tion with ethyl acetate afforded 0.75 g. of material that crystallized slowly from ether-petroleum ether (b.p. 28–38°) to yield 0.26 g. of the monoacetate **4b**, m.p. 92–94°; $[\alpha]_D$ +45°; λ_{max} 2.74, 5.79 μ.

Anal. Calcd. for $C_{26}H_{44}O_3$: C, 77.17; H, 10.96. Found: C, 77.35; H, 10.92.

A second crop of material, 0.15 g., m.p. 90–94°, also was obtained. The sole differences in the infrared of this compound as compared to starting material were maxima at 2.7–2.9 μ and minor intensity changes at 7.22, 10.71, and 11.29 μ.

3-(3β,17β-Diacetoxy-5-androsten-17α-yl)propyl Acetate (5a).—A slurry of 78 g. of 3-(3β,17β-dihydroxy-5-androsten-17α-yl)-propanol[6] in 0.8 l. of *i*-propenyl acetate and 1.9 g. of *p*-toluenesulfonic acid was heated at the boiling point with slow distillation of the solvent. The compound dissolved within 15 min. After 3 hr. the solution was cooled and filtered to remove insoluble inorganic material (a contaminant of the very insoluble starting material). The filtrate was washed twice with aqueous potassium bicarbonate and then with water, and the solution was concentrated to dryness. The resulting oil was crystallized from methanol yielding 54.5 g., m.p. 114–116°, of the triacetate **5a**. A second crop of 27 g., m.p. 112–114°, was obtained from aqueous methanol. Recrystallization of 1.5 g. of the first crop afforded 1.3 g. of the pure triacetate, m.p. 115–116°; $[\alpha]_D$ −76°; λ_{max} 5.78 μ; $\Delta\nu$ 220 (OAc), 222 (OAc), 223 (OAc), 243 c.p.s. (C-22-H).

Anal. Calcd. for $C_{28}H_{42}O_6$: C, 70.85; H, 8.92. Found: C, 71.10; H, 9.06.

3-(3β,17β-Diacetoxy-5-androsten-17-α-yl)propanol (5b) and 3-(3β-Hydroxy-17β-acetoxy-5-androsten-17α-yl)propanol (5c).—A solution of 80 g. of the triacetate **5a** in 1 l. of benzene was dried by the distillation of 100 ml. of solvent and was adsorbed on 2.5 kg. of Alcoa F-20 alumina. After 65 hr. the column was washed with 4 l. of benzene affording 2.0 g. of starting material (identification by infrared comparison). Ethyl acetate (10 l.) was passed through the column. On evaporation of the solvent 74 g. of crystalline residue remained. This was recrystallized from aqueous ethanol to afford 51 g. of the monohydroxy compound **5b**, m.p. 101–102°, and 11.5 g., m.p. 99–102°. Recrystallization of 1.1 g. of the first crop from petroleum ether (b.p. 60–68°) yielded 0.77 g. of pure material, m.p. 104–105°; $[\alpha]_D$ −85°; λ_{max} 2.74, 5.79 μ; $\Delta\nu$ 120 (OAc), 122 (OAc), 213, 218, and 223 c.p.s. (C-22-H).

Anal. Calcd. for $C_{26}H_{40}O_5$: C, 72.19; H, 9.32. Found: C, 72.31; H, 9.26.

The only bands in the infrared distinguishing the monohydroxy compound from starting material were those at 2.7–2.9 μ and minor intensity changes at 6.91 and 9.12 μ.

Further elution of the column with 4 l. of methanol afforded 7.5 g. of material which was recrystallized from methanol–ethyl acetate to yield 2.7 g. of the dihydroxy compound **5c**, m.p. 200–204°. A further recrystallization from aqueous methanol yielded 1.35 g. of analytically pure material, m.p. 202–205°; $[\alpha]^{EtOH}_D$ −83°; λ^{KBr}_{max} 3.00, 5.78 μ.

Anal. Calcd. for $C_{24}H_{38}O_4$: C, 73.80; H, 9.81. Found: C, 73.73; H, 9.74. Low chloroform solubility prevented obtention of an infrared spectrum of its solution.

Both the mono- and diacetates **5b** and **5c** were readily converted in good yields to the starting triacetate **5a** by treatment in acetic anhydride–pyridine at 100° for 20 min. The identification in each case was made by comparison of the infrared and n.m.r. spectra.

