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

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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.

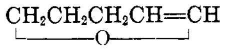
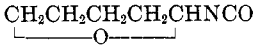
In a previous paper[1] it was reported that hydroxy isocyanates can be obtained by the addition of isocyanic acid to certain carbonyl compounds. This paper describes a new route to the little-studied α-alkoxy isocyanates through the addition of isocyanic acid to α,β-unsaturated ethers.

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

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

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

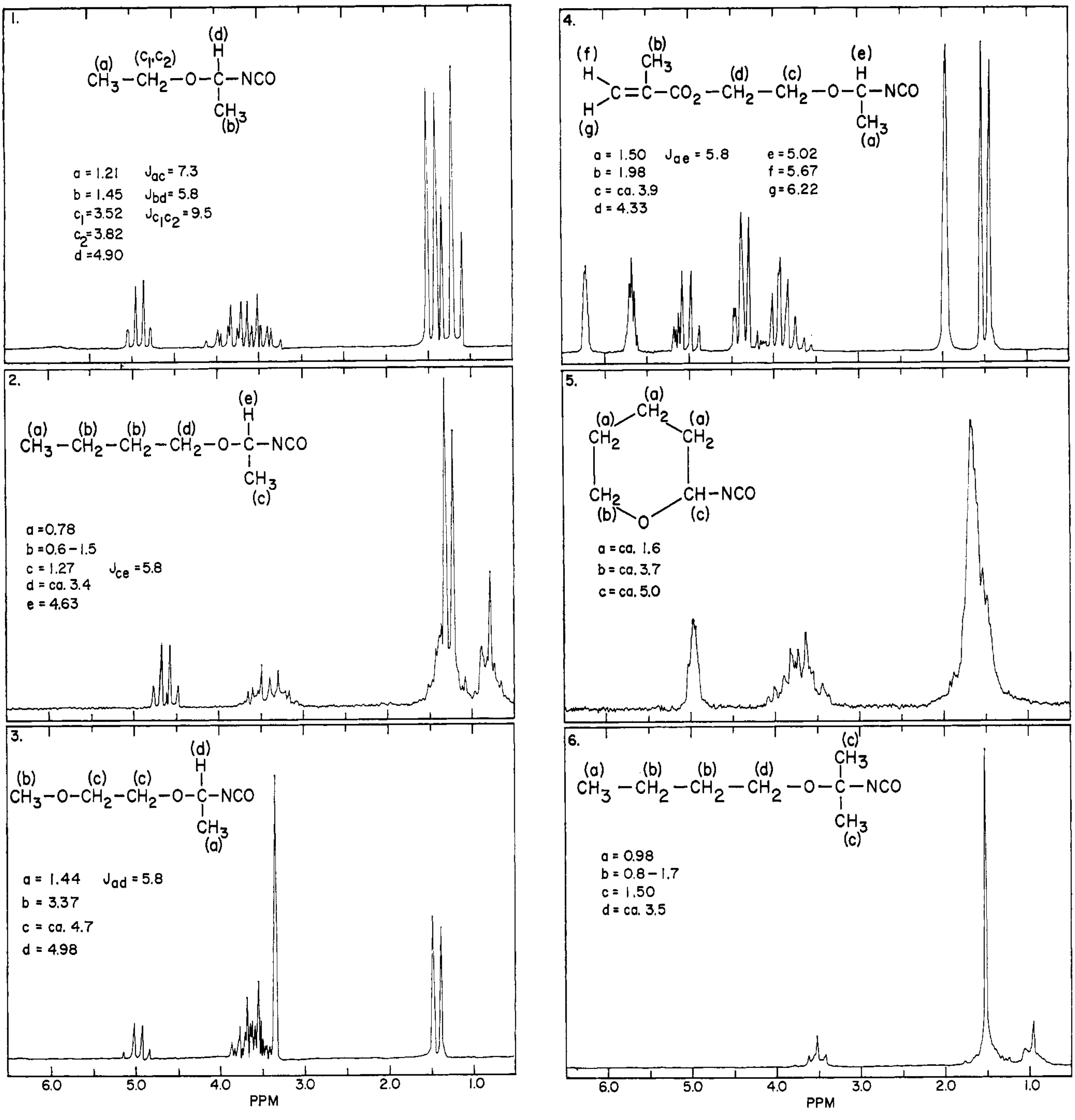

Fig. 1.—N.m.r. spectra of certain isocyanates using tetramethylsilane as an internal standard at 0.0. For spectrum 3, c = *ca.* 3.7 instead of the 4.7 given.

$C_4H_9OCH(CH_3)NCO$ with ethanol at 24° is 8 × 10^{-5} l. $mole^{-1}$ $sec.^{-1}$, compared with $K_{23°}$ 2.5 × 10^{-4} for phenyl isocyanate.[2] Replacement of the α hydrogen with an alkyl group results in much lower reactivity, apparently because of greater steric hindrance. Thus, $C_4H_9OC(CH_3)_2NCO$ reacts very slowly with ethanol in a complex manner to give several products, including ethyl allophanate and ethyl carbamate.

Polymers were obtained by the reaction of the diisocyanate from the divinyl ether of ethylene glycol with glycols or amines. The urea $C_4H_9OCH(CH_3)NHCONHC_6H_5$, obtained from aniline and 1-butoxyethyl isocyanate, underwent a disproportionation reaction on heating in acetone to give the bisurea $(C_6H_5NHCONH)_2CHCH_3$.

In the course of this study, it was found that isocyanic acid and diethyl ether form a maximum boiling point azeotrope (b.p. 48°) containing about 27 mole % isocyanic acid.

