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.), $\lambda_{\max}^{\mathrm{CHCl_3}}$ 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°, $\lambda_{\max}^{\mathrm{CHCl_3}}$ 2.81 μ.

Anal. Calcd. for $C_{30}H_{22}O$: 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 Vogel[1] 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^{20}_D	R^a_D	$(N\equiv C)^a$	$(Mn^{20}_D)^a$
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
n-Pr	99–100	0.7665	1.3832	21.04	5.17	28.27
n-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]

$(N\equiv C)$ determined from each of these alkyl isocyanides is greater than $(C\equiv N)$ 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 cyanides[1] 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 nitrogen 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. Linnett[5] has suggested that these pairs are in some way connected with the lower value for the $N\equiv C$ force constant in methyl isocyanide as compared with that of $C\equiv N$ in methyl cyanide.

Methyl isocyanide has a lower boiling point and smaller dipole moment[6] 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 fractioned 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 results[1] 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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Discussion and Results

Compounds I, II, and III were chlorinated under a wide variety of conditions and the results are recorded on Tables I, II, and III.

TABLE I

PHENYL ETHER CHLORINATION

Chlorinating system	% 2-	% 4-
No catalyst, Cl_2,CCl_4, R.T.	8.4	91.6
No catalyst, Cl_2, HOAc, 0°	11.0	89.0
$SnCl_4$, Cl_2, CCl_4, 0°	25.2	74.8
$FeCl_3$, Cl_2, CCl_4, 0°	17.0	83.0
$AlBr_3$, Cl_2, CCl_4, 0°	7.7	92.3

TABLE II

2-CHLOROPHENYL ETHER CHLORINATION

Chlorinating system	% 2,6-	% 2,4-	% 2,2'-	% 2,4'-
No catalyst, Cl_2, HOAc, 0°	...	0.9	10.7	88.4
$SnCl_4$, Cl_2, CCl_4, 0°	Trace	1.4	23.1	75.5
$FeCl_3$, Cl_2, CCl_4, 0°	Trace	2.0	22.9	75.1
$AlBr_3$, Cl_2, CCl_4, 0°	1.2	5.4	21.5	72.0

TABLE III

4-CHLOROPHENYL ETHER CHLORINATION

Chlorinating system	% 2,4-	% 2,4'-	% 4,4'-
No catalyst, Cl_2, HOAc, 0°	...	8.8	91.2
$SnCl_4$, Cl_2, CCl_4, 0°	0.3	23.2	76.5
$FeCl_3$, Cl_2, CCl_4, 0°	1.0	20.2	78.8
$AlBr_3$, Cl_2, CCl_4, 0°	3.7	19.6	76.7

Examination of Table I provides some explanation of why II was not found in previously reported noncatalytic chlorinations since it is formed in relatively minor amounts. The most interesting feature of Table I is the manner in which the *ortho/para* ratio rises and falls with increasing activity of the chlorinating species. A possible explanation for this is discussed elsewhere.[2,3] Briefly, we believe the increase in *ortho/para* ratio is due to a decrease in steric interactions in the transition state as more reactive chlorinating species are used. We feel the *ortho/para* ratio passing through a maximum is also correlated with increasing activity of the chlorinating species, since the dipolar interaction between the ether group (-I) and the incoming partially positive chlorine atom increases.

Tables II and III show the same general trend to a lesser extent, which is somewhat puzzling.[4] They also show that some substitution takes place in the already chlorinated nucleus and this increases as the activity of the chlorinating species increases. The data in Table III clearly demonstrate that IV[5] is not formed in measurable amounts nor is any product of meta substitution produced in any of the systems[5] in measurable amounts.

Experimental

General Chlorination Method.—A solution of 0.01 mole of I, II, or III in 10 ml. of solvent (acetic acid or carbon tetrachloride) was prepared and cooled in an ice bath. To this solution was added 0.01 g. of catalyst (stannic chloride, ferric chloride, or aluminum bromide), if any. The resulting mixture was combined with a cold solution of 0.003 mole of chlorine in 4 ml. of solvent. The reaction mixture was allowed to stand in an ice bath for 1 hr. (The noncatalytic chlorination of I in carbon tetrachloride was carried out at room temperature and stored in the dark for 48 hr.) At the end of the reaction period, the mixture was poured into water, carbon tetrachloride added if necessary, the organic layer dried, evaporated, and the oily residue used directly for vapor phase chromatographic analysis.

Analytical Procedure.[6] The analyses were performed on a Barber-Colman Model 20 gas chromatograph equipped with a 200-ft. apiezon "L" capillary column and an argon ionization detector. Although areas were found to be nearly proportional to mole per cent, any deviation from linearity was corrected for by use of calibrated standard samples.

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[2] H. Weingarten, *J. Org. Chem.*, **26**, 4347 (1961).

[3] J. R. Knowles, R. O. C. Norman, and G. K. Radda, *J. Chem. Soc.*, **4885** (1960).

[4] Treatment of II under much more severe conditions (30 min. at 140° with aluminum chloride or aluminum bromide and no solvent) produced no detectable isomerization.

[5] Standard samples of the possible *meta* substituted compounds were prepared for comparison by usual Ullmann methods.

[6] Details of the analytical procedure are identical to those reported by H. Weingarten, W. D. Ross, J. M. Schater, and G. Wheeler, Jr., *Anal. Chim. Acta*, **26**, 391 (1962).

The Synthesis and Properties of N,N-Dialkylaminovinylindoles

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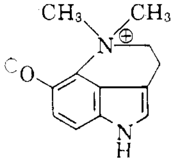
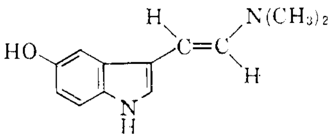
Recently the structure of dehydrobufotenine, isolated from the parotid gland of the South American toad, *Bufo marinus*, has been established as the tricycle I[1,2] superseding the old enamine formula II.[3] Because of interest in the hallucinogenic activity of alkylated tryptamines[4] we are reporting here the synthesis and some properties of enamines of type II.[5,6]



I



II

The starting materials, namely 3-indoleacetaldehyde[7] and 5-benzyloxy-3-indoleacetaldehyde were prepared by the oxidation of the corresponding tryptophans according to the method of Gray.[7]

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