

444. *N-Oxides and Related Compounds. Part XII.\* Infrared Spectra of Some Carbonyl Compounds.*

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The positions of the carbonyl stretching band in esters and ketones show that the pyridine 1-oxide ring can release electrons to the 4-position more easily than to the 3-position, but that the reverse is true of the pyridine ring.

All the bands in a monosubstituted pyridine or oxide may be correlated with those of other compounds containing either (a) the same nucleus or (b) the same substituent. Positions and apparent extinction coefficients of bands characteristic of carbonyl compounds are treated statistically, and tentative assignments are made.

PREVIOUS papers in this series recorded dipole moments which indicated that the ring in pyridine 1-oxide,<sup>2</sup> but not the ring in pyridine-boron trichloride,<sup>3</sup> could release electrons

\* Part XI, Hands and Katritzky, *J.*, 1958, 1754.

<sup>1</sup> For general review see Katritzky, *Quart. Rev.*, 1956, **10**, 395.

<sup>2</sup> Part IV, Katritzky, Randall, and Sutton, *J.*, 1957, 1769.

<sup>3</sup> Parts VIII and IX, Bax, Katritzky, and Sutton, *J.*, 1958, 1254, 1258.

to a substituent in the 4-position. To gain more evidence on this point, and to investigate 2- and 3-substituted compounds, in which non-linearity makes interpretation of dipole moments difficult, we have studied the infrared spectra of methyl and ethyl esters and methyl ketones. Carbonyl compounds were selected because they have already been

TABLE I. *Ethyl esters.*

No.	Ring †	1		2		3		4		5		6		7	
		CO	ε <sub>A</sub>	Chain	ε <sub>A</sub>	Et, CH <sub>2</sub> scissor	ε <sub>A</sub>	Et, CH <sub>3</sub> bend (as)	ε <sub>A</sub>	Et, CH <sub>3</sub> bend (s)	ε <sub>A</sub>	Et, CH <sub>2</sub> wag	ε <sub>A</sub>	cm. <sup>-1</sup>	ε <sub>A</sub>
<i>Compounds X·CO<sub>2</sub>Et</i>															
1	Ph	1716	360	—	—	1467 * 30	—	(—)	—	1391	30	1369	90	1313	120
2	4P <sup>a</sup>	1730	360	—	—	1465	25	1445	25	1393 * 45	—	1370	105	1326	135
3	3P	1724	360	—	—	1470	30	1447	25	1392	30	1370	100	1328	60
4	2P	1723	280	—	—	1465 † 55	—	(—)	—	1390	35	1369	115	1305	450
5	4PO	1722	390	—	—	1470 * 60	—	(—)	—	1390	35	1369	125	1303	270
6	3PO	1732	340	—	—	1468 * 55	—	(—)	—	1394	30	1370	110	1298 † 560	—
7	2PO	1741	260	—	—	1464	40	(—)	—	1391	25	1369	75	—	—
8	4PBCl <sub>3</sub>	1739	290	—	—	1460	35	(—)	—	1390	35	1370	110	1325	90
9	4PBBBr <sub>3</sub>	1739	330	—	—	1469	30	1447 * 35	—	1397	30	1371	100	1326	100
10	3PBCl <sub>3</sub>	1737	360	—	—	1464	50	(—)	—	1393	35	1371	110	1321	100
<i>Compounds X·CH<sub>2</sub>·CO<sub>2</sub>Et</i>															
11	Ph	1730	330	1415 *	25	1465 * 25	—	(—)	—	1391	20	1369	75	1325	55
12	4P	1736	270	(—)	—	1465 * 15	—	1450 * 20	—	1390	20	1370	75	1325 *	55
13	3P	1730	310	(—)	—	(—)	—	1444	35	1391	30	1367	85	1327	70
14	3PO	1737	360	1420 *	35	(—)	—	(—)	—	1395	30	1370	90	1334	70
<i>Compounds X·CH<sub>2</sub>·CH<sub>2</sub>·CO<sub>2</sub>Et</i>															
15	Ph	1730	330	1415	30	(—)	—	(—)	—	1391 * 35	—	1373	90	1340	40
16	4P	1731	330	(—)	—	1465 * 25	—	1445 * 45	—	(—)	—	1374	90	1339	45
17	3P	1731	320	(—)	—	(—)	—	1447	45	1391 * 35	—	1375	85	1345	40
<i>Compounds X·CH:CH·CO<sub>2</sub>Et</i>															
18	Ph	1711	380	1640	220	1465 * 25	—	(—)	—	1390	30	1369	110	1328	150
19	4P	1715	350	1648	85	1465	25	1445	25	1392	30	1367	105	1335	70
20	3P	1715	350	1646	150	(—)	—	1447	25	1390	25	1368	90	1335	30
21	2P	1712	370	1648	85	(—)	—	(—)	—	1392	25	1368	95	1317	290
22	4PO	1715	350	1644	140	(—)	—	(—)	—	1389	30	1368	100	1319 *	260
23	3PO	1715	330	1650	85	(—)	—	(—)	—	1391	30	1368	100	1319	270
24	2PO	1715	320	1639	65	1468 * 35	—	(—)	—	1392	35	1369	95	—	—
25	4PBCl <sub>3</sub> <sup>b</sup>	1723	425	1638	270	(CHCl <sub>3</sub> )	—	(CHCl <sub>3</sub> )	—	1390 * 40	—	1369	130	1336	70
<i>Compounds X·CO<sub>2</sub>Et</i>															
1	1277	530	1249 *	100	1174	70	1110	230	1100 * 130	1028 † 140	—	—	—	870	<15
2	1282	530	1249 *	90	1174	25	1120	170	1095	35	1018	65	—	{ 871	25
													—	{ 851	30
3	1284	500	(—)	—	1167	35	{ 1128 * 160	—	1086 * 40	1027 † 170	—	—	—	853	15
							{ 1110	205							
4	1293	250	1244	200	1171	50	{ 1135 * 185	—	1087	65	1015	45	—	852	25
							{ 1125	240							
5	1284 *	280	1258 † 570	(—)	(—)	—	1120	125	1091 *	85	1015	95	—	(—)	—
6	(—)	(—)	(1232 200)	(—)	(—)	—	1108	220	1077	30	1014 † 230	—	—	861	20
7	1311	270	(—)	—	1175 *	55	{ 1132	175	1094 † 120	1011	45	—	—	{ 878 *	35
							{ 1112 *	45						{ 866	40
8	1283	500	1245	95	1170	20	{ 1130	90	1091 *	60	1010	75	—	{ 870	60
							{ 1115 *	50						{ 855	35
							{ 1139 *	90							
9	1285	490	1240	90	1175	30	{ 1132	95	1093 *	45	1012	70	—	{ 870	55
							{ 1119 *	55						{ 856	35
10	1302	360	1258	55	1173	60	{ 1133	190	(—)	1010	75	—	—	857	65
							{ 1117	190							
<i>Compounds X·CH<sub>2</sub>·CO<sub>2</sub>Et</i>															
11	1296	90	1250	120	1155	130	1140 * 130	1094	30	1028 † 130	—	—	—	—	—
12	1300	75	1256	110	1156	95	1136 * 80	1095	25	1028	100	—	—	—	—
13	1300	75	1256	125	1153	120	1138 * 110	1094	40	1027 † 180	—	—	—	—	—
14	1303 *	105	(—)	—	1156 † 350	—	(—)	1093	25	1027	145	—	—	—	—