Experimental[3]

The following examples illustrate the procedures employed in this study for preparing α-alkoxy isocyanates.

1-Butoxyethyl Isocyanate. Method A.—To a stirred mixture of 100 ml. of benzene, 52.8 g. (1.2 moles) of isocyanic acid, and 0.1 g. of *p*-toluenesulfonic acid was added 110 g. (1.1 moles) of butyl vinyl ether over a period of 11 min.; the temperature rose to 56°. As soon as the temperature dropped to about 30°, the product was distilled rapidly at 1 mm. Redistillation gave

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(2) I. C. Kogon, *J. Org. Chem.*, **24**, 438 (1959).

(3) All melting points (Fisher-Johns apparatus) and boiling points are uncorrected. Proton n.m.r. spectra were obtained with a Varian A60 spectrometer on neat samples.

100 g. (64%) of 1-butoxyethyl isocyanate, b.p. 62° (24 mm.), $n^{25}D$ 1.4080.

Anal. Calcd. for $C_7H_{13}NO_2$: C, 58.75; H, 9.09; N, 9.80. Found: C, 59.17; H, 9.07; N, 10.27.

The infrared spectrum of this product showed strong absorption at 3.38 μ and 3.47 μ (saturated CH); 4.45 μ (NCO); 7.25 μ (C—CH_3); and 8.87 μ (C—O—C).

When a dioxane solution of this compound was treated with a drop of concentrated hydrochloric acid and then added to a solution of 2,4-dinitrophenylhydrazine, the hydrazone of acetaldehyde (m.p. 163–165°, no depression with an authentic sample) was obtained.

Method B.—1-Butoxyethyl isocyanate also was obtained by adding a mixture of 50 g. of vinyl butyl ether and 14.9 ml. of isocyanic acid dropwise to a stirred mixture of 50 ml. of diethyl ether and 0.1 g. of *p*-toluenesulfonic acid. The rate of addition was adjusted so that a temperature of 38–40° was maintained. On distillation, there was obtained 53 g. (90% yield) of 1-butoxyethyl isocyanate.

