

reflux for 3 hr., then cooled and poured into water (100 ml.). The resulting mixture was extracted with three 50-ml. portions of dichloromethane and the combined extracts were washed with water, dilute hydrochloric acid, water, and saturated brine, and dried over anhydrous sodium sulfate. Removal of the solvent under reduced pressure left the crude product as a viscous, brown oil (8 g.), $\lambda_{\text{max}}^{\text{CHCl}_3}$ 6.01, 6.29 μ . A solution of 0.8 g. of this oil in carbon tetrachloride (30 ml.) was treated with a solution of bromine (1.5 g.) in carbon tetrachloride (10 ml.) and the mixture was boiled under reflux for 1 hr. It was then cooled and treated with aqueous sodium bisulfite to discharge the excess of bromine. The organic layer was separated and washed with water, aqueous sodium bicarbonate, water, and saturated brine. It was dried over anhydrous sodium sulfate and stripped of solvent under reduced pressure. The residue was crystallized from benzene-petroleum ether to give the phenol IX, m.p. 244–245°, $\lambda_{\text{max}}^{\text{CHCl}_3}$ 2.81 μ .

Anal. Calcd. for $\text{C}_{20}\text{H}_{22}\text{O}$: C, 90.42; H, 5.57. Found: C, 90.47; H, 5.61.

Isocyanide Bond Refraction

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Extensive tabulations of bond refractions have been made by Vogel¹ and by Gillis.² The isocyanide bond refraction, which has not previously been determined, is now reported for comparison with that of the cyanide bond. The new value is based on the properties of four alkyl isocyanides shown in Table I.

TABLE I
PROPERTIES OF ALKYL ISOCYANIDES

R	B.P.	d_{20}^4	n_D^{20}	R_D^{20}	$(\text{N}\equiv\text{C})^a$	$(\text{Mn}^{20})^a$
Me	59–60	0.7497	1.3466	11.68	5.10	29.16
Et	78–79	0.7478	1.3658	16.49	5.27	28.51
<i>n</i> -Pr	99–100	0.7665	1.3832	21.04	5.17	28.27
<i>n</i> -Bu	129–130	0.7818	1.3976	25.64	5.12	28.26
			Mean	5.17	28.55	

^a The symbolism is Vogel's.¹

($\text{N}\equiv\text{C}$) determined from each of these alkyl isocyanides is greater than ($\text{C}\equiv\text{N}$) determined from the corresponding alkyl cyanide,¹ and the difference of the means is significant at the 0.01 level. (The bond refraction coefficients 28.55 for isocyanides and 29.91 for cyanides¹ are also significantly different.) This result is in contrast with the low bond refractions normally associated with systems containing dative bonds.^{2–4} It is probably owing to the effect of the lone pairs of electrons on the nitro-

gen and carbon atoms, because the bond refraction as determined is a measure of the polarizability of the six electrons in the bond plus that of the lone pair in each case. Linnett⁵ has suggested that these pairs are in some way connected with the lower value for the $\text{N}\equiv\text{C}$ force constant in methyl isocyanide as compared with that of $\text{C}\equiv\text{N}$ in methyl cyanide.

Methyl isocyanide has a lower boiling point and smaller dipole moment⁶ than methyl cyanide. These facts are compatible with the terminal lone pair in isocyanide being less strongly bound than in cyanides. Further evidence is being sought from retention data on various donor and acceptor stationary phases in gas chromatography.

Experimental

The isocyanides were prepared from the corresponding iodide and silver cyanide by the method of Jackson and McCusick.⁷ It was advantageous to dilute the reaction mixture with a little ethylene glycol which made the pasty complex easier to stir. The products were fractionated in a column packed with helices, and physical properties were determined^{2,3} on fractions shown to be homogeneous by gas chromatography.

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Chlorination of Phenyl Ether

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Previous studies of phenyl ether (I) chlorination are very sparse in the chemical literature, possibly due to the difficulty in separating the liquid or low melting products. Vapor phase chromatography has allowed us to examine this system in a much more precise way. We were particularly anxious to check some previously reported results¹ which we considered anomalous. They are (a) monochlorination of I in acetic acid yields no detectable amounts of 2-chlorophenyl ether (II), and (b) chlorination of 4-chlorophenyl ether (III) yields a significant amount of 3,4-dichlorophenyl ether (IV). Although the first seemed not too improbable, the second would require some revision of our concept of electrophilic substitution.

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