TABLE I. (Continued.)

No.	8		9		10		11		12		13		14		15	
	CCO				CO·O				Et		OEt		HC:CH		?	
cm. <sup>-1</sup>	$\epsilon_A$	cm. <sup>-1</sup>	$\epsilon_A$	cm. <sup>-1</sup>	$\epsilon_A$	cm. <sup>-1</sup>	$\epsilon_A$	cm. <sup>-1</sup>	$\epsilon_A$	cm. <sup>-1</sup>	$\epsilon_A$	cm. <sup>-1</sup>	$\epsilon_A$	cm. <sup>-1</sup>	$\epsilon_A$	
Compounds X·CH <sub>2</sub> ·CH <sub>2</sub> ·CO <sub>2</sub> Et																
15	1297	90	1257	90	1180	125	{ 1159 125 1149 * 110	1094	40	{ 1035 85 1015 50	—	—	—	—	—	—
16	1296	90	1247 *	105	1182	135	1151 105	1094	30	{ 1034 60 1018 40	—	—	855	20	—	—
17	1299	85	1252 *	100	1183	150	1154 90	1097 *	40	{ 1034 * 70 1019 * 40	—	—	—	—	—	—
Compounds X·CH:CH·CO <sub>2</sub> Et																
18	1310	280	1271	180	1179	310	—	1094	45	1033	105	980	115	{ 882 20 860 40	—	—
19	{ 1310 300 1297 * 190	—	1266	145	1175	230	—	1093	30	1028	95	{ 981 150 957 * 20	842	20	—	—
20	1311	290	1268	155	1175	200	—	1094	30	1025 †	110	981	110	{ 880 20 865 25	—	—
21	1299	260	1266	140	1161	170	—	1092 †	55	1029	100	981	120	872	<15	—
22	1311	270	(—)	—	1177 *	330	—	1093	55	1032 †	185	978	155	884	15	—
23	1303	160	(—)	—	1179	260	—	1093	30	1030	115	977	160	{ 875 * 15 836 15	—	—
24	1309	300	1242	200	1184	200	—	1094	30	1031 *	95	982	90	902	20	—
25	1309	390	(CHCl <sub>3</sub> )	(CHCl <sub>3</sub> )	—	—	—	(—)	—	1027	110	{ 978 165 968 60	(CHCl <sub>3</sub> )	—	—	—

\* Shoulder.