A mixture of 4.5 g. (0.03 mole) of 1-butoxyethyl isocyanate and 8.0 g. (0.17 mole) of ethanol was allowed to stand for 20 hr. Distillation gave 4.7 g. (79%) of ethyl N-(1-butoxyethyl)carbamate, b.p. 53° (0.04 mm.), $n^{25}D$ 1.4177.

Anal. Calcd. for $C_9H_{19}NO_2$: C, 57.11; H, 10.02; N, 7.38. Found: C, 57.38; H, 10.02; N, 7.38.

When 0.36 g. of 1-butoxyethyl isocyanate was added to a solution of 0.28 g. of aniline and 2 ml. of acetone, a precipitate formed which, after recrystallization from acetone, melted at 102–103°. The infrared spectrum and elemental analyses were in agreement with the structure $C_6H_5NHCONHCH(CH_3)OC_4H_9$.

Anal. Calcd. for $C_{13}H_{20}N_2O_2$: C, 66.10; H, 8.50. Found: C, 66.22; H, 8.60.

Some disproportionation of the product occurred when this reaction was carried out on a larger scale. Thus, from 14.3 g. of 1-butoxyethyl isocyanate, 10 g. of aniline, and 40 ml. of acetone, there was obtained 21.3 g. of slightly off-color product, m.p. 95–100°. On recrystallization of this product from acetone there was obtained 5 g. of a product, m.p. 218°, that was not soluble in acetone, chloroform, carbon tetrachloride, ethanol, 1,2-dimethoxyethane, or benzene. It was readily soluble in dimethylformamide and was recrystallized from a mixture of dimethylformamide and ethanol. Its infrared spectrum and elemental analyses were consistent with the structure $(C_6H_5NHCONH)_2CHCH_3$.

Anal. Calcd. for $C_{16}H_{18}N_4O_2$: C, 64.40; H, 6.05; N, 17.77. Found: C, 64.40; H, 6.08; N, 17.70.

A solution of 7.2 g. of 1-butoxyethyl isocyanate, 16.4 g. of *p*-chloroaniline, and 45 ml. of acetone was prepared at 10° and allowed to stand at 4° for 2 days during which time a precipitate formed. Collection of the product by filtration gave 8.2 g. (60%) of N-(1-butoxyethyl)-N′-*p*-chlorophenylurea, m.p. 108–109°.

Anal. Calcd. for $C_{13}H_{19}N_2O_2Cl$: N, 10.35; Cl, 13.10. Found: N, 10.57; Cl, 13.46.

The rate of the reaction of 1-butoxyethyl isocyanate with ethanol in carbon tetrachloride at 24 ± 1° was determined using near-infrared spectrophotometry[2] to follow the formation of carbamate (NH, 1.48 μ) and disappearance of ethanol (OH, 1.43 μ). Solutions (0.25 *M*) of the reactants were mixed in equal amounts, and the concentration of carbamate and ethanol were determined from time to time. The plot of

$$\frac{x}{a(a-x)}\ vs.\ t$$

where x is concentration of carbamate and a is initial isocyanate or ethanol concentration gave a nearly straight line over a 90-hr. reaction period. The value of k, the second-order rate constant, was 8×10^{-5} l. mole^{-1} sec.$^{-1}$.

The following monoisocyanates were prepared in ether by the procedure (method B) used for preparing 1-butoxyethyl isocyanate.

1-Ethoxyethyl Isocyanate.—B.p. 58° (114 mm.); $n^{25}D$ 1.3975; yield 50%.

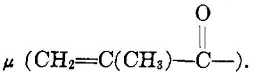
Anal. Calcd. for $C_5H_9NO_2$: C, 52.16; H, 7.88; N, 12.17. Found: C, 52.76; H, 7.91; N, 11.88.

Infrared: 3.35 μ and 3.45 μ (saturated CH); 4.44 μ (NCO); 7.24 μ (C—CH_3); and 8.85 μ (C—O—C).

1-(2-Methacryloxyethoxy)ethyl Isocyanate.—B.p. 70° (0.3 mm.); $n^{25}D$ 1.4436; yield 83%.

Anal. Calcd. for $C_9H_{13}NO_4$: C, 54.26; H, 6.58; N, 7.03. Found: C, 54.46; H, 6.40; N, 7.01.

Infrared: 3.23 μ shoulder (=CH); 3.35 μ and 3.41 μ (saturated CH); 4.44 μ (NCO); 5.80 μ (ester >C=O); 6.08 μ (—C=C—); 7.24 μ (C—CH_3); 8.55 μ and 8.85 μ (C—O—C); and 10.59



μ ($CH_2{=}C(CH_3){-}\overset{\overset{O}{\|}}{C}{-}$).

1-(2-Methoxyethoxy)ethyl Isocyanate.—B.p. 47° (4.5 mm.); $n^{25}D$ 1.4150; yield 48%.

Anal. Calcd. for $C_6H_{11}NO_3$: C, 49.64; H, 7.64; N, 9.65. Found: C, 49.70; H, 7.65; N, 9.36.

1-Phenoxyethyl Isocyanate.—B.p. 42° (0.4 mm.); $n^{25}D$ 1.5057; yield, 80%.

Anal. Calcd. for $C_9H_9NO_2$: C, 66.30; H, 5.52; N, 8.60. Found: C, 66.04; H, 5.57; N, 8.23.

Infrared: 3.25 μ and 3.27 μ (=CH); 3.32 μ and 3.39 μ (saturated CH); 4.42 μ (NCO); 6.25 μ and 6.68 μ (aromatic —C=C—); 7.23 μ (C—CH_3); 8.17 μ (C_6H_5—O—C); and 13.27 μ and 14.47 μ (monosubstituted aromatic bands).

The proton n.m.r. showed five aromatic hydrogens, three methyl hydrogens, and a tertiary hydrogen in accordance with this structure.

2-Tetrahydropyranyl Isocyanate.—B.p. 72° (25 mm.); $n^{25}D$ 1.4500; yield 80%.

Anal. Calcd. for $C_6H_9NO_2$: C, 56.68; H, 7.13; N, 11.02. Found: C, 56.82; H, 7.65; N, 11.06.

Infrared: 3.4 μ and 3.5 μ (saturated CH); 4.46 μ (NCO); and bands in 9–10-μ region (C—O—C).

The n.m.r. spectrum is shown in Fig. 1 (see spectrum 5). In decoupling experiments, c could be decoupled from a to give a singlet. Also, b could be decoupled from a to give a wssw pattern, but b would not decouple from c. These data are in agreement with the assigned structure.

1,1′-(Ethylenedioxy)diethyl Diisocyanate.—The divinyl ether of ethylene glycol (22.8 g., 0.2 mole) was added with stirring to a mixture of 36 g. (0.84 mole) of isocyanic acid, 100 ml. of benzene, and 0.1 g. of *p*-toluenesulfonic acid over a period of 20 min., during which time the temperature rose to 55°. The reaction mixture was stirred for 20 additional min. and the product distilled under reduced pressure. After removal of the solvent and excess isocyanic acid, the residue was distilled through a short-pass still at 0.3 mm. to separate the distillable products from the polymeric products. The distillate was then redistilled through a short Vigreux column to give 31.8 g. (80% yield) of 1,1′-(ethylenedioxy)diethyl diisocyanate, b.p. 65° (0.6 mm.), $n^{25}D$ 1.4360.

Anal. Calcd. for $C_8H_{12}N_2O_4$: N, 14.00. Found: N, 13.93.

The infrared spectrum showed absorption at 3.35 μ, 3.42 μ, and 3.46 μ (saturated CH); 4.44 μ (NCO); 7.24 μ (C—CH_3); and 8.94 μ (C—O—C).

1,1′-(Ethylenedioxy)diethyl diisocyanate reacted with ethylene glycol at room temperature to form a clear, viscous polymer and with hexamethylenediamine to form a white polymer that melted at about 150°.