Isocyanides. III.[1,2] Electron Impact Study of Aliphatic Isocyanides

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Our interest in isocyanides has led us to study the isocyanide bond refraction[1] and solvent effects on the isocyanide stretching fundamental in the infrared.[2] The results of both studies could be interpreted consistently in terms of greater polarizability of the lone pair of electrons on the terminal carbon atom of the isocyanide group as compared with the nitrogen lone pair of the cyanide group. We now report a continuation of this work in comparing the behavior of aliphatic isocyanides in a mass spectrometer with the corresponding cyanides.

TABLE I

MASS SPECTRA OF ALIPHATIC ISOCYANIDES AND CYANIDES[a]

m/e	MeNC	MeCN	EtNC	EtCN	PrNC	PrCN	BuNC	BuCN
15	**8**	**1**	5	6	4	2	2	3
26	2	2	20	16	6	5	6	5
27	4	1	52	14	38	26	39	34
28	8	4	93	100	15	7	37	19
29			**100**	**3**	51	57	33	16
30			2		5	1	3	
37				1	4	3	1	2
38	13	10	5	2	5	3	3	3
39	20	19	8	2	17	8	19	15
40	49	55	29	4	10	4	7	4
41	*100*	*100*	2		100	100	100	100
42	3	3			44	3	9	5
43					**10**	**1**	56	97
44			2	1	1		3	4
50			2	2			1	1
51			9	9	2	2	2	2
52			15	11	3	3	2	3
53			3	7			2	2
54			33	61	25	2	9	54
55			*78*	*10*	2	1	43	21
56			4	1			25	3
57							**47**	
58							2	
68					11		2	1
69					*5*	<*1*		2
70						1		
82							2	4
83							<*1*	<*1*
84								1

[a] Peaks less than 1% of base peak omitted; molecular ions, italic; $M - 26$ ions, boldface.

The fragmentation patterns for methyl, ethyl, *n*-propyl, and *n*-butyl isocyanides and cyanides are shown in Table I. The agreement between our results for cyanides and those recently reported by McLafferty[3] is satisfactory. The base peak of propyl and butyl isocyanides is at m/e 41 as for the corresponding cyanides. This indicates that β-bond cleavage is the principal mode of fragmentation in the isocyanides. McLafferty has already shown this to be the case in cyanides, and postulated a six-membered cyclic transition state. The identical geometry of the two species makes this transition state equally probable for the isocyanides. Ethyl isocyanide shows stronger peaks than ethyl cyanide at m/e 39, 40, and 41 (which are not base peaks), again demonstrating the importance of β-cleavage.

However, α-bond cleavage, which is of minor importance in cyanides, is very noticeable in isocyanides. This is seen by comparing the intensities of the $M - 26$ peaks (m/e 15, 29, 43, and 57, respectively). This indicates that the R–N bond of the isocyanide molecular ion is considerably weaker than the R–C bond of cyanide. It appears that the isocyanide molecular ion retains the destabilizing effect of the resonance of the molecule, which tends to place a negative charge on the

$$R{-}\overset{+}{N}{=}\overset{-}{C} \longleftrightarrow \overset{-}{R}{=}\overset{+}{N}{=}C$$

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[1] Part I, R. G. Gillis, *J. Org. Chem.*, **27**, 4103 (1962).

[2] Part II, R. G. Gillis, and J. L. Occolowitz, *Spectrochim. Acta*, **19**, 873 (1963).

[3] F. W. McLafferty, *Anal. Chem.*, **34**, 26 (1962).

alkyl group. In addition to the greater tendency to α-fission, it is noticeable that hydrogen rearranges or is lost more easily. This can be seen from the relative intensities of the $M - 26$ ($-CN$), $M - 27$ ($-HCN$), and $M - 28$ ($-H_2CN$) peaks.

Cyanide mass spectra have an $M + 1$ peak which is pressure sensitive (and therefore is caused by an "ion-molecule" reaction), and McLafferty has shown how this can be used to identify molecular ions in mixtures.[3] The isocyanides also show a pressure dependent $M + 1$ peak which must be caused by hydrogen transfer in an ion-molecule reaction.

A further object of this work was to measure the appearance potentials of the molecular ions. Only five compounds gave a sufficiently intense molecular peak to make the necessary measurements. The results were 11.8, 11.2, and 11.1 e.v. for methyl, ethyl and propyl isocyanides, and 12.3 and 11.9 e.v. for methyl and ethyl cyanides. The last two values are in good agreement with the results of Morrison and Nicholson,[4] 12.39 and 11.85 e.v., respectively. Other ionization potentials determined by electron impact which are recorded for methyl cyanide are 12.52,[5] 12.48,[6] and 12.42 e.v.[7]

In the methyl and ethyl pairs of isomers the ionization potential of the isocyanide is smaller. It requires approximately 0.6 e.v. less energy to remove one electron from the isocyanide molecule. While this electron undoubtedly comes from the isocyanide group, it is not possible to determine whether it is from the bonding electrons or the lone pair.