† Abbreviations used are: P = pyridine. PO = pyridine 1-oxide. PBCl<sub>3</sub> = pyridine-boron trichloride. PBBr<sub>3</sub> = pyridine-boron tribromide. Preceding numerals denote position of substituent.‡ Peak considered to be formed by the superimposition of two bands, which will consequently appear twice. — Absence of band. (—) Band is masked by other stronger absorption. (CHCl<sub>3</sub>) Band masked by solvent.\* Other band at 3310 cm.<sup>-1</sup> (20) (overtone?). † 0.02M-Solution in 1 mm. cell.

extensively studied (for reviews see refs. 4a, 5a) and it is well established that in a given series the C=O stretching frequency decreases as the electron-releasing power of an attached group increases.<sup>4a, 5a</sup> For consistency the spectra were all measured at 0.2M-concentration in chloroform in a 0.117 mm. cell. The bands could be divided into those characteristic of the nucleus and those characteristic of the substituent. This paper records the latter; the nuclear bands will be discussed elsewhere,<sup>6</sup> together with those of rings containing other substituents, with which excellent correlations are shown. Bands ( $\epsilon \geq 15$ ) characteristic of neither nucleus nor substituent, of which there are few, are indicated by lettered footnotes.

Chloroform was used because more compounds are soluble in it than in, e.g., carbon disulphide or carbon tetrachloride. In a 0.1 mm. cell only the bands at 3020—3000, 1240—1200 and below 805 cm.<sup>-1</sup> are obscured by solvent absorption.<sup>4c</sup> Apparent molecular extinction coefficients are recorded; they are comparable between themselves, although considerably different from the true molecular extinction coefficients, both because of the variation of  $\epsilon_A$  with concentration,<sup>7, 8</sup> and because of the finite slit widths used;<sup>4d, 7</sup> in addition, corrections have not been made for absorption by the finite mole fraction of solvent displaced,<sup>4e</sup> and the difference in densities<sup>4e</sup> and refractive indices<sup>4f</sup> of solvent and solution; there are also other sources of error.<sup>4g</sup> Also at 0.2M-concentration

<sup>4</sup> Jones and Sandorfy in Weissberger, "Technique of Organic Chemistry, Vol. IX. Chemical Applications of Spectroscopy," Interscience Publ. Inc., London, 1956: (a) p. 443 ff., (b) p. 473 ff., (c) p. 300, (d) p. 273, (e) p. 265, (f) p. 263, (g) p. 269, (h) p. 471, (i) pp. 369, 374, 377 ff., (j) p. 502 ff., (k) p. 482.

<sup>5</sup> Bellamy, "The Infrared Spectra of Complex Molecules," Methuen, London, 1956: (a) p. 114—163, (b) p. 119 ff., (c) p. 21, (d) p. 161 ff., (e) p. 163.

<sup>6</sup> Katritzky *et al.*, following papers; Katritzky, Coates, Beard, Hands, and Lagowski, to be published.

<sup>7</sup> Thompson, *Spectrochim. Acta*, 1956, **9**, 133.

<sup>8</sup> Jones, *ibid.*, p. 235.

in the 0.117 mm. cell, values outside the range 50—250 will be very approximate, because they correspond to optical densities outside the optimum range for measurement. The

