monia was evaporated. The residue was treated with 100 ml. of water and 110 ml. of concentrated hydrochloric acid, and most of the *t*-butyl alcohol was distilled. After cooling, the acid solution was made alkaline with sodium hydroxide solution, and the resulting mixture was extracted with ether. The ether extract was dried, and the solvent removed. The residue was distilled to give 28.9 g. (89%) of 1-dimethylamino-1-phenylpropane (IVb), b.p. 58–58.5° at 2.5 mm., n_D^{25} 1.5016. The picrate, m.p. and mixed m.p 167–168°, was recrystallized from ethanol.

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[CONTRIBUTION FROM THE ROHM & HAAS COMPANY]

Vinylation of Pentaerythritol

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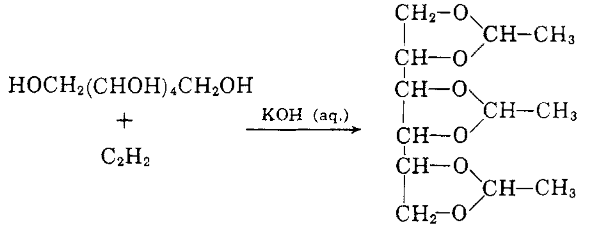
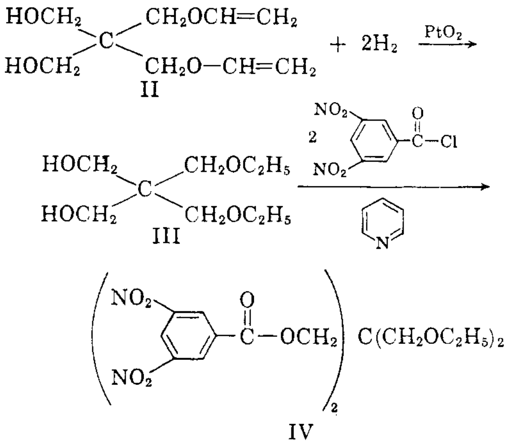
The catalytic vinylation of pentaerythritol in aqueous base afforded a mixture of products from which the pure divinyl ether II was isolated in 22% yield. The total mixture of compounds obtained from the aqueous vinylation was treated further with acetylene under non-aqueous basic conditions to give a mixture of the tetravinyl ether of pentaerythritol (V) (60–70%) and 5,5-di(vinyloxymethyl)-2-methyl-1,3-dioxane (VII) (30–40%). There appears to be a relationship between the acidity of an alcohol and its tendency to undergo vinylation in an aqueous solution. Simple monohydric aliphatic alcohols do not undergo base-catalyzed vinylation in water, whereas, polyhydroxy compounds capable of forming intramolecular hydrogen bonds react with acetylene in aqueous base to give products of vinylation.

It is well known that phenols[1,2] and mercaptans[3] undergo vinylation smoothly in aqueous base to give aryl vinyl ethers and vinyl sulfides, respectively; indeed, these reactions proceed even in the presence of weakly basic catalysts (sodium carbonate, potassium carbonate, amines, etc.). With one exception,[4] previously reported vinylations of aliphatic polyhydroxy compounds appear to have been conducted exclusively under non-aqueous conditions.[5] Shtishevskii and Obolonskaya[4] treated mannitol with acetylene in aqueous potassium hydroxide and obtained mannitol triacetal (I) along with a complex mixture of products which could not be separated.



I

The base-catalyzed vinylation of pentaerythritol has not heretofore been reported. Owing to the high melting point of pentaerythritol and its low solubility in most organic solvents, an aqueous medium was employed for the reaction. The treatment of an aqueous solution of pentaerythritol with acetylene under 10–30 atm. pressure in the presence of a catalytic quantity of potassium hydroxide at 145–175° afforded a distillable liquid mixture of products in 50–70% yield. From the mixture which contained hydroxyl, vinyl ether, and acetal functionality, only the divinyl ether II (yield 22%) was isolated. The structure of the colorless crystalline ether II was established by analytical and spectroscopic data, as well as by quantitative hydrogenation to the diethyl ether of pentaerythritol (III), from which the crystalline di-3,5-dinitrobenzoate ester (IV) was prepared.