The divinyl ether of ethylene glycol used in this experiment was prepared[4] in about 65% yield by heating a mixture of 220 g. of ethylene glycol, 12 g. of potassium hydroxide pellets, and acetylene in an autoclave at 150° for 22 hr.

When a mixture of 2.04 g. of 1,1′-(ethylenedioxy)diethyl diisocyanate and 99 g. of ethanol was allowed to stand for 4 days at room temperature, the dicarbamate (0.78 g.), m.p. 120–122°, precipitated. This dicarbamate was insoluble in water but was hydrolyzed by boiling water to give acetaldehyde as one of the products.

Anal. Calcd. for $C_{12}H_{24}N_2O_4$: C, 49.30; H, 8.27; N, 9.58. Found: C, 49.33; H, 7.67; N, 9.45.

1-Butoxy-1-methylethyl Isocyanate.—2,2-Dibutoxypropane, prepared[5] in 56% yield from 1-butanol and isopropenyl acetate, was converted to butyl isopropenyl ether by the following procedure adapted from the literature.[6] A mixture of 105 g. of 2,2-dibutoxypropane, 80 g. of quinoline, and 87 g. of potassium

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(4) A. E. Favorskiĭ and M. F. Shostakovskii, *J. Gen. Chem. USSR* (Eng. Transl.), **13**, 1 (1943).

(5) W. J. Croxall, F. S. Glavis, and H. T. Neher, *J. Am. Chem. Soc.*, **70**, 2805 (1948).

(6) H. P. Crocker and R. H. Hall, *J. Chem. Soc.*, 2052 (1955).

hydroxide was heated to 190° and 56 g. of distillate was collected. A foam-producing reaction set in near the end of the run. After treatment with 10 g. of sodium hydride (in oil) to remove the alcohol, the crude product was distilled. There was obtained 22 g. (35%) of butyl isopropenyl ether, b.p. 111–114°, n^{25}D 1.4076.

Anal. Calcd. for $C_7H_{14}O$: C, 73.64; H, 12.36. Found: C, 73.19; H, 12.26.

To a stirred mixture of 12.6 g. (0.29 mole) of isocyanic acid, 25 ml. of benzene, and 0.05 g. of *p*-toluenesulfonic acid was added 22 g. (0.19 mole) of butyl isopropenyl ether over a period of 24 min. with a temperature rise to 44°. On distillation, there was obtained 22.2 g. (71%) of 1-butoxy-1-methylethyl isocyanate, b.p. 58° (18 mm.), n^{25}D 1.4104.

Anal. Calcd. for $C_8H_{15}NO_2$: C, 61.12; H, 9.62; N, 8.91. Found: C, 61.56; H, 9.60; N, 9.08.

The infrared spectrum showed absorption at 3.33 μ and 3.38 μ and 3.47 μ (saturated CH); 4.45 μ (NCO); 7.23 μ and 7.32 μ ($C(CH_3)_2$); and 8–10-μ region (C—O—C).

In an attempt to obtain the carbamate by reaction of this isocyanate with ethanol, a slow complex reaction occurred with the formation of ethyl carbamate and ethyl allophanate. The stoichiometry corresponded to about 2.3 moles of ethanol consumed per mole of isocyanate. Apparently, the initial reaction involved displacement of NCO with OC_2H_5 to give HNCO, which underwent further reaction with ethanol to form ethyl carbamate and ethyl allophanate.

On the Nature of the Catalytic Agent in Friedel–Crafts Isomerization

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Infrared spectra of solutions containing aluminum bromide, 1,2,4-trichlorobenzene, and small quantities of water suggest that Al_2Br_5OH is a possible catalytic species in the "homogeneous" isomerization of *n*-hexane in these systems.