TABLE 2. *Methyl esters.*

No.	Ring	1 CO		2 Chain		3 OMe CH <sub>3</sub> bend (s)		4		5 CCO		6	
		cm. <sup>-1</sup>	ε <sub>A</sub>	cm. <sup>-1</sup>	ε <sub>A</sub>	cm. <sup>-1</sup>	ε <sub>A</sub>	cm. <sup>-1</sup>	ε <sub>A</sub>	cm. <sup>-1</sup>	ε <sub>A</sub>	cm. <sup>-1</sup>	ε <sub>A</sub>
<i>Compounds X·CO<sub>2</sub>Me</i>													
26	Ph	1724	370	—	—	1437	100	1315	140	1279	480	1250 *	65
27	4P	1735	390	—	—	1440	120	1327	160	1286	540	1254 *	75
28	3P	1730	370	—	—	1438	90	1328	65	1285	370	(—)	—
29	2P	1730	340	—	—	1446	135	1310	310	1294	190	1246	190
30	4PO	1727	390	—	—	1437	140	1304	270	(—)	—	1261 †	600
31	3PO	1741	360	—	—	1442 †	270	1307 †	570	(—)	—	(1236	230)
32	2PO	1749	260	—	—	1442	240	—	—	1317	260	(—)	—
33	4PBCl <sub>3</sub>	1745	340	—	—	1439 *	180	1325	110	1291	500	1242	80
34	3PBCl <sub>3</sub>	1745	420	—	—	1441 †	250	1324 *	130	1304	450	1255	35
<i>Compounds X·CH<sub>2</sub>·CO<sub>2</sub>Me</i>													
35	Ph	1735	310	1418 *	25	1439	95	1341	60	1299	65	1255	110
36	4P	1740	300	(—)	—	1440	90	1346	50	1300	60	1260	110
<i>Compounds X·CH<sub>2</sub>·CH<sub>2</sub>·CO<sub>2</sub>Me</i>													
37	Ph	1731	320	1418 *	25	1440	110	1365	60	1295	75	1260 *	80
38	4P *	1732	280	(—)	—	1438	110	1365	50	{ 1310 *	55	1260 *	80
<i>Compounds CH:CH·CO<sub>2</sub>Me</i>													
39	Ph	1714	350	1640	200	1436	90	1330	195	1315	210	1278	200
40	4P	1718	360	1648	85	1435	115	1337	120	{ 1312	320	1278	180
<i>Compounds X·CO·O</i>													
No.	Ring	7		8		9 ?		10 OMe		11 CH:CH		12 ?	
		cm. <sup>-1</sup>	ε <sub>A</sub>	cm. <sup>-1</sup>	ε <sub>A</sub>	cm. <sup>-1</sup>	ε <sub>A</sub>	cm. <sup>-1</sup>	ε <sub>A</sub>	cm. <sup>-1</sup>	ε <sub>A</sub>	cm. <sup>-1</sup>	ε <sub>A</sub>
<i>Compounds X·CO<sub>2</sub>Me</i>													
26	Ph	{ 1192 *	50	1114	195	1100 *	75	967	30	—	—	823	<15
		{ 1175	65										
27	4P	1192 *	60	1124	210	—	—	967	60	—	—	850	30
28	3P	1188 †	50	1112 *	140	1085	25	960	20	—	—	825	30
29	2P	1193 *	85	1128	220	1089 †	45	966	40	—	—	833	25
30	4PO	(—)	—	1122	100	1091	50	964	65	—	—	—	—
31	3PO	1192 *	70	1109	220	1080 *	25	983	85	—	—	(—)	—
32	2PO	(—)	—	1136	220	1094 †	90	958	25	—	—	815	<15
33	4PBCl <sub>3</sub>	(—)	—	{ 1130	105	—	—	960	70	—	—	870	30
				{ 1121 *	45								
34	3PBCl <sub>3</sub>	1192 †	70	1135	250	1081 *	60	960	25	—	—	—	—
<i>Compounds X·CH<sub>2</sub>·CO<sub>2</sub>Me</i>													
35	Ph	1158	125	1140 *	105	—	—	1013	60	—	—	—	—
36	4P	1156	95	1140 *	85	—	—	1012	50	—	—	—	—
<i>Compounds X·CH<sub>2</sub>·CH<sub>2</sub>·CO<sub>2</sub>Me</i>													
37	Ph	1194	90	1160	110	—	—	{ 1028 †	35	—	—	—	—
								{ 987	30				
38	4P *	1191	90	1170	110	—	—	{ 1023	20	—	—	{ 832	25
								{ 981	35			{ 810	45
<i>Compounds CH:CH·CO<sub>2</sub>Me</i>													
39	Ph	{ 1187 *	125	—	—	—	—	{ 1039	40	{ 987 *	65	863	45
		{ 1172	290					{ 1014	45	{ 980	110		
40	4P	{ 1190 *	110	—	—	—	—	{ 1035	50	{ 980	150	{ 859	20
		{ 1170	270					{ 1010	30	{ 955	15	{ 842	20

\* Other band at 1339 cm.<sup>-1</sup> (35). See also footnotes to Table 1.

standardised conditions under which the spectra were measured are given on p. 2191. ε<sub>A</sub> was reproducible with a standard deviation of about 8%.

*The Carbonyl Stretching Band.*—(i) When a carbonyl group is directly attached to the ring, a definite pattern of changes is observed. All the heterocyclic compounds have

higher C=O stretching frequencies than the corresponding benzene derivative; the increments in wave numbers are shown in Table 5. As the differences were small, the position of the CO band for the ethyl esters was also measured at 5 times the normal resolution; the results were within  $\pm 2$  cm.<sup>-1</sup> of those obtained in the normal way.

TABLE 3. *Methyl ketones.*

No.	Ring	1		2		3		4		5		6		7		8			
		CO	$\epsilon_A$	Me?	$\epsilon_A$	Me	$\epsilon_A$	cm. <sup>-1</sup>	$\epsilon_A$	cm. <sup>-1</sup>	$\epsilon_A$	cm. <sup>-1</sup>	$\epsilon_A$	cm. <sup>-1</sup>	?	$\epsilon_A$	cm. <sup>-1</sup>	$\epsilon_A$	
41	Ph <sup>a</sup>	1680	290	1420	30	1358	135	{ 1309 1295	{ 25 25	1264	290	1245	*	70	(—)		954	45	
42	4P <sup>b</sup>	1700	230	(—)		1361	135	1322	20	1263	310	1242	*	105	1082		15	960	25
43	3P	1690	340	(—)		1359	130	—		1270	280	(CHCl <sub>3</sub> )		1089		25	956	45	
44	2P	1695	240	1417	25	1358	165	1297	70	1283	160	(1234 105)		1087	*	<15	954	45	
45	4PO	1692	260	(—)		1359	150	1300	85	1280	* 130	(—)		1080		15	959	55	
46	3PO	1707	190	(—)		1361	115	1295	* 240	(—)		(CHCl <sub>3</sub> )		1084		30	961	15	
47	2PO	1691	220	(—)		1357	115	—		1300	190	(1235 140)		1075		30	968	15	

<sup>a</sup> Other band at 1177 cm.<sup>-1</sup> (20). <sup>b</sup> Shoulder at 1146 cm.<sup>-1</sup> (50). See also footnotes to Table 1.

