organic Analysis via Functional Groups*, Wiley, New York, 1949, p. 106.

(8) S. Siggia, *Quantitative Organic Analysis via Functional Groups*, Wiley, New York, 1949, p. 8.

dine (18 ml.), boiled at 103° (0.2 mm.) and 130° (2.0 mm.), n_D^{25} 1.5095, d_4^{25} 1.170, yield 10.1 g. (80%); reported b.p. 144–145° (2 mm.), n_D^{17} 1.5145, d_4^{17} 1.618.[9] A strong absorption band ascribable to the carbonyl function appeared at 1710 cm.$^{-1}$ in the infrared spectrum of the ester (liquid); there was no hydroxyl absorption.

Anal. Calcd. for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35; mol. wt., 222.2. Found: C, 65.12; H, 6.23; mol. wt. (ebullioscopic in acetone), 225.

From the sodium salt of III and methyl iodide in *N*-methylpyrrolidone, the methyl ether of III was synthesized, b.p. 49–50° (18 mm.), n_D^{25} 1.4128; reported b.p. 56–58° (23 mm.), n_D^{17} 1.4177.[9] The infrared spectrum (liquid) of the colorless derivative was consistent with its assigned structure, exhibiting no significant absorption above 3000 cm.$^{-1}$ A portion of the ether (1.24 g.; 0.0094 mole) was hydrolyzed in dilute acid as previously described. Periodate analysis[8] of the hydrolyzate showed that the solution contained a total of 0.0092 equivalent (98%) of vicinal hydroxyl functions.

(c) When the vinylation of glycerol was conducted as described in part (b) for a period of 7 hr. at 137–150°, the dioxolane II and the trivinyl ether I were obtained in 65 and 5% yield, respectively.

Continuous vinylation of glycerol in a condensed-phase coil reactor.[10] Under a pressure of 20 atm., *N*-methylpyrrolidone was saturated with acetylene at 12.0°. The solution was pumped continuously at a rate of 9.0 ml./min. under a pressure of 100–135 atm. (sufficient to prevent the formation of a vapor phase) through a tubular reactor heated to 190°. A solution of potassium hydroxide (7.9 wt.%) in glycerol was injected into the hot acetylene solution at a rate (3.2 ml./min.) such that the molar ratio of acetylene to glycerol was greater than 3:1. After a reaction time of 9.2 min., the reaction mixture passed out of the reactor through a pressure relief valve. The excess acetylene was vented and the product solution was added to twice its volume of water. The organic layer was separated and the aqueous layer was washed several times with ether. The products were isolated by fractional distillation under reduced pressure. Under these conditions, glycerol was converted to the trivinyl ether I (50%) and the dioxolane II (30%).

Acknowledgment. The authors wish to express their sincere appreciation to Dr. Newman M. Bortnick and Dr. Clayton M. Huggett for many helpful suggestions and constructive criticisms during the course of this work.

PHILADELPHIA, PA.

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[9] The benzoate ester of III, prepared according to the procedure of Hill, Hill, and Hibbert (see Table I, footnate a), had a b.p. of 104° (0.24 mm.). It was shown to be identical with the derivative described above by a comparison of the infrared spectra and the other physical constants.

[10] J. J. Nedwick and C. M. Huggett, U. S. Pat. 2,969,400 (1961).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF MEERUT COLLEGE]

Behavior of Halogenated Nitrobenzenes with β-Diketones.
II. 6-Nitroanthranil from 2,4-Dinitrophenylacetone

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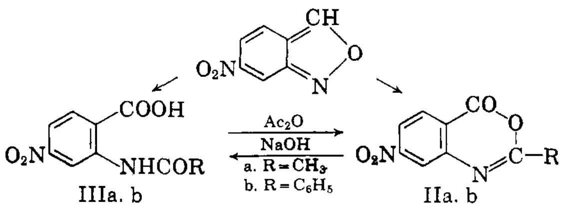
Received March 10, 1961

6-Nitroanthranil, formed by the action of concentrated sulfuric acid on 2,4-dinitrophenylacetone, has been further characterized. Like anthranil, it adds to mercuric chloride, can be acetylated and benzoylated, but unlike anthranil itself it forms indazole derivatives with aniline, phenylhydrazine, and hydrazine acetate. The acyl derivatives can be transformed into *o*-acylaminobenzamides and subsequently to quinazolone derivatives.

In a previous communication[1] it was stated that the compound formed by the action of concentrated sulfuric acid on 2,4-dinitrophenylacetone may be 6-nitroanthranil (I). It has been further observed that like anthranil[2] the compound I with alcoholic mercuric chloride forms a molecular compound from which it is recovered with hot water. When heated with acetic anhydride and zinc acetate, it gives an acetyl derivative which is found to be identical with 4-nitroacetanthranil (or 7-nitro-2-methylbenzoxazone) (IIa), a product obtained by treatment of 4-nitroacetylanthranilic acid (IIIa) with acetic anhydride.[3] On heating with benzoyl chloride and pyridine, it yields 4-nitrobenzoylanthranil (or 7-nitro-2-phenylbenzoxazone) (IIb) and 4-nitro-*N*-benzoylanthranilic acid (IIIb), which are also obtained by benzoylation of 2-amino-4-nitrobenzoic acid. These compounds IIb and IIIb are interconvertible by treatment with acetic anhydride and dilute caustic soda solution respectively.[4]



A simple mechanism for the formation of 4-nitrobenzoylanthranil (IIb) from 6-nitroanthranil (I) through 4-nitro-*N*-benzoylanthranilic acid (IIIb) as an intermediate, which is also isolated, is given as follows:

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[1] *J. Am. Chem. Soc.*, **78**, 2222 (1956).

[2] O. Buhlmann and A. Einhorn, *Ber.*, **34**, 3788 (1901).

[3] M. T. Bogert and S. H. Steiner, *J Am. Chem. Soc.*, **27**, 1330 (1905).

[4] P. Ruggli and W. Leonhardt, *Helv. Chim. Acta*, **7**, 808 (1926).