Experimental

Spectra were determined in an Atlas mass spectrometer, a 60°, 20-cm. radius instrument using magnetic scanning. The inlet temperature was maintained at 90° and the ion source at 250°; the electron energy was 70 e.v. Appearance potentials were measured by the energy compensation method.[8] Argon was used as reference and its ionization potential was taken as 15.7 e.v. The argon was admitted to the ion source at the same time as the sample. The reproducibility of argon and sample readings was 0.05 e.v., so that the over-all accuracy is ±0.1 e.v. The resolution ($m/\Delta m$) available was 800 at 1%. This was adequate to distinguish argon from C_3H_4 or C_2H_2N, but not to distinguish those fragments from one another. The preparation of the isocyanides has been described[1]; all compounds were repurified by gas chromatography.

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[4] J. D. Morrison and A. J. C. Nicholson, *J. Chem. Phys.*, **20**, 1021 (1952).

[5] C. A. McDowell and J. W. Warren, *Trans. Faraday Soc.*, **48**, 1084 (1952).

[6] B. C. Cox, thesis, University of Liverpool, 1953, quoted by R. W. Kiser; "Tables of Ionization Potentials," U. S. Atomic Energy Commission, 1960.

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[8] R. W. Kiser and E. J. Gallegos, *J. Phys. Chem.*, **66**, 947 (1962).

The Phenolysis of N-Bromomethylphthalimide. A Correction

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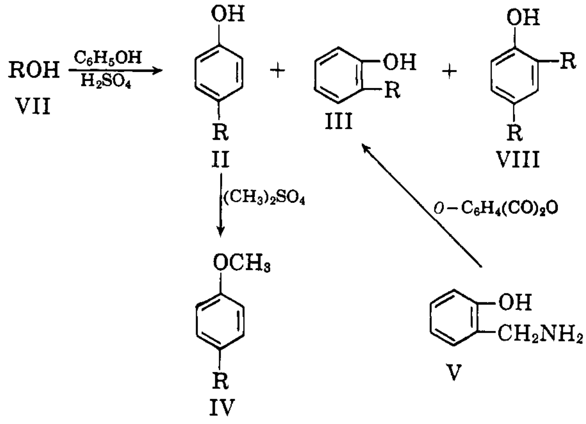
Because of the high solvolytic reactivity of its bromine atom and the ready isolation of derived products, N-bromomethylphthalimide (I) twice has been recommended as an identification reagent for alcohols.[1,2] Both groups of workers extended its use to the characterization of phenol; and, by analogy to the products obtained from alcohols, they assigned the phenyl ether structure VI to their derivatives. However, their melting points (171–172°[1] and 205°[2]) did not agree.

This discrepancy, coupled with the original observation of Tscherniac[3] that ring substitution of phenol by N-methylolphthalimide VII (in strong sulfuric acid) furnishes a derivative, m.p. 205°, suggested that phenolysis of the bromide I occurs with alkylation at carbon rather than at oxygen. Position isomerism could then be invoked to account for the melting point discrepancy. This note reports the verification of this expectation.

Preliminary work demonstrated that the crude products obtained by the prescribed[1,2] procedures did indeed possess free hydroxyl groups. The Tscherniac[3] condensation of phenol with N-methylolphthalimide was then repeated and the products were identified (Scheme I). The material, m.p. 205–206°, assumed by Tscherniac to be the *para* isomer II, indeed possesses the expected structure. Methylation of it gave the ether IV identical with an authentic sample.[4]

SCHEME I
(R = *o*-$C_6H_4(CO)_2NCH_2-$)



The corresponding *ortho* isomer III, m.p. 177°, was synthesized independently by treatment of *o*-hydroxybenzylamine (V)[5] with phthalic anhydride. Its presence in the Tscherniac reaction mixture was then demonstrated by means of qualitative thin-layer silica gel chromatography. Further application of a quantitative column chromatographic technique (see Experimental) to the mixture of monosubstitution products showed that the *para* isomer II had been formed in 38% yield and *ortho* isomer III in 9% yield. An insoluble material, m.p. 297–298°, characterized as a disubstituted product was also obtained in 33% yield. Although its structure was not rigorously proved, confinement of monosubstitution in this reaction to the *ortho* and *para* positions enables the reasonably confident assignment to it of the 2,4-disubstituted structure VIII.

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[5] Prepared by reduction of salicylamide with lithium aluminum hydride.