TABLE 4. *Aldehydes.*

No.	Ring	1		2		3		4		5		6		7		8	
		CH str.	$\epsilon_A$	cm. <sup>-1</sup>	$\epsilon_A$	cm. <sup>-1</sup>	CO str.	$\epsilon_A$	cm. <sup>-1</sup>	?	$\delta$ CH	$\epsilon_A$	cm. <sup>-1</sup>	$\epsilon_A$	cm. <sup>-1</sup>	?	$\epsilon_A$
48	Ph <sup>a</sup>	2850	35	2740	35	1705	350	1652	30	1389	20	1309	75	1165	70	828	120
49	4P	2840	25	2750	<15	1721	280	1674	30	1388	35	1322	85	1190	65	835	50
50	3P	2850	30	2740	20	1712	370	1667	* 30	1388	40	1326	55	1190	* 35	832	100
51	2P	2830	30	2740	* <15	1717	300	1656	* 20	1365	25	1294	20	(CHCl <sub>3</sub> )		832	100

<sup>a</sup> Other band at 1195 cm.<sup>-1</sup> (20). See also footnotes to Table 1.

TABLE 5. *Carbonyl stretching bands. Increments in wave numbers over that for the corresponding benzenoid compound.*

	4P	3P	2P	4PO	3PO	2PO	4PBCl <sub>3</sub>	3PBCl <sub>3</sub>
CO <sub>2</sub> Et .....	14	8	7	6	16	25	23	21
CO <sub>2</sub> Et <sup>*</sup> .....	14	8	10	9	18	28	24	25
CO <sub>2</sub> Me .....	11	6	6	3	17	25	21	21
COMe .....	20	10	15	12	27	11	—	—
CHO .....	16	7	12	—	—	—	—	—

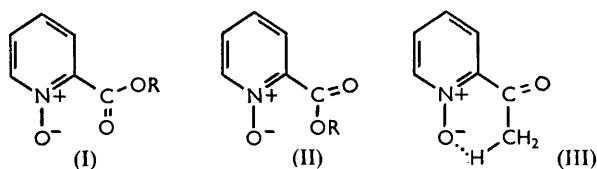
<sup>\*</sup> Differences obtained at high resolution. The CO frequency in ethyl benzoate was 1714. See also footnote † to Table 1.

For 3- and 4-substituted compounds, in each series, the increments are in the order: Ph < 4-pyridyl 1-oxide ~ 3-pyridyl < 4-pyridyl < 3-pyridyl 1-oxide < 3- or 4-position of pyridine-boron trichloride. Thus the rings should have electron-releasing ability in the stated positions in the opposite order. This agrees with evidence from dipole moments,<sup>2,3</sup> ultraviolet spectra,<sup>9</sup> and chemical reactivity (electrophilic reagents attack pyridines in the 3-, but pyridine 1-oxides in the 4-position<sup>1</sup>), and with theoretical predictions. In no important canonical form of pyridine 1-oxide does a negative charge appear at the 3-position, and inductive effects make the 1-oxide less able than the pyridine to release electrons at that position. The ring of pyridine-boron trichloride is still less able to release electrons in both the 3- and the 4-position.

Consideration of the 2-substituted compounds is more difficult owing to possible steric hindrance (in the 1-oxides) and direct field effects. The increments for the 2-substituted pyridine 1-oxide esters are much greater than for 2-acetylpyridine 1-oxide. This may be because both the planar configurations (I and II) of the ester are unfavoured owing to steric and direct field effects, but the ketone can adopt the configuration (III) with

<sup>9</sup> Katritzky and Monro, unpublished work.

possibly a weak hydrogen bond. The reluctance of pyridine oxides to undergo electrophilic substitution in the 2-position is probably due to the direct field effect.<sup>1</sup> Electron-availability at the 2-position in pyridines appears to be intermediate between that in the 3- and the 4-position.



(ii) For compounds  $X\cdot CH_2\cdot CO_2Et$ , the effect seems to persist weakly, for the frequencies are in the order:  $Ph \sim 3\text{-pyridyl} < 4\text{-pyridyl} \sim 3\text{-pyridyl 1-oxide}$ ; but in compounds  $X\cdot CH_2\cdot CH_2\cdot CO_2Et$  the position of the CO band is constant at  $1731\text{ cm}^{-1}$  and in compounds  $X\cdot CH\cdot CH\cdot CO_2Et$  it is relatively constant at  $1715\text{ cm}^{-1}$ , somewhat lower, as expected,<sup>4a</sup> than the  $1735$  and  $1720\text{ cm}^{-1}$  recorded in non-polar solvents for fatty and  $\alpha\beta$ -unsaturated esters respectively.<sup>4a</sup>

(iii) The intensities of the carbonyl bands are in the ranges: ethyl esters ( $260\text{--}390$ ) [ $(335 \pm 35)$ ]; \* methyl esters ( $260\text{--}420$ ) [ $(340 \pm 45)$ ]; methyl ketones ( $190\text{--}340$ ) [ $(250 \pm 50)$ ]; and aldehydes ( $280\text{--}370$ ). These values are lower than those which were recorded for similar compounds when a calcium fluoride prism was used<sup>10</sup> (e.g.,  $Ph\cdot CH_2\cdot CO_2Et$   $540$ ,  $Ph\cdot CO_2R$  ca.  $700$ <sup>10c</sup>), but they agree with Cross and Rolfe's measurements<sup>11</sup> with sodium chloride optics ( $Ph\cdot COMe$   $310$ ,  $R\cdot CO_2R$  ca.  $350$ ,  $Ph\cdot CHO$   $320$ ).