The "homogeneous" isomerization of *n*-hexane was studied recently using 1,2,3-, 1,2,4-, and 1,3,5-trichlorobenzene as solvents and aluminum bromide promoted with small amounts of water as the co-catalyst.[1] Water is known to be a good promoter of Friedel–Crafts catalysts, and several reasons have been advanced for this phenomenon.[2] Typical arguments are that water reacts with aluminum bromide: to form hydrogen bromide which adds to trace quantities of olefins to form alkyl bromides which serve as carbonium ion initiators, to form a protonic acid which converts trace olefins to carbonium ions, or to form a protonic acid which interacts directly with and causes the rearrangement of a paraffin without carbonium ion formation.

The object of the present study was to obtain a better understanding of this co-catalyst system by determining the infrared absorption of solutions of aluminum bromide, trichlorobenzene, and small amounts of water.

Results and Discussion

It was observed that, when a small quantity of water is gradually added to a solution of aluminum bromide in 1,2,4-trichlorobenzene, some of it reacts at the surface to form a precipitate, possibly a hydrated aluminum oxide or very basic aluminum bromide, while the major portion dissolves to form a "homogeneous" solution. The precipitate would account only for a small portion of the added water and it was not further characterized, but the clear solution was examined by infrared. It was found that an OH band in the 2.9-μ (3450-cm.$^{-1}$) region of the spectrum developed in intensity as the nominal water–aluminum bromide mole ratio increased from 0 to 0.5. Adding more water resulted in a *decrease* in the 2.9-μ band (Fig. 1). This behavior suggests that the species in solution possessing an OH group is altered or removed by further reaction with excess water.

Also, in the spectra of these solutions no bands were observed at ~6.1 μ. A band in this spectral region is indicative of an H–O–H bending vibration, and its absence indicates that the added water did not simply form a hydrate with aluminum bromide, $Al_2Br_6 \cdot xH_2O$. For example, typical hydrates such as $LiClO_4 \cdot H_2O$ have a sharp band at 6.1 μ.[3] These spectra indicate that water reacts with aluminum bromide in 1,2,4-trichlorobenzene and forms a soluble complex containing a hydroxyl group.

While infrared absorption at 2.9 μ thus went through a maximum at a water–aluminum bromide mole ratio of 0.5, an exactly parallel behavior occurred in the 14.5–15-μ spectral region. Infrared bands in this region are due to the C–Cl vibrations of 1,2,4-trichlorobenzene.[4] This parallel behavior in the two spectral regions suggests that the soluble aluminum bromide complex interacts with trichlorobenzene to form a species which has infrared bands both at 14.5–15 and 2.9 μ. The interaction between 1,2,4-trichlorobenzene and the soluble aluminum bromide complex is weak, since the addition of excess water permitted the original spectrum of the solvent to be recovered (Fig. 2).

The result that water and aluminum bromide interact in 1,2,4-trichlorobenzene to form a species whose concentration is a maximum at a water–aluminum bromide mole ratio of 0.5 is supported by *n*-hexane isomerization rate measurements. In general, it was found previously that the *n*-hexane isomerization and cracking rates increased as the water–aluminum bromide mole ratio varied from 0 to 0.5,[1] but the solutions containing excess water, water–aluminum bromide >1, had no catalytic activity. Also, a slow evolution of hydrogen bromide from these solutions was detected during all of the *n*-hexane isomerization experiments. While hydrogen bromide may serve as a co-catalyst with aluminum bromide, hydrogen bromide adding to trace quantities of olefins to form alkyl bromides which serve as carbonium ion initiators, its contribution must be small since previous work[1] has shown that even in the presence

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(1) G. M. Kramer, R. M. Skomoroski, and J. A. Hinlicky, *J. Org. Chem.*, **28**, 1029 (1963).

(2) H. Pines, "Advances in Catalysis," Vol. I, Academic Press, New York, N. Y., 1948, p. 201.

(3) F. A. Miller and C. H. Wilkins, *Anal. Chem.*, **24**, 1253 (1952).

(4) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958.