IV

Acetylene was absorbed slowly by the basic aqueous solution of pentaerythritol even after 14 hours of reaction. A comparison of the data for two experiments (Table I, Exp. No. 3 and 4) conducted under identical conditions except for the time of reaction shows that although twice as

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(1) M. Ban, T. Tamamoto, and S. Otsuka, *Nippon Kagaku Zasshi*, **77**, 176 (1956); *Chem. Abstr.*, **52**, 300 (1958).

(2) M. F. Shostakovskii, A. V. Bogdanova, and G. K. Krasil'nikova, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 339 (1957); *Chem. Abstr.*, **51**, 14653 (1957).

(3) H. J. Schneider, U. S. Patent No. **2,910,480** (1959).

(4) V. V. Shtishevskii and N. A. Obolonskaya, *J. Gen. Chem.* (*U.S.S.R.*), **20**, 671 (1950); *Chem. Abstr.*, **44**, 7766 (1950).

(5) W. Reppe, *Ann.*, **601**, 100 (1956); B. I. Mikhant'ev and V. L. Lapenko, *J. Gen. Chem.* (*U.S.S.R.*), **27**, 2972, 2840 (1957), *Chem. Abstr.*, **52**, 8054, 8055 (1958); N. Shachat, H. J. Schneider, J. J. Nedwick, G. Murdoch, and J. J. Bagnell, *J. Org. Chem.*, *in press.*

much acetylene was absorbed in the longer run, each afforded about the same amount of product. The excess acetylene appeared in the residue, the composition of which was not investigated. It is reasonable to suspect that under the conditions of the reaction, acetylene is slowly converted to acetaldehyde which may undergo aldol-type polymerization. The highest product to residue ratio was observed in the experiment conducted for the shortest period of time (Table I, Exp. No. 1).

When the total liquid mixture of products obtained from the vinylation in aqueous solution was subjected to further reaction with acetylene in the presence of a catalytic amount of base in a nonaqueous medium, complete vinylation was effected smoothly. Three products, two in substantial quantities and one in trace amounts, which could not be separated by distillation, were obtained. The major product (60–70%), the tetravinyl ether of pentaerythritol (V), was partly separated from the mixture by crystallization; its structure was confirmed by analytical and infrared data and by quantitative hydrogenation to the known tetraethyl ether (VI). The other major component (30–40%) was shown to be 5,5-di(vinyloxymethyl)-2-methyl-1,3-dioxane (VII) by hydrogenation to 5,5-di(ethoxymethyl)-2-methyl-1,3-dioxane (VIII) followed by *in situ* hydrolysis to the known diethyl ether of pentaerythritol (III).[6] The trace constituent, ascribed the diacetal structure IX, afforded pentaerythritol on hydrolysis. The structure proof for the products of the complete vinylation of pentaerythritol was conveniently carried out on the total mixture as illustrated diagramatically in Fig. 1.

Although simple monohydric aliphatic alcohols do not condense with acetylene in aqueous base under conditions normally employed for vinylation, it has not been generally recognized that polyhydric alcohols capable of forming intramolecular hydrogen bonds do react under these conditions to yield products of vinylation.[7] The base-catalyzed vinylation of an alcohol is best explained by a mechanism involving a nucleophilic attack on acetylene (Eq. I and II).

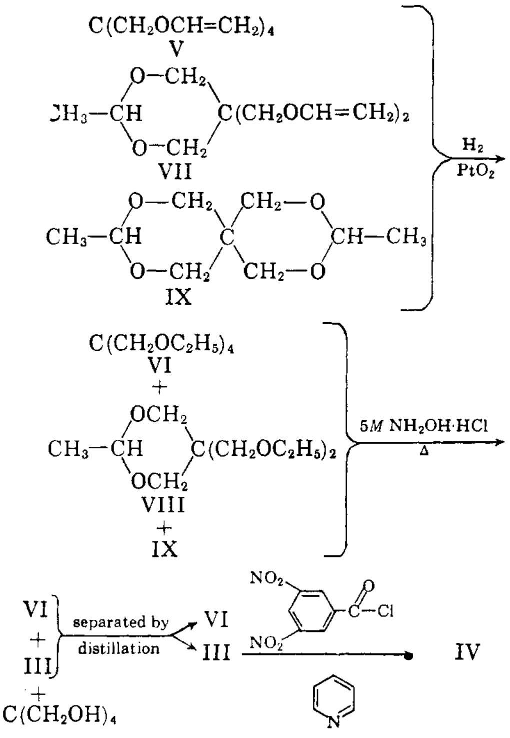


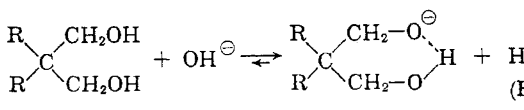
Figure 1

$$RO^{\ominus} + HC{\equiv}CH \xrightarrow{k} ROCH{=}CH^{\ominus} \xrightarrow{ROH} ROCH{=}CH_2 + RO^{\ominus} \quad \text{(Eq. I)}$$

$$\text{rate} = k[HC{\equiv}CH][RO^{\ominus}] \quad \text{(Eq. II)}$$

$$ROH + OH^{\ominus} \rightleftarrows RO^{\ominus} + H_2O \quad \text{(Eq. III)}$$

In an aqueous medium, the equilibrium concentration of the nucleophile $RO^{\ominus}$ (given by Eq. III) would be low for alcohols which are not considerably more acidic than water. This suggests an explanation for the observed failure of monohydric aliphatic alcohols to react with acetylene in aqueous base, whereas, the more acidic phenols and thiols undergo vinylation smoothly.[8] So too, the acidity of certain polyhydroxy compounds, promoted by intramolecular hydrogen bonding (Eq. IV), appears sufficient to allow base-catalyzed vinylation in aqueous solution to proceed at a significant rate.



(Eq. IV)

$$R_2C(CH_2OH)_2 + OH^{\ominus} \rightleftarrows R_2C(CH_2O^{\ominus}\cdots H\cdots OCH_2) + H_2O$$

EXPERIMENTAL[9]

Vinylation of pentaerythritol in aqueous base. A mixture of 880 ml. of water, 120 g. (1.8 moles) of 85% potassium hydrox-

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(6) It is interesting to note that the acetal functions were not readily hydrolyzed under mild conditions. Success was achieved ultimately by treatment with 5*M* hydroxylamine hydrochloride under reflux for about 7 hours. A. Skrabel and M. Zlatewa, *Z. Physik. Chem.*, 119, 305–18 (1926), found that the acetal of ethyl alcohol undergoes acid hydrolysis 10^4 times faster than the cyclic acetal of pentaerythritol. This effect is most likely a result of the steric hindrance generally associated with neopentyl systems.

(7) In addition to pentaerythritol, we have also effected the base-catalyzed vinylation of 1,1,1-trimethylolpropane, glycerol, neopentyl glycol, and sorbitol in water. The experimental details are not complete enough, however, to warrant inclusion in this paper. The failure of isopropyl alcohol and *n*-butyl alcohol to react with acetylene in aqueous base under the conditions normally employed for vinylation was also demonstrated experimentally.

(8) Because they do not bear directly on the argument, the factors relating to the nucleophilicity of the attacking anion have not been included in the discussion. One should not overlook, however, when comparing different compounds, that the rate of vinylation is also a function of the nucleophilicity of the anion which may be influenced by electronic, inductive, steric, and solvation effects.

(9) All melting points and boiling points are uncorrected.

ide, and 410 g. (3.0 moles) of pentaerythritol was placed in a 3-l., mechanically stirred reactor. The system was pressure tested with nitrogen, flushed with nitrogen, and then flushed with acetylene. The mixture was heated at 145–160° for 5 hr. while acetylene was introduced at a pressure of 300–470 p.s.i.g. During this period of time, 281 g. (10.8 moles) of acetylene was absorbed. The crude product mixture consisted of two layers. The upper organic layer was separated from the aqueous layer and the latter was washed several times with ether. The ether washes were combined with the organic layer and the ether was removed by distillation. The product mixture was crudely separated under reduced pressure into two distillates and a brown, glassy, partly water-soluble residue.

	Wt. (g.)	(B.P./mm.)	pot T.
Distillate 1	421	to 130/0.67	to 149
Distillate 2	122	to 114/0.44	to 159
Residue	201	—	—

The residue was not investigated further. Distillate 2, the divinyl ether of pentaerythritol (II), was a solid at room temperature which gave a yellow precipitate with 2,4-dinitrophenylhydrazine and underwent polymerization in the presence of boron trifluoride etherate. The compound boiled at 99.5–100.5° (0.16–0.28 mm.). Recrystallization from cyclohexane afforded silky, colorless needles, m.p. 63–64°. Its infrared spectrum (chloroform solution) exhibited intense hydroxyl (3520 and 1050 cm.$^{-1}$) and vinyl ether (1628, 1614, 1192, and 1082 cm.$^{-1}$) absorption. By vapor phase chromatography it was shown that Distillate 2 consisted almost entirely of II, yield 122 g. (22%).

Anal. Calcd. for $C_9H_{16}O_4$: C, 57.43; H, 8.57; hydrolyzable aldehyde, 10.6 meq./g.; vinyl ether, 10.6 meq./g.; hydroxyl number, 596. Found: C, 57.31; H, 8.50; hydrolyzable aldehyde,[10] 9.4 meq./g.; vinyl ether,[11] 10.3 meq./g.; hydroxyl number, 612.

A portion of Distillate 1 was carefully separated into twelve fractions (total wt. 245 g.) and a viscous, amber liquid residue (32 g.) by distillation under reduced pressure [boiling range, 65–95° (0.13–0.15 mm.); n_D^{25} 1.4454–1.4781]. The first eleven fractions (liquids) were shown to be mixtures of products by vapor phase chromatography. The infrared spectra of several of the fractions exhibited both hydroxyl and vinyl ether absorptions. The last cut (19 g.; solid) provided an additional quantity of the divinyl ether II, m.p. 63°. Further efforts to isolate pure compounds from the mixtures were unsuccessful.

The data obtained from several similar vinylation experiments are summarized in Table I.

Hydrogenation of the divinyl ether of pentaerythritol (II). A mixture of 2.4 g. (0.0128 mole) of the divinyl ether II, a few milligrams of platinum dioxide and 25 ml. of ethanol absorbed 700 ml. (0.0285 mole) of hydrogen smoothly at room temperature under atmospheric pressure. The catalyst was removed by filtration and the solvent, by distillation. The colorless liquid product, the diethyl ether of pentaerythritol (III), was treated with 3,5-dinitrobenzoyl chloride in the usual manner.[12] The di-3,5-dinitrobenzoate ester of III was a colorless crystalline solid, m.p. 123–125°.

Anal. Calcd. for $C_{23}H_{24}O_{14}N_4$ (IV): C, 47.59; H, 4.17; N, 9.65. Found: C, 47.59; H, 4.20; N, 9.53.

Vinylation of liquid distillate from aqueous vinylation. Potassium metal (1.6 g.; 0.041 g.-atom) was dissolved in 30 ml. of absolute ethanol. To the solution was added 88 g. of

TABLE I

VINYLATIONS OF PENTAERYTHRITOL IN AQUEOUS BASE

Exp. No.	Wt. of Starting Materials (g.)			C_2H_2 Absorbed (g.)	Time (hr.)	T. (°C.)	P (p.s.i.g.)	Wt. of Products (g.)[a]		Analyses of Distillate		
	$C(CH_2OH)_4$	KOH	H_2O					Distillate	Residue	Hydrolyzable aldehyde (meq./g.)	Vinyl ether (meq./g.)	Hydroxyl number
1	34.0	10.1	63.8	21.0	1.5	146–175	160–390	28.0	10.0	11.58[b]	—	336
2	34.4	10.0	63.9	36.0	3.8	145–178	205–440	32.4	19.0	12.36[c]	—	—
3	410	120	898	213	5.0	150–158	248–430	402	214	10.11[d]	9.75	391
4	410	120	872	437	14.2	150–158	260–445	413	395	12.22[d]	10.67	279

[a] The total organic product, removed from the reaction mixture by extraction with ether, was stripped of the extraction solvent and separated into a liquid distillate and a solid residue by flash distillation to minimum pot temperature of 140° at <0.5 mm. [b] The analyses for this experiment are for a heart cut obtained by fractionation of the total product distillate. The material boiled at 73° (0.08 mm.); n_D^{25} 1.4739; *Anal.* Found: C, 60.09; H, 8.64. [c] The total product distillate was fractionated. The analysis was obtained from an early fraction, b.p. 63° (0.25 mm.); n_D^{25} 1.4631. [d] These analyses were performed on the total product distillate.

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(10) S. Siggia, *Quantitative Organic Analysis via Functional Groups*, John Wiley and Sons, Inc., New York, 1949, p. 63.

(11) S. Siggia, *Quantitative Organic Analysis via Functional Groups*, John Wiley and Sons, Inc., New York, 1949, p. 106.

(12) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, *The Systematic Identification of Organic Compounds*, Fourth ed., John Wiley & Sons, Inc., New York, 1956, p. 212.

the total liquid distillate which was obtained from the vinylation of pentaerythritol in aqueous base. The mixture was heated at 137–166° for a period of 4 hr. in a magnetically stirred reactor while acetylene gas (34 g.; 1.31 moles) was pressed into the solution at a pressure of 250–470 p.s.i.g. Distillation afforded in addition to 24 g. of ethyl vinyl ether, 85 g. of a liquid product mixture and 25 g. of a brown solid residue. The liquid product mixture was separated into eleven liquid fractions (total wt. 82 g.) by distillation under reduced pressure; boiling range, 90°/0.75 mm. to 68°/0.09 mm.; n_D^{25}, 1.4659–1.4881. Examination of the fractions by vapor phase chromatography showed that each consisted of a mixture of three components, two in major amounts and one in trace quantities. To be certain that vinylation was complete, the fractions were combined, dissolved in 1,2-dimethoxyethane, treated with a catalytic amount of sodium methoxide and heated in the presence of acetylene for 20 hr. as described above. Again, the three compounds which could not be separated by distillation were obtained. On cooling, the tetravinyl ether of pentaerythritol (V) was precipitated from the mixture. The compound was removed by filtration and recrystallized from ethanol, m.p. 47–49°. It was demonstrated to be the major product in the mixture (estimated to be present to the extent of about 60–70%) by a vapor phase chromatographic comparison. Further precipitation of V could be induced by seeding and by the addition of ethanol to the product mixture; however, complete separation could not be effected in this manner. The infrared spectrum of V (melt) exhibited intense absorption at 1634, 1615, 1197, and 1082 cm.$^{-1}$ (vinyl ether) and did not contain absorption bands ascribable to hydroxyl or acetal functions.

Anal. Calcd. for $C_{13}H_{20}O_4$: C, 64.98; H, 8.39; mol. wt., 240.3; hydrolyzable aldehyde, 16.6 meq./g. Found: C, 64.72; H, 8.28; mol. wt. (ebullioscopic in acetone), 251; hydrolyzable aldehyde, 16.5 meq./g.

The tetravinyl ether V absorbed 4 moles of hydrogen quantitatively over platinum oxide at room temperature under atmospheric pressure. It absorbed bromine readily and polymerized vigorously in the presence of boron trifluoride etherate to give a solid, highly cross-linked polymer.

Hydrogenation of the products of the complete vinylation of pentaerythritol. A mixture of the products of the complete vinylation of pentaerythritol was examined by infrared spectroscopy and vapor phase chromatography. The infrared spectrum (liquid) did not exhibit hydroxyl absorption; the vapor phase chromatogram showed three components, one corresponding to about 60–70% of the mixture (previously shown to be the tetravinyl ether of pentaerythritol), one corresponding to approximately 30–40% of the mixture, and one in trace amounts.

Anal. Found: hydrolyzable aldehyde, 13.4 meq./g.; vinyl ether, 12.8 meq./g.; hydroxyl number, 25.

A portion of the mixture (52.1 g.) absorbed 0.67 mole of hydrogen over platinum oxide (0.5 g.) at room temperature under 4–30 p.s.i.g. pressure.

Hydrolysis of the saturated product mixture. The hydrogenation catalyst was removed by filtration and the filtrate was heated under gentle reflux with 200 ml. of 5.0*M* hydroxylamine hydrochloride solution for 7.25 hr. The layers were separated and the aqueous layer was washed with several portions of ether. The ether washes were combined with the organic layer and the solution was dried over anhydrous sodium sulfate. The ether was removed by distillation at atmospheric pressure, and the product mixture, which showed two VPC peaks with an approximate area ratio 7:3, was separated by distillation under reduced pressure. The tetraethyl ether of pentaerythritol (VI) boiled at 63–65° (0.3 mm.), n_D^{25} 1.4196, yield 27.3; reported b.p. 83° (5 mm.).[13]

Anal. Calcd. for $C_{13}H_{28}O_4$: C, 62.90; H, 11.30. Found: C, 63.11; H, 11.19.

The diethyl ether of pentaerythritol (III) had a b.p. of 92–94° (0.25 mm.), n_D^{25} 1.4465, yield 11.8 g.; reported b.p. 115° (5 mm.).[13] The infrared spectrum (liquid) exhibited both strong hydroxyl (3400 and 1050 cm.$^{-1}$) and ether (1090–1130 cm.$^{-1}$) absorption.

Anal. Calcd. for $C_9H_{20}O_4$: C, 56.22; H, 10.49. Found: C, 56.57; H, 10.26.

The di-3,5-dinitrobenzoate ester of III was synthesized, m.p. 123–125°. A mixture melting point with the di-3,5-dinitrobenzoate ester previously prepared from the hydrogenation product of II was undepressed. The infrared spectra of the two derivatives were superimposable.

Several experiments were necessary to establish conditions under which complete hydrolysis of the vinyl ether and acetal functions would occur. During one experiment in which only partial hydrolysis was effected by means of 5% hydrochloric acid, a small amount of pentaerythritol, m.p. *ca.* 260°, was isolated from the concentrated aqueous phase.

PHILADELPHIA 37, PA.

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[13] E. Berlow, R. H. Barth, and J. E. Snow, *The Pentaerythritols*, Reinhold Publishing Corp., New York, 1949, pp. 121–122.

[CONTRIBUTION FROM THE RESEARCH CENTER, UNITED STATES RUBBER COMPANY]

Catalysis of Isocyanate Reactions. II. Pyridine *N*-Oxide Catalysis

J. BURKUS

Received June 12, 1961

Pyridine *N*-oxide is an effective catalyst for the reaction of phenyl isocyanate with butanol-1. The rate is directly proportional to the pyridine *N*-oxide concentration. Pyridine *N*-oxide does not catalyze the phenyl isocyanate–phenol reaction appreciably. Pyridine *N*-oxide in combination with an alkylene oxide causes the trimerization of phenyl isocyanate.

The triethylamine catalysis of the reaction of phenyl isocyanate with alcohols,[1a–] phenol,[1b] and mercaptans[2a,b] has been published. This paper reports some observations concerning the catalysis of isocyanate reactions with pyridine *N*-oxide.

EXPERIMENTAL

Conventional published procedures were used in the preparation of reactants and solvents. The kinetic method has been described previously.[3]

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(1)(a) J. W. Baker and J. B. Holdsworth, *J. Chem. Soc.*, 713 (1947). (b) J. W. Baker and J. Gaunt, *J. Chem. Soc.*, 9 (1949). (c) J. Burkus, *J. Org. Chem.*, **26**, 779 (1961).

(2)(a) E. Dyer and J. F. Glenn, *J. Am. Chem. Soc.*, **79**, 366 (1957). (b) J. F. Smith and E. C. Friedrich, *J. Am. Chem. Soc.*, **81**, 161 (1959).

(3) J. Burkus and C. F. Eckert, *J. Am. Chem. Soc.*, **80**, 5948 (1958).