*The 3000  $cm^{-1}$  Region.*—Of the CH stretching bands, because of solvent interference,<sup>6</sup> the sodium chloride prism resolved only the band due to the hydrogen atom of the CHO group; in each of the aldehydes a doublet was found near  $2850$  and  $2750\text{ cm}^{-1}$  ( $\leq 40$ ) (Table 4, cols. 1 and 2); such doublets have been observed and discussed for other aldehydes by Pinchas.<sup>12</sup>

*The 1650  $cm^{-1}$  Region.*—(i) Compounds  $X\cdot CH\cdot CH\cdot CO_2Et$  (Table 1, col. 2) and  $X\cdot CH\cdot CH\cdot CO_2Me$  (Table 2, col. 2) show the C:C stretching band at  $1651\text{--}1638$  [ $1644 \pm 4$ ]  $cm^{-1}$ ; it had been reported<sup>4c</sup> that for the C:C band in  $\alpha\beta$ -unsaturated ketones the intensity increased and the position was lowered by ca.  $30\text{ cm}^{-1}$ , from the  $1678\text{--}1668\text{ cm}^{-1}$  of unconjugated compounds. The intensity and frequency ( $cm^{-1}$ ) of the bands are in the order:

Ph	3-Pyridyl	4-Pyridyl 1-oxide	4-Pyridyl	3-Pyridyl 1-oxide	2-Pyridyl	2-Pyridyl 1-oxide
220	> 150	~ 140	> 85	~ 85	~ 85	> 65
1640	< 1646	~ 1644	< 1649	~ 1650	~ 1648	> 1639

thus it appears that the greater the electron-donating power of the ring, the greater is the intensity of the band, and the lower its frequency (*i.e.*, the greater the single-bond character). The frequency for the 2-substituted pyridine oxide, and the frequency and intensity for the 4-substituted pyridine-boron trichloride are out of line with this generalisation; possibly here receipt of electrons by the ring from the double bond becomes of overriding importance.

The bands for the two available compounds  $X\cdot CH\cdot CH\cdot CO_2Me$  agree well with those for corresponding ethyl esters.

\* Values in parentheses are apparent molecular extinction coefficients. Values in square brackets are arithmetical means and standard deviations, calculated by omitting those compounds where the band is present as a shoulder, and, in the case of  $\epsilon_A$ , those in which it is superimposed on another band or measured in a 1 mm. cell.

<sup>10</sup> (a) Jones, Ramsay, Keir, and Dobriner, *J. Amer. Chem. Soc.*, 1952, **74**, 80; (b) Marion, Ramsay, and Jones, *ibid.*, 1951, **73**, 305; (c) Hampton and Newell, *Analyt. Chem.*, 1949, **21**, 914.

<sup>11</sup> Cross and Rolfe, *Trans. Faraday Soc.*, 1951, **47**, 354.

<sup>12</sup> Pinchas, *Analyt. Chem.*, 1957, **29**, 334.

(ii) The aldehydes show a weak band or shoulder (Table 4, col. 4) at 1674—1652  $\text{cm}^{-1}$  (20—30), possibly due to contamination by the corresponding acid.

*The 1500—1350  $\text{cm}^{-1}$  Region.*—Previous workers have noticed that intensities of methyl and methylene C-H deformations are enhanced when the groups are near an oxygen atom,<sup>5c,13</sup> and we confirm this.\*

(i) Where these frequencies are at  $>1410 \text{ cm}^{-1}$  they are overlapped by nuclear bands,<sup>6</sup> and interpretation of the spectrum can be difficult; but the known<sup>13,14</sup> asymmetrical bending vibrations of  $\text{CO}_2\text{Me}$  groups at 1446—1435  $\text{cm}^{-1}$  (90—140 except for the 2-pyridyl 1-oxide derivative where it is overlapped) [ $1439 \pm 3 \text{ cm}^{-1}$  ( $110 \pm 15$ )] is easily distinguished (Table 2, col. 3). In methyl acetate the band occurs at 1435  $\text{cm}^{-1}$  (130).<sup>15</sup> The ethyl esters show weaker bands at 1470—1460  $\text{cm}^{-1}$  (25—50) and 1447—1444  $\text{cm}^{-1}$  (25—45) (Table 1, cols. 3 and 4), corresponding respectively to the scissors methylene vibration and the asymmetrical bending of the (ethoxy) methyl group found by Jones and Nolin<sup>16</sup> at respectively 1464 (35) and 1446  $\text{cm}^{-1}$  (40) for ethyl acetate. For the only two methyl ketones where the region is not obscured, bands are found at 1420—1417  $\text{cm}^{-1}$  (25—30) (Table 3, col. 2). Weak bands or shoulders at 1418—1415  $\text{cm}^{-1}$  are sometimes found for the esters  $\text{X}\cdot\text{CH}_2\cdot\text{CO}_2\text{R}$  and  $\text{X}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{R}$  (Table 1, col. 2; Table 2, col. 2).

(ii) The known methyl CH deformation for acetyl groups (ref. 13, at *ca.* 1364  $\text{cm}^{-1}$ ; ref. 17, at 1370  $\text{cm}^{-1}$ ) was found at 1361—1357  $\text{cm}^{-1}$  (115—165) [ $1359 \pm 1.5 \text{ cm}^{-1}$  ( $135 \pm 20$ )] (Table 3, col. 3).

(iii) The ethyl esters show bands at 1397—1389  $\text{cm}^{-1}$  (20—35) [ $1391.5 \pm 2 \text{ cm}^{-1}$  ( $30 \pm 5$ )] and 1375—1367  $\text{cm}^{-1}$  (75—125) [ $1370 \pm 2 \text{ cm}^{-1}$  ( $100 \pm 10$ )] (Table 1, cols. 5 and 6), corresponding respectively to the (ethoxy) methyl symmetrical bending and methylene wagging modes found by Nolin and Jones<sup>16</sup> at respectively 1393 (35) and 1359  $\text{cm}^{-1}$  (60) for ethyl acetate; the latter was found at *ca.* 1372  $\text{cm}^{-1}$  by Francis<sup>13</sup> for some simple ethyl esters.

(iv) The aldehydes show a weak band at 1389—1365  $\text{cm}^{-1}$  (20—40) (Table 4, col. 5), which is probably the CH in-plane deformation mode shown in Raman spectra as a strong band at *ca.* 1390  $\text{cm}^{-1}$ .<sup>18</sup>



*The 1350—1240  $\text{cm}^{-1}$  Region.*—The absorption in this region is assigned to the group (IV) because corresponding methyl and ethyl esters show almost identical absorption there (Table 1, cols. 7—9; Table 2, cols. 4—6) and the absorption of the methyl ketone (IV; X = C instead of O) is similar (Table 3, cols. 4—6), but that of the aldehydes is very different (Table 4, col. 6). The absorption depends on the environment of the carbon atom to which the carbonyl group is attached. Interpretation of this region in the oxides is sometimes difficult because of overlap with the intense  $\text{N}^+\text{---}\text{O}^-$  band. Strong absorption by esters has been found previously in this region,<sup>4i, 5d</sup> and assigned to C—O stretching modes. Where the acid radical is kept constant and the alkyl radical changed the position of the band varies inversely with that of the C=O stretching band;<sup>4k</sup> this is neither expected nor found in our compounds.

(i) Compounds  $\text{X}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$  and  $\text{X}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$  and the corresponding methyl esters all show three bands, which steadily increase in intensity towards lower frequencies.

\* In  $\gamma$ -picoline oxide the intensity of the  $\text{CH}_3$  symmetrical deformation is  $<10$ , but in  $\alpha$ -picoline oxide it is 25, doubtless owing to the proximity of the  $\text{N}^+\text{---}\text{O}^-$  group (Katritzky, Beard, and Monro, unpublished observations).

<sup>13</sup> Francis, *J. Chem. Phys.*, 1951, **19**, 942.

<sup>14</sup> Jones, Cole, and Nolin, *J. Amer. Chem. Soc.*, 1952, **74**, 5648, 5662.

<sup>15</sup> Nolin and Jones, *Canad. J. Chem.*, 1956, **34**, 1382.

<sup>16</sup> *Idem*, *ibid.*, p. 1392.

<sup>17</sup> Thompson and Torkington, *J.*, 1945, 640.

<sup>18</sup> Kohlrausch, "Ramanspektren," Becker and Erler, Leipzig, 1943, pp. 281—282.

The first band is at  $1365\text{ cm}^{-1}$  for  $\text{X}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$ , at  $1346\text{--}1341\text{ cm}^{-1}$  for  $\text{X}\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$ , at  $1345\text{--}1339\text{ cm}^{-1}$  for  $\text{X}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , and at  $1334\text{--}1325\text{ cm}^{-1}$  for  $\text{X}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ ; the intensities are all  $(40\text{--}70)$  [ $55 \pm 10$ ]. All the compounds show the other bands at  $1300\text{--}1295\text{ cm}^{-1}$  ( $60\text{--}90$ ) [ $1298 \pm 2\text{ cm}^{-1}$  ( $80 \pm 10$ )] and at  $1260\text{--}1250\text{ cm}^{-1}$  ( $90\text{--}125$ ) [ $1256 \pm 3\text{ cm}^{-1}$  ( $110 \pm 10$ )]. The first of these three bands may be due to a wagging mode of the group adjacent to the carbonyl, which shows at  $1356\text{ cm}^{-1}$  in methyl propionate and at  $1347\text{ cm}^{-1}$  in ethyl propionate.<sup>13</sup>

(ii) Compounds  $\text{X}\cdot\text{CO}_2\text{Et}$ ,  $\text{X}\cdot\text{CO}_2\text{Me}$ ,  $\text{X}\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{Et}$ , and  $\text{X}\cdot\text{COMe}$  also show in general three bands in this region; the positions and intensities depend in a regular way both on the ring and on the substituent. Absorption in the two compounds  $\text{X}\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{Me}$  available closely resembles that in the corresponding compounds  $\text{X}\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{Et}$ .

(a) The first of these bands for compounds  $\text{X}\cdot\text{CO}_2\text{Me}$ ,  $\text{X}\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{Et}$ , and  $\text{X}\cdot\text{COMe}$  are respectively at the following positions relative to that for  $\text{X}\cdot\text{CO}_2\text{Et}$ :  $0\text{--}5$  [ $1.5 \pm 1.5$ ] higher,  $7\text{--}15$  [ $10.5 \pm 3$ ] higher and  $3\text{--}8$  [ $5 \pm 2$ ]  $\text{cm}^{-1}$  lower, and  $0.69\text{--}1.22$  [ $1.06 \pm 0.19$ ],  $0.50\text{--}1.25$  [ $0.80 \pm 0.30$ ], and  $0.15\text{--}0.31$  [ $0.21 \pm 0.07$ ] times as intense. If the benzenoid compounds (intensity  $120\text{--}150$  in the esters,  $25$  in the ketone) are taken as standards, the bands in the corresponding 3- and 4-pyridyl derivatives and their boron trichloride compounds are  $7\text{--}15$  [ $11 \pm 3$ ]  $\text{cm}^{-1}$  higher and of intensity  $(30\text{--}160)$  [ $90 \pm 40$ ] for the esters and  $(20)$  for the ketone. For the 2-pyridyl and 4- and 3-pyridyl 1-oxide derivatives the bands are  $5\text{--}15$  [ $10 \pm 3$ ]  $\text{cm}^{-1}$  lower and of intensity  $(270\text{--}450)$  [ $310 \pm 80$ ] for the esters and *ca.*  $(80)$  for the ketones.

(b) The second band is at a relatively constant position  $1311\text{--}1299$  [ $1308 \pm 4$ ]  $\text{cm}^{-1}$  and intensity  $(160\text{--}300)$  [ $265 \pm 50$ ] in the compounds  $\text{X}\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{Et}$ . The in-plane *trans*- $\text{CH}=\text{CH}$  deformation mode would be expected in this region, but the band is weak, at least in non-conjugated olefins.<sup>19</sup>

Fluctuations in position and intensity are again parallel for compounds  $\text{X}\cdot\text{CO}_2\text{Et}$ ,  $\text{X}\cdot\text{CO}_2\text{Me}$ , and  $\text{X}\cdot\text{COMe}$ . Bands for corresponding compounds in the last two series are respectively at positions  $1\text{--}8$  [ $3\frac{1}{2} \pm 2\frac{1}{2}$ ]  $\text{cm}^{-1}$  higher, and  $10\text{--}19$  [ $13 \pm 3$ ]  $\text{cm}^{-1}$  lower than, and of intensity  $0.74\text{--}1.25$  [ $0.95 \pm 0.17$ ] and  $0.55\text{--}0.70$  [ $0.61 \pm 0.06$ ] times, those of the  $\text{X}\cdot\text{CO}_2\text{Et}$  series.

In compounds  $\text{X}\cdot\text{CO}_2\text{Et}$ ,  $\text{X}\cdot\text{CO}_2\text{Me}$ , and  $\text{X}\cdot\text{COMe}$  the position relative to the corresponding phenyl compound varies in the order: 2-pyridyl 1-oxide  $34\text{--}38$ , 3-pyridyl-boron trichloride  $24\text{--}25$ , 2-pyridyl  $15\text{--}19$ , 4-pyridyl-boron trichloride  $6\text{--}12$ , 3-pyridyl  $6\text{--}7$ , and 4-pyridyl  $-1$  to  $7$  wavenumbers higher. The intensities for methyl and ethyl pyridine-2-carboxylate and their oxides are  $(190\text{--}280)$  [ $240 \pm 35$ ], and for the ketones  $(160\text{--}190)$ ; whereas in the 3- and 4-pyridyl series, as well as for their boron chloride compounds and the phenyl series, the esters have an intensity of  $(360\text{--}540)$  [ $475 \pm 65$ ], and the ketones  $(280\text{--}310)$ .

(c) The third band is too often obscured by solvent or  $\text{N}^+\text{--O}^-$  absorption for any definite conclusions to be legitimate about its position or intensity.

(iii) The aldehydes show a single band at  $1326\text{--}1294\text{ cm}^{-1}$  ( $20\text{--}85$ ).

*The 1200--1100 cm<sup>-1</sup> Region.*—Absorption in this region is assigned to the group (V), for ketones do not absorb here, and aldehydes show merely a single band at *ca.*  $1190\text{ cm}^{-1}$  ( $\leq 70$ ) (Table 4, col. 7), but the absorption in corresponding methyl and ethyl esters is very similