spectrum a saturated ketone and an enone absorption, and benzene–ethyl acetate (7:3) eluted 114 mg. (50%) of $\Delta^{9(11)}$-testosterone. Crystallization from aqueous ethyl alcohol and methylene chloride–hexane afforded colorless crystals, m.p. 153–154°, identical in all respects with an authentic sample.[10]

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[10] The authors are indebted to the Upjohn Co., Kalamazoo, Mich., for kindly supplying an authentic sample of $\Delta^{9(11)}$-testosterone.

Studies Concerning the Infrared Spectra of Some Substituted Benzofuran Derivatives

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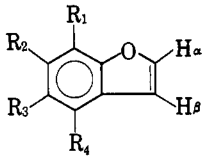
Although a number of studies of the infrared spectra of furan-type compounds have been reported,[1-8] these investigations with one exception[1] have been limited to monosubstituted or simple polysubstituted derivatives. Three groups of these workers have made some generalizations concerning characterizing bands. Katritzky and Lagowski[2] found nine bands to be common and identified with the furan nucleus in 24 2-monosubstituted furans. Kubota[3] after considering the spectra of 43 furano compounds has suggested three bands as being characteristic of the furan group. On the basis of 20 compounds most of which were 2,3-disubstituted furan derivatives of complex furanoquinoline alkaloids and furanocoumarins, Briggs and Colebrook[1] proposed that seven bands characterized the furano group. However, there has been little effort directed toward empirical correlations between given bands and specific furan hydrogens.

As a result of synthetic work directed toward furanocoumarins and other benzofuran derivatives, we have been able to gather and study the infrared spectra of a number of simple and complex substituted benzofurans. The findings of this study seem to indicate a relationship between the presence or absence of furan hydrogens and medium to strong bands in the 1180–1020-cm.$^{-1}$ region. It is not surprising that a relationship exists since Katritzky and Lagowski[9] have shown that in the six-membered ring heteroaromatic series, and presumably in the five-membered series as well, the number and relative orientations of the hydrogen atoms determine the positions of the in- and out-of-plane bending modes. The strong absorption of the out-of-plane bending modes of aromatic hydrogen have long been used to establish substitution patterns while the in-plane bending modes are not of much diagnostic use because they usually give only weak bands and there are other types of absorption in the same region. The C–H in-plane bending bands (1270–1015 cm.$^{-1}$) of furans are much stronger and more easily distinguished than those for the more normal aromatic compounds presumably due to the polar nature of the hetero atom.

The compounds studied were divided into two groups. One group (Table I) included only substances with two furan hydrogens. This group had two bands, one in the range 1160–1125 cm.$^{-1}$ and one in the 1087–1029-cm.$^{-1}$ region which we suggest are associated with the in-plane bending modes of the β- and α-hydrogens on the furan nucleus and tend to be characteristic of furans with adjacent α- and β-hydrogens. The second group (Table II) has compounds with only a single furan hydrogen and in the β-position. These compounds all showed a band in the range 1172–1121 cm.$^{-1}$ and no medium or strong, sharp bands in the 1087–1029-cm.$^{-1}$ region which we feel is characteristic of the β-hydrogen.

TABLE I

BENZOFURAN DERIVATIVES WITH TWO FURAN HYDROGENS



Compd.				Bands (cm.$^{-1}$)	
R_1	R_2	R_3	R_4	Hα	Hβ
H	H	H	H	1029 (s)	1125 (s)
OH	H	H	$COCH_3$[a]	1047 (m)	1138 (m)
H	H	OCH_3	Et[a]	1048 (ms)	1142 (s)
H	H	OH	$COCH_3$[a]	1073 (m)	1160 (ms)
H	OCH_3	OCH_3	H[b]	1045 (m)	1139 (s)
H	OH	$COCH_3$	H[c]	1042 (m)	1139 (s)
H	OH	COOH	H[c]	1041 (s)	1140 (s)
OH	OCH_3	OCH_3	H[d]	1087 (m)	1134 (s)
$OOCCH_3$	OCH_3	OCH_3	H[d]	1070 (m)	1136 (s)
OCH_3	OH	$COCH_3$	OCH_3[e,f]	1064 (s)	1143 (ms)

[a] P. K. Ramachandran, A. T. Tefteller, G. O. Paulson, T. Cheng, C. T. Lin, and W. J. Horton, *J. Org. Chem.*, **28**, 398 (1963). [b] Unpublished work by P. K. Ramachandran and W. J. Horton. [c] P. K. Ramachandran, T. Cheng, and W. J. Horton, *J. Org. Chem.*, **28**, 2744 (1963). [d] Unpublished work of C. T. Lin and W. J. Horton. [e] Unpublished work of E. Paul and W. J. Horton. [f] Spectrum run in carbon tetrachloride.

It is not known if this generalization can be applied to simple furan derivatives but Quilico, Piozzi, and Pavan[7] report that dendrolosin and tetrahydrodendrolosin, both monosubstituted furan derivatives, do have medium to strong bands at 1156 and 1075 cm.$^{-1}$.

Since the region of the spectrum under consideration is one where many types of absorptions occur, the generalization discussed above should be used cautiously and perhaps in a negative sense rather than a positive one, *i.e.*, the absence of a 1160–1125- or 1087–1020-cm.$^{-1}$ band indicating the lack of an α- or β-H on a benzofuran nucleus, rather than the occurrence of the proper absorption indicating the definite presence of the α- or β-H.

Experimental

All the infrared spectra were taken on a Beckman IR 5 with sodium chloride optics. Chloroform was used as solvent unless

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[1] L. H. Briggs and L. D. Colebrook, *J. Chem. Soc.*, 2458 (1960).

[2] A. R. Katritzky and J. M. Lagowski, *ibid.*, 657 (1959).

[3] T. Kubota, *Tetrahedron*, **4**, 68 (1958).

[4] A. H. J. Cross, S. G. E. Stevens, and T. H. E. Watts, *J. Appl. Chem.* (London), **7**, 562 (1957).

[5] L. W. Daasch, *Chem. Ind.* (London), 1113 (1958).

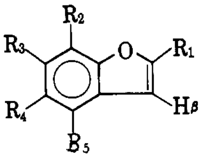
[6] A. H. J. Gross and T. H. E. Watts, *ibid.*, 1161 (1958).

[7] A. Quilico, F. Piozzi, and M. Pavan, *Tetrahedron*, **1**, 177 (1957).

[8] R. Royer, E. Bisagui, C. Hudry, A. Cheutin, and M. L. Desvaye, *Bull. soc. chim. France*, 1003 (1963).

[9] A. R. Katritzky and J. M. Lagowski, *J. Chem. Soc.*, 4155 (1958).

Table II.—Benzofuran Derivatives with One Furan Hydrogen



Compd.					Band, cm.$^{-1}$, H_{β}
R_1	R_2	R_3	R_4	R_5	
$COCH_3$	H	H	H	H^{a}	1135 (s)
$COOCH_3$	H	H	H	H	1143 (ms)
$COOCH_3$	H	H	OH	H^{b}	1152 (ms)
$COOCH_3$	H	H	OCH_3	H^{b}	1152 (ms)
$COOCH_3$	H	H	NH_2	H^{c}	1157 (s)
$COOCH_3$	H	H	$NHCOCH_3$	H^{c}	1152 (s)
$COOCH_3$	H	H	$COCH_3$	H^{c}	1126 (m)
$COOCH_3$	H	H	$C(CH_3)=NOH$	H^{c}	1163 (s)
$COOCH_3$	H	H	Cl	H^{c}	1122 (w)
COOH	H	H	C_2H_5	H^{c}	1142 (ms)
$CH(CH_3)_2$	H	H	$COCH_3$	H^{c}	1152 (ms)
$COH(CH_3)_2$	H	H	Cyclic ketal of $COCH_3$	H^{c}	1152 (ms)
$COOCH_3$	H	H	OH	$C_2H_5^{b}$	1152 (m) or 1131 (m)
$COOCH_3$	H	H	OH	$COCH_3^{b}$	1129 (m)
$C=CH_2CH_3$	H	OH	CONH	H^{c}	1142 (s)
$COOCH_3$	H	$OOCCH_3$	$COCH_3$	H^{c}	1136 (s)
$COOCH_3$	H	OH	Cyclic ketal of $COCH_3$	$H^{c,d}$	1156 (m) or 1129 (m)
$COOCH_3$	OCH_3	OCH_3	H	$H^{d,e}$	1165 (m) or 1135 (m)
$COOCH_3$	$COOCH_3$	H	H	OCH_3^{b}	1143 (m)
$COOCH_3$	NH_2	H	H	OCH_3^{b}	1172 (ms)
COOH	OH	H	H	$COCH_3^{b,f}$	1135 (s)
$COOCH_3$	$COCH_3$	H	C_2H_5	H^{c}	1136 (ms)
$COOCH_3$	OCH_3	H	NO_2	H^{g}	1125 (m)
$COOCH_3$	OCH_3	OCH_3	H	$OCH_3^{d,e}$	1149 (ms)
$COOCH_3$	OCH_3	OCH_3	H	NH_2^{g}	1157 (s)
$COOCH_3$	OCH_3	OCH_3	H	$NHCOCH_3^{g}$	1149 (s)
$COOCH_3$	OCH_3	OCH_3	H	$COCH_3^{g}$	1125 (s)
$COOCH_3$	OCH_3	OCH_3	H	$C(CH_3)=NOH^{g}$	1121 (s)
$COCH_3$	OH	OCH_3	OCH_3	H^{h}	1130 (s)
$COCH_3$	$OOCCH_3$	OCH_3	OCH_3	H^{h}	1134 (s)
$COCH_3$	OCH_3	OCH_3	OCH_3	H^{h}	1130 (s)
$COOCH_3$	OH	OCH_3	$COCH_3$	OH^{e}	1135 (s)
$COOCH_3$	$OOCCH_3$	OCH_3	$COCH_3$	OH^{e}	1149 (s)
$COOCH_3$	$OOCCH_3$	OCH_3	$COCH_3$	$OOCCH_3^{e}$	1138 (s)
COOH	OCH_3	OCH_3	$COCH_3$	OCH_3^{e}	1152 (s)
COOH	OCH_3	OCH_3	Br	OCH_3^{e}	1136 (s)
COOH	OCH_3	OCH_3	CH_3	OCH_3^{e}	1121 (s)
$COOCH_3$	OCH_3	OCH_3	CH_3	$OCH_3^{d,e}$	1150 (s)
$COCH_3$	$OOCCH_3$	OCH_3	$OOCCH_3$	$COCH_3^{h}$	1127 (m)
$COCH_2COCH_3$	$OOCCH_3$	OCH_3	$OOCCH_3$	$COCH_3^{h}$	1130 (m)

[a] J. I. Degraw and W. A. Bonner, *Tetrahedron*, **18**, 1295 (1962). [b] Footnote *a*, Table I. [c] Footnote *c*, Table I. [d] Spectrum run in carbon tetrachloride. [e] Footnote *e*, Table I. [f] Spectrum run as Nujol mull. [g] Footnote *b*, Table I. [h] Footnote *d*, Table I.

otherwise indicated. The preparation of the compounds listed in Tables I and II as previously unreported will be the subject of a later communication.

5H-Pyrimido[4,5-*b*][1,4]thiazin-6(7H)-one. The Product of a Novel Cyclization Reaction[1]

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Heteroaromatic-substituted alkanethiols, such as 2-benzimidazolemethanethiol (I), became of interest in a search for an effective heterocyclic modification of 2-aminoethanethiol as an antiradiation drug.[2] The reported[3] synthesis of I by the acid-catalyzed condensation of *o*-phenylenediamine and mercaptoacetic acid provided a good method for the synthesis of 2-benzimidazoleethanethiol (II) by a similar condensation in which 3-mercaptopropionic acid was used. The insolubility of 4,5-diaminopyrimidine (III) in ethyl mercaptoacetate, however, precluded the condensation expected to give the analogous purine-8-methanethiol (IV) under conditions suggested by Albert's synthesis of purine-8-methanol from III and ethyl glycolate.[4]

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[1] This investigation was supported by the U. S. Army Medical Research and Development Command under Contract No. DA-49-193-MD-2028.

[2] (a) T. P. Johnston and A. Gallagher, *J. Org. Chem.*, **27**, 2452 (1962); (b) J. R. Piper and T. P. Johnston, *ibid.*, **28**, 981 (1963); (c) T. P. Johnston and A. Gallagher, *ibid.*, **28**, 1305 (1963).

[3] G. K. Hughes and F. Lions, *J. Proc. Roy. Soc. N. S. Wales*, **71**, 209 (1938); *Chem. Abstr.*, **32**, 5830 (1938).

[4] A. Albert, *J. Chem. Soc.*, 2690 (1955).