was initiated on II. Thereafter, the butene-2 derivative IV was decomposed in ethylene dichloride and trichloroethane, 1 g. of IV in 39 g. of solvent with added ferric chloride catalyst (see Table I).

5. (*trans*[15]?)-1,4-Diisocyanatobutene-2

A solution of 10.0 g. (0.031 mole) of IV, 30 mg. of ferric chloride (hexahydrate), and 90 g. of ethylene dichloride was refluxed (83°), while passing a gentle stream of nitrogen to entrain volatiles, for 25 hr., then cooled, filtered, and concentrated to a brownish oil. The oil was distilled *in vacuo*, b.p. 106–111° (13–19 mm.), affording 2.8 g. (65%) of a clear oil, $n^{23}\text{D}$ 1.4728, m.p. −2 to 0°; $\lambda_{\max}^{\text{CHCl}_3}$ 2.75, 3.24, 4.45, 6.92, 7.10, 7.45, 10.3, 11.6 μ. The bismethylurethane (glistening flakes from methanol) had m.p. 143–144° (reported[8] m.p. 137°). The isocyanate turned brown on standing several days.

6. 1,3-Bis-*t*-butyl-2-imidazolidinone (VII)

When 17.2 g. (0.1 mole) of N,N′-bis-*t*-butylethylenediamine was added to 0.2 mole of a phosgene (20 g.)–triethylamine (20.2 g.) complex in cold benzene, followed by stirring and gentle warming, the reddish brown mixture gave a 67% yield of triethylamine hydrochloride and a filtrate which, on evaporation, gave a semicrystalline oil, 22.2 g. Crystallization (hexane) or distillation afforded solid, soft needles, m.p. 73–74°, b.p. 127° (16.5 mm.), b.p. 245° (760 mm.); $\lambda_{\max}^{\text{CHCl}_3}$ 5.98, also 6.75, 6.85, 7.13, 7.35, and 7.8–8.3 μ.

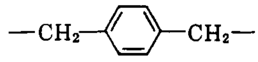
Anal. Calcd. for $C_{11}H_{22}N_2O$: C, 66.60; H, 11.18; N, 14.13. Found: C, 66.73; H, 11.14; N, 14.27.

The distillation yielded a considerable forecut, b.p. 80° (16 mm.), b.p. 180–185° (760 mm.), identified additionally as diethylcarbamoyl chloride [reported[4i] b.p. 81–85° (20 mm.)] by isolation of diethylamine (spectrum identical with authentic material) by mild alkaline hydrolysis.

7. Properties of the Intermediate Amines (See Table II)

TABLE II

t-BUTYLAMINES $R—NH—C(CH_3)_3$

Compound (R–)	M.p., °C.	B.p., °C (mm.)	Ref. index
$CH_2{=}CH—CH_2—$	...	112 (760 mm.)	$n^{22.5}\text{D}$ 1.4160
$CH_3CH_2CH_2CH_2—$	...	83 (140 mm.)	$n^{22.7}\text{D}$ 1.4086
		91 (177 mm.)	
	68–70	...	...
$—CH_2CH_2—$[b]	(42)[a]	99 (32 mm.)[c]	...
$—CH_2CH{=}CH—CH_2—$	(40–50)[a]	95–100 (6 mm.)	$n^{22}\text{D}$ 1.4494

[a] Hydrates. [b] Base equivalent, 85.8 (theory 86.15). [c] Lit. b.p. 198° (760 mm.).[4f]

Acknowledgment.—The authors wish to express their gratitude to Mr. F. Geremia and Mr. E. Foster for valuable assistance in infrared and analytical determinations.

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[15] The starting 1,4-dichlorobutene-2 (Eastman) was labeled *trans*.

Direct Syntheses of Some Cyano and Nitro Derivatives of Carbohydrates by Nucleophilic Displacement[1]

JAMES M. SUGIHARA, WILFORD J. TEERLINK, RODERICK MACLEOD,[2] SAMUEL M. DORRENCE, AND CHARLES H. SPRINGER[2]

Department of Chemistry, University of Utah, Salt Lake City, Utah

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Methyl 2,3,4-tri-*O*-acetyl-6-deoxy-6-iodo-α-D-glucopyranoside (I) and 2,3,4,5-di-*O*-benzylidene-1,6-dideoxy-1,6-diiodo-D-mannitol (II) reacted with sodium cyanide and with sodium nitrite in *N*,*N*-dimethylformamide to give the cyano and nitro derivatives expected following nucleophilic displacement of iodide. 6-Deoxy-6-iodo-1,2:3,4-di-*O*-isopropylidene-D-galactopyranose (III) was appreciably less reactive toward sodium cyanide. *O*-Benzylidenepentaerythritol dibenzenesulfonate (IX) reacted with sodium nitrite in *N*,*N*-dimethylformamide at the reflux temperature to form *O*-benzylidenepentaerythritol benzenesulfonate (XII).

In previous investigations,[3] 1,2-*O*-isopropylidene-D-glucofuranose 6-*p*-toluenesulfonate and 1,3-*O*-benzylidene-L-arabinitol 5-*p*-toluenesulfonate reacted with potassium cyanide to afford the corresponding cyano derivatives. In these reactions, the carbon undergoing displacement is removed from the rings by an intervening carbon bearing a hydroxyl group, which was proposed[3] to form an intermediate epoxide that then added hydrogen cyanide to give product. Success realized in effecting nucleophilic displacement reactions of neopentyl-type sulfonate esters with cyanide ion[4] prompted an investigation in which carbohydrate derivatives with functional groups without hydroxyls on the adjacent carbon were subjected to similar reaction conditions with the objective of achieving direct displacement, which was previously reported[3] to have failed. Iodides were selected over sulfonate esters since the former tend to be more reactive[5] than the latter in reactions with SN2-type character and moreover are readily preparable from the latter.[6] Methyl 2,3,4-tri-*O*-acetyl-6-deoxy-6-iodo-α-D-glucopyranoside (I),[7] 2,3,4,5-di-*O*-benzylidene-1,6-dideoxy-1,6-diiodo-D-mannitol (II),[8] and 6-deoxy-6-iodo-1,2:3,4-di-*O*-isopropylidene-D-galactopyranose (III)[9] were selected as substrates for displacement reactions with sodium cyanide in *N*,*N*-dimethylformamide (DMF). Both I and II reacted readily to give the expected products of displacement, methyl 2,3,4-tri-*O*-acetyl-6-deoxy-α-D-*gluco*-heptopyranurononitrile (IV) and 3,4,5,6-di-*O*-benzylidene-2,7-dideoxy-D-*manno*-octaronitrile (V), respectively, in yields of 54 and 51%.

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[1] Abstracted from portions of the Ph.D. theses of W. J. T. and S. M. D.

[2] Members of the "Research Participation for Teacher Training" Program at the University of Utah, 1962, sponsored by the National Science Foundation.

[3] R. Grewe and G. Rockstroh, *Chem. Ber.*, **86**, 536 (1953); R. Grewe and H. Pachaly, *ibid.*, **87**, 46 (1953).

[4] J. M. Sugihara, D. L. Schmidt, V. D. Calbi, and S. M. Dorrence, *J. Org. Chem.*, **28**, 1406 (1963).

[5] C. A. Bishop and C. H. DePuy, *Chem. Ind.* (London), 297 (1959).

[6] R. S. Tipson, *Advan. Carbohydrate Chem.*, **8**, 180 (1953).

[7] B. Helferich and E. Himmen, *Ber.*, **61**, 1825 (1928).

[8] R. T. Haskins, R. M. Hann, and C. S. Hudson, *J. Am. Chem. Soc.*, **65**, 1419 (1943).

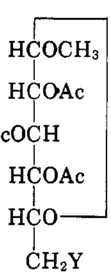
[9] K. Freudenberg and K. Raschig, *Ber.*, **60**, 1633 (1927).

III was appreciably less reactive and gave 6-deoxy-1,2:3,4-di-*O*-isopropylidene-D-*galacto*-heptopyranurononitrile (VI) in 28% yield. Each of the products obtained exhibited absorption peaks in the infrared spectra at 4.43 μ, characteristic of aliphatic nitriles, and reacted with moist alcoholic base to release ammonia.

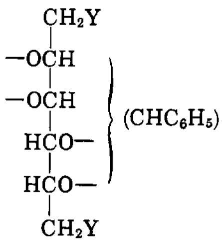
The marked difference in reactivity of III as compared to I may be rationalized by considering field effects influencing the approach of the nucleophilic reagent.[10] Placing the iodine atom away from neighboring oxygens, the backside of the primary carbon atom undergoing displacement is relatively accessible to cyanide ion in I. In III the axial oxygen at C-4 might be expected to impede the approach of the charged nucleophilic reagent. Rationalization of reactivity of II does not appear to be possible since the location of the benzylidene groups in this compound has not been established.

This direct method of increasing the length of the carbon skeleton presents the possibility of synthesis of a wide variety of novel or previously synthesized carbohydrate derivatives with deoxy carbons at the α-, α'-, or α,α'-positions. In all probability the nitriles obtained may undergo the same types of reactions described for the cyanohydrins derived in the classical Kiliani-Fischer method.[11] Another synthetic possibility afforded with these compounds is condensation reactions of β-carbons *via* both intramolecular and intermolecular processes.

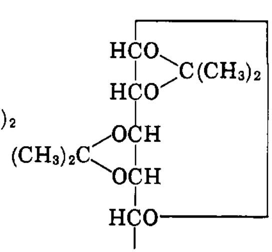
The nucleophilic displacement reactions have been extended to those using nitrite ion as the nucleophilic reagent. Kornblum and co-workers[12] have demonstrated that alkyl halides react with sodium nitrite in dimethylformamide to give good yields of nitro compounds. There are complications attending this reaction since any nitrite esters formed competitively may react with aliphatic nitro compounds.[13] The presence of phloroglucinol in the reaction mixture was very effective in scavenging nitrite esters and allowed synthesis of α-nitro esters in high yields.[14] Another side reaction is the interaction of alkyl halides with dimethylformamide to give products of dehydrohalogenation and salts.[15] Compounds I and II reacted smoothly with sodium nitrite in the presence of phloroglucinol in a dimethylformamide solution at low temperatures (30–40°) to form the corresponding nitro compounds, methyl 2,3,4-tri-*O*-acetyl-6-deoxy-6-nitro-α-D-glucopyranoside (VII) and 2,3,4,5-di-*O*-benzylidene-1,6-dideoxy-1,6-dinitro-D-mannitol (VIII), in yields of 64 and 44%. Infrared spectra of each compound showed absorbance at 6.43 and 7.29–7.33 μ, indicative of aliphatic nitro compounds, and no peaks suggestive of nitrite esters. Moreover, the presence of the nitrite ester scavenger, phloroglucinol,[14] precludes these products. This method of synthesis constitutes an independent path to primary nitro derivatives available by the well established nitromethane method.[16] Displacement with nitrite ion is likely to be influenced by field effects in the same manner as found with cyanide ion.



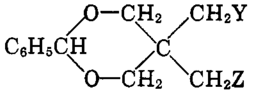
I, $Y = I$
IV, $Y = CN$
VII, $Y = NO_2$



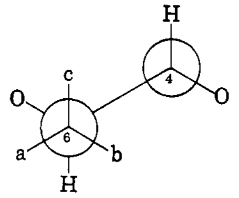
II, $Y = I$
V, $Y = CN$
VIII, $Y = NO_2$



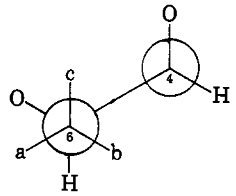
III, $Y = I$
VI, $Y = CN$



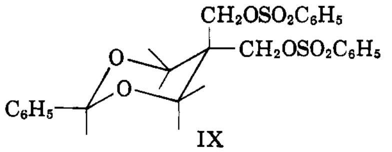
IX, $Y = Z = OSO_2C_6H_5$
X, $Y = OSO_2C_6H_5, Z = I$
XI, $Y = Z = I$
XII, $Y = OSO_2C_6H_5, Z = OH$



I, I at a, b, or c



III, I at a or b



IX

1,2,3,4 - Tetra - *O* - acetyl - 6 - deoxy - 6 - iodo - β-D-glucopyranose,[17] mixed with sodium cyanide or sodium nitrite in a dimethylformamide solution, gave water-soluble products with a portion of the starting material as the sole isolable compound when reaction was effected at low temperature. Apparently, reaction occurred at the anomeric carbon, suggesting that all substrates with acyloxy functions at C-1 may be unsatisfactory for these displacement reactions.

When the foregoing reaction conditions for displacement by nitrite ion were applied to derivatives of *O*-benzylidenepentaerythritol, the dibenzenesulfonate (IX), the benzenesulfonate iodide (X), and the diiodide (XI), considerable starting material was recovered as the only isolable product except in one instance in which a small amount of *O*-benzylidenepentaerythritol benzenesulfonate (XII) was obtained. On the other hand, the reaction of *O*-benzylidenepentaerythritol dibenzenesulfonate with sodium nitrite in boiling dimethylformamide for brief periods with or without phloroglucinol gave 42% of XII, resulting from the over-all substitution of one benzenesulfonyloxy with a hydroxyl group. The nature of the compound was established by converting it into the known[4] dibenzenesulfonate (IX) by reaction with benzenesulfonyl chloride. The

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[10] M. L. Wolfrom, J. Bernsmann, and D. Horton, *J. Org. Chem.*, **27**, 4505 (1962).

[11] C. S. Hudson, *Advan. Carbohydrate Chem.*, **1**, 1 (1945).

[12] N. Kornblum, H. O. Larson, R. K. Blackwood, D. D. Mooberry E. P. Oliveto, and G. E. Graham, *J. Am. Chem. Soc.*, **78**, 1497 (1956).

[13] N. Kornblum, R. K. Blackwood, and D. D. Mooberry, *ibid.*, **78**, 1501 (1956); N. Kornblum and J. H. Eicher, *ibid.*, **78**, 1494 (1956).

[14] N. Kornblum, R. K. Blackwood, and J. W. Powers, *ibid.*, **79**, 2507 (1957).

[15] N. Kornblum and R. K. Blackwood, *ibid.*, **78**, 4037 (1956).

[16] J. C. Sowden, *Advan. Carbohydrate Chem.*, **6**, 291 (1951).

[17] B. Helferich, H. Dressler, and R. Griebel, *J. prakt. Chem.*, **153**, 285 (1939).

infrared spectrum indicated the absence of intramolecular hydrogen bonding[18]; thus a *trans* relationship of hydroxyl to phenyl appeared likely since the *cis* isomer should allow the hydroxyl group to hydrogen bond to the ring oxygens. The reaction of *O*-benzylidenepentaerythritol with limited amounts of benzenesulfonyl chloride gave IX, XII, and a third substance, intermediate in mobility on an alumina column between IX and XII. This material has not been obtained in a homogeneous form but in all probability is the isomer of XII.

The relative inertness of the *O*-benzylidenepentaerythritol derivatives is undoubtedly a consequence of steric factors. Since the nitrite ion appears to have greater steric requirement in the formation of a C–N bond than in the formation of a C–O bond,[19] the predominant reaction may lead to nitrite ester, which is then hydrolytically cleaved or which reacts with phloroglucinol when introduced. As an alternative explanation, some type of salt may be formed initially[19]; it is then hydrolytically cleaved.

Experimental[20]

Methyl 2,3,4-Tri-*O*-acetyl-6-deoxy-α-D-*gluco*-heptopyranurononitrile (IV).—A mixture of 10.0 g. of methyl 2,3,4-tri-*O*-acetyl-6-deoxy-6-iodo-α-D-glucopyranoside (I),[21] 4.0 g. of sodium cyanide, and 100 ml. of redistilled *N*,*N*-dimethylformamide was stirred mechanically for 4 hr. at 45°. The resulting red-brown reaction mixture was poured into 500 ml. of ice and water and allowed to stand overnight in a refrigerator. The following day the light brown solid which had precipitated was filtered, washed with water, and dried to yield 3.93 g. (51%) of crude methyl 2,3,4-tri-*O*-acetyl-6-deoxy-α-D-*gluco*-heptopyranurononitrile, m.p. 134–136°. Recrystallization first from ten parts methanol and then from chloroform–ligroin (b.p. 60–90°) gave fine white needles, m.p. 135–135.5°, $[\alpha]^{23}_{\mathrm{D}}$ +139° (*c* 1.88, chloroform).

Anal. Calcd. for $C_{14}H_{19}NO_8$: C, 51.06; H, 5.82; N, 4.25. Found: C, 50.66; H, 5.67; N, 4.25.

3,4,5,6-Di-*O*-benzylidene-2,7-dideoxy-D-*manno*-octaronitrile (V).—A mixture of 10.0 g. of 2,3,4,5-di-*O*-benzylidene-1,6-dideoxy-1,6-diiodo-D-mannitol (II),[22] 10.0 g. of sodium cyanide, and 150 ml. of redistilled *N*,*N*-dimethylformamide was stirred mechanically for 4 hr. at 50–55°. The resulting amber-colored reaction mixture was processed in the same manner as described for IV. The solid obtained was extracted with 40 ml. of boiling acetone and the extract concentrated to half its original volume. Upon adding 20 ml. of hot ethanol to the extract and cooling, 3.5 g. (54%) of fine white needles crystallized, m.p. 196–201° dec. After two recrystallizations from chloroform–ligroin (b.p. 60–90°), 3,4,5,6-di-*O*-benzylidene-2,7-dideoxy-D-*manno*-octaronitrile, m.p. 204–206° dec., $[\alpha]^{23}_{\mathrm{D}}$ +82.0° (*c* 0.45, chloroform), was obtained.

Anal. Calcd. for $C_{22}H_{20}N_2O_4$: C, 70.20; H, 5.36; N, 7.44. Found: C, 69.81; H, 5.28; N, 7.39.

6-Deoxy-1,2:3,4-di-*O*-isopropylidene-D-*galacto*-heptopyranurononitrile (VI).—A mixture of 8.00 g. of 6-deoxy-6-iodo-1,2:3,4-di-*O*-isopropylidene-D-galactopyranose (III),[23] 3.2 g. of sodium cyanide, and 80 ml. of redistilled *N*,*N*-dimethylformamide was stirred mechanically for 4 hr. at 105°. The resulting dark brown reaction mixture was poured with stirring into 500 ml. of ice and water. After standing 2 hr., the aqueous solution was extracted with six 100-ml. portions of chloroform and the combined chloroform extracts were washed with six 100-ml. portions of water, dried over anhydrous sodium sulfate, and evaporated first under reduced pressure (aspirator) on a steam bath and then at 2 mm. The resulting sirup was dissolved in 15 ml. of absolute ethanol and cooled to −15°. Crystallization occurred after several hr. to yield 0.81 g. of impure III, m.p. 57–60°. Resulting filtrate was evaporated to a thick sirup, dissolved in 7 ml. of absolute ethanol and 7 ml. of ligroin (b.p. 40–48°), and the resulting solution cooled to −15°. Crystallization occurred slowly following seeding to yield 1.65 g. (28%) of 6-deoxy-1,2:3,4-di-*O*-isopropylidene-D-*galacto*-heptopyranurononitrile, m.p. 61–63°. Seed crystals were first obtained by allowing an ethanol solution of the sirup to stand on the shelf for a period of 6 months, during which time solvent slowly evaporated. Several recrystallizations from absolute ethanol–ligroin (b.p. 40–48°) (1:2, by volume) gave rods, m.p. 65.5–66.5°, $[\alpha]^{23}_{\mathrm{D}}$ −67.7° (*c* 0.83, chloroform).

Anal. Calcd. for $C_{13}H_{19}O_5N$: C, 57.98; H, 7.11; N, 5.20. Found: C, 58.10; H, 7.02; N, 5.38.

The infrared spectra of potassium bromide disks of IV, V, and VI showed peaks at 4.43 μ characteristic of the carbon–nitrogen stretching frequency of aliphatic nitriles. The three compounds liberated ammonia when refluxed in moist alcoholic sodium hydroxide.

Methyl 2,3,4-Tri-*O*-acetyl-6-deoxy-6-nitro-α-D-glucopyranoside (VII).—A mixture of 5.00 g. (0.0116 mole) of methyl 2,3,4-tri-*O*-acetyl-6-deoxy-6-iodo-α-D-glucopyranoside (I),[21] 1.50 g. (0.0218 mole) of sodium nitrite, 3.00 g. (0.0185 mole) of phloroglucinol dihydrate, and 150 ml. of redistilled *N*,*N*-dimethylformamide was maintained at 30–40° for 18 hr. The reaction solution was poured into 700 ml. of ice and water to precipitate a white solid, which was filtered. After a single recrystallization from ethanol, 2.61 g. (64.4%) of methyl 2,3,4-tri-*O*-acetyl-6-deoxy-6-nitro-α-D-glucopyranoside, m.p. 175–177°, was obtained. An analytical sample, m.p. 181–182°, $[\alpha]^{25}_{\mathrm{D}}$ +143° (*c* 1.82, chloroform), was prepared by recrystallization once from benzene–ligroin (b.p. 90–120°) and twice more from ethanol.

Anal. Calcd. for $C_{13}H_{19}NO_{10}$: C, 44.70; H, 5.48. Found: C, 44.79; H, 5.44.

2,3,4,5-Di-*O*-benzylidene-1,6-dideoxy-1,6-dinitro-D-mannitol (VIII).—*A mixture of 5.78* g. (0.010 mole) of 2,3,4,5-di-*O*-benzylidene-1,6-dideoxy-1,6-diiodo-D-mannitol (II),[22] 2.8 g. (0.041 mole) of sodium nitrite, 5.5 g. (0.034 mole) of phloroglucinol dihydrate, and 150 ml. of redistilled *N*,*N*-dimethylformamide was maintained at 35–40° for 16 hr. The resulting reaction mixture was poured into 800 ml. of ice and water, and the resulting suspension was allowed to stand at 0° for 18 hr. The solid was filtered and recrystallized three times from ethanol, three times from chloroform–ligroin (90–120°), and once from toluene–ligroin to provide 1.82 g. (44%) of 2,3,4,5-di-*O*-benzylidene-1,6-dideoxy-1,6-dinitro-D-mannitol, m.p. 162.5–164°. An analytical sample, m.p. 164.4–164.8°, $[\alpha]^{25}_{\mathrm{D}}$ +41.7° (*c* 0.64, chloroform), was prepared by two additional recrystallizations from chloroform–ligroin.

Anal. Calcd. for $C_{20}H_{20}N_2O_8$: C, 57.69; H, 4.84; N, 6.73. Found: C, 57.58; H, 4.95; N, 6.74.

The infrared spectra of chloroform solutions of VII and VIII showed peaks at 6.43 and 7.33 μ and 6.43 and 7.29 μ, respectively.

Reactions of 1,2,3,4-Tetra-*O*-acetyl-6-deoxy-6-iodo-β-D-glucopyranose with Sodium Cyanide and Sodium Nitrite.—1,2,3,4-Tetra-*O*-acetyl-6-deoxy-6-iodo-β-D-glucopyranose[24] was mixed with sodium cyanide in *N*,*N*-dimethylformamide at room temperature and at 0°. Considerable heat evolution was observed with immediate coloration of the mixture. Pouring the reaction mixture into ice and water after varying periods of time produced water-soluble materials only. A mixture of 1,2,3,4-tetra-*O*-acetyl-6-deoxy-6-iodo-β-D-glucopyranose and sodium nitrite in *N*,*N*-dimethylformamide darkened considerably after 24 hr. at room temperature. Approximately 40% of the organic substrate was recovered after pouring the reaction mixture into ice and water, collecting the insoluble portion, extracting the aqueous phase with chloroform, and combining the crystalline material.

***O*-Benzylidenepentaerythritol Benzenesulfonate (XII).**—A mixture of 30.0 g. (0.0596 mole) of *O*-benzylidenepentaerythritol dibenzenesulfonate,[4] 30 g. (0.43 mole) of sodium nitrite, and 300 ml. of *N*,*N*-dimethylformamide was brought to the reflux point in about 5 min. and then refluxed for 10 min. During this time brown vapors of nitrogen dioxide were visible above the reaction mixture. (Addition of phloroglucinol to the original reaction

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(18) B. Dobinson and A. B. Foster, *J. Chem. Soc.*, 2338 (1961).

(19) N. Kornblum, R. A. Smiley, R. K. Blackwood, and C. D. Iffland, *J. Am. Chem. Soc.*, **77**, 6269 (1955).

(20) Melting points are corrected. Microanalyses by K. W. Zimmerman, Australian Microanalytical Service, University of Melbourne.

(21) Prepared by the procedure of J. Compton, *J. Am. Chem. Soc.*, **60**, 395 (1938).

(22) Prepared by the procedure of G. S. Skinner, L. A. Anderson, and C. G. Gustafson, Jr., *ibid.*, **80**, 3788 (1958).

(23) Prepared by the procedure of A. L. Raymond and E. F. Schroeder, *ibid.*, **70**, 2785 (1948).

(24) Prepared by the procedure of E. Hardegger and R. M. Montavon, *Helv. Chim. Acta*, **29**, 1199 (1946).

mixture prevented nitrogen dioxide formation, but the same recovery of reaction product was observed.) After cooling the mixture, 500 ml. of water was added and the resulting suspension was placed in a refrigerator overnight. Filtration gave 9.2 g. (42%) of crude *O*-benzylidenepentaerythritol benzenesulfonate, m.p. 112–115.5°. Repeated recrystallizations from ethanol gave an analytical sample, m.p. 115.5–116°. The infrared spectrum in a chloroform (ethanol-free) solution showed an absorption at 2.74 μ, indicative of nonhydrogen-bonded hydroxyl stretching.

Anal. Calcd. for $C_{18}H_{20}O_6S$: C, 59.33; H, 5.53; S, 8.80. Found: C, 59.16; H, 5.61; S, 8.84.

Reaction of *O*-benzylidenepentaerythritol dibenzenesulfonate (IX), *O*-benzylidene-*O*-benzenesulfonylpentaerythritol iodide (X)[4], or *O*-benzylidenepentaerythritol diiodide (XI)[4] with sodium nitrite in *N*,*N*-dimethylformamide with or without phloroglucinol gave the starting compound as the main product when reaction was effected at 40–50°. With X, a very small amount of XII was also recovered. At higher temperatures, X and XI gave oily reaction products and the starting materials.

***O*-Benzylidenepentaerythritol Dibenzenesulfonate (IX) from *O*-Benzylidenepentaerythritol Benzenesulfonate (XII).**—To a solution of 0.91 g. (0.0025 mole) *O*-benzylidenepentaerythritol benzenesulfonate in 1.8 ml. of anhydrous pyridine cooled to 0°, 0.53 g. (0.0030 mole) of redistilled benzenesulfonyl chloride was added dropwise. The reaction mixture was maintained at 0° for 4 hr. during which time a large mass of crystals appeared. Then 0.5 ml. of ethanol was added and the resulting mixture allowed to stand for 0.5 hr. at room temperature. Cold water was added and the solid was filtered. After one recrystallization from ethanol–acetone, *O*-benzylidenepentaerythritol dibenzenesulfonate was obtained in 1.09 g. (87%) yield, m.p. and m.p. upon admixing with an authentic sample, 148.5–150°.

Reaction of *O*-Benzylidenepentaerythritol with Benzenesulfonyl Chloride.—A variety of reaction mixtures of benzenesulfonyl chloride and *O*-benzylidenepentaerythritol, in molar ratios of slightly less than one to more than two, in anhydrous pyridine at −10 to 0° for varying lengths of time gave *O*-benzylidenepentaerythritol dibenzenesulfonate in yields of less than 5 to some 86%. Separation was accomplished readily by suspending reaction mixture in acetone–water (40:60, by volume), in which the fully substituted compound has but slight solubility. Filtrates were evaporated and residues obtained dissolved in benzene and chromatographed on alumina. Very small amounts of the dibenzenesulfonate appeared in the first fractions followed by materials with melting points in the range 60–80°. Then the monobenzenesulfonate, m.p. 112–115°, obtained by the reaction of *O*-benzylidenepentaerythritol dibenzenesulfonate and sodium nitrite in *N*,*N*-dimethylformamide, was eluted in relatively small yields, up to 30%. Attempts to prepare a homogeneous sample of the lower melting fraction have not been successful.

Chemistry of Isocyanic Acid. II. Reactions with α,β-Unsaturated Ethers

F. W. HOOVER AND H. S. ROTHROCK

Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Inc., Wilmington, Delaware

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The addition of isocyanic acid to such α,β-unsaturated ethers as butyl vinyl ether, vinyloxyethyl methacrylate, and butyl isopropenyl ether proceeds readily to form α-alkoxy isocyanates.

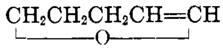
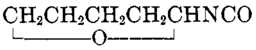
In a previous paper[1] it was reported that hydroxy isocyanates can be obtained by the addition of isocyanic acid to certain carbonyl compounds. This paper describes a new route to the little-studied α-alkoxy isocyanates through the addition of isocyanic acid to α,β-unsaturated ethers.

$$C_4H_9OCH{=}CH_2 + HNCO \longrightarrow C_4H_9OCH(CH_3)NCO$$

This is apparently the first reported addition of isocyanic acid to a carbon–carbon double bond.

TABLE I

NEW ISOCYANATES FROM ISOCYANIC ACID AND α,β-UNSATURATED ETHERS

α,β-Unsaturated ether	Isocyanate
$C_2H_5OCH{=}CH_2$	$C_2H_5OCH(CH_3)NCO$
$C_4H_9OCH{=}CH_2$	$C_4H_9OCH(CH_3)NCO$
$C_4H_9OC(CH_3){=}CH_2$	$C_4H_9OC(CH_3)_2NCO$
$C_6H_5OCH{=}CH_2$	$C_6H_5OCH(CH_3)NCO$
$(CH_2OCH{=}CH_2)_2$	$(CH_2OCH(CH_3)NCO)_2$
$CH_3OCH_2CH_2OCH{=}CH_2$	$CH_3OCH_2CH_2OCH(CH_3)NCO$
$CH_2{=}C(CH_3)CO_2CH_2CH_2OCH{=}CH_2$	$CH_2{=}C(CH_3)CO_2CH_2CH_2OCH(CH_3)NCO$
 $\underbrace{CH_2CH_2CH_2CH{=}CH}_{O}$	 $\underbrace{CH_2CH_2CH_2CH_2CHNCO}_{O}$

The reaction of α,β-unsaturated ethers and isocyanic acid is strongly exothermic and proceeds rapidly, especially in the presence of *p*-toluenesulfonic acid or other strong acids. Solvents, such as diethyl ether or benzene, are desirable to moderate the reaction and to stabilize the isocyanic acid against trimerization. Polymerization of the unsaturated ether is the principal competitive reaction and is minimized by using an excess of isocyanic acid. It is usually desirable to add the unsaturated ether to the solution of isocyanic acid. With the divinyl ether of ethylene glycol, a severalfold excess of isocyanic acid is necessary to obtain a good yield of the diisocyanate. The addition of isocyanic acid to α,β-unsaturated ethers is apparently quite general as indicated by the variety of structures (see Table I) that undergo this reaction.

The structures of these new isocyanates are confirmed by hydrolysis, infrared, and proton magnetic resonance data. For example, hydrolysis of the isocyanates from vinyl ethers gives acetaldehyde in good yields, showing that the NCO group and ether oxygen are attached to the same carbon atom. Moreover, the proton n.m.r. spectra (see Fig. 1) of these compounds show a single hydrogen split into a quadruplet and methyl hydrogens split into a doublet as required for the $RCH_2OCH(CH_3)NCO$ structure. Interestingly, the n.m.r. spectra also show that the hydrogens of the methylene group next to the oxygen are nonequivalent even though this group is not attached directly to the asymmetric carbon atom. Thus, with $CH_3CH_2OCH(CH_3)NCO$, these hydrogens appear as four quadruplets.

Isocyanates of the structure $ROCH(CH_3)NCO$, containing a hydrogen on the same carbon as the NCO group, are moderately reactive, forming ureas and carbamates with amines and alcohols, respectively. The second-order rate constant for the reaction of

(1) F. W. Hoover, H. B. Stevenson, and H. S. Rothrock, *J. Org. Chem.*, **28**, 1825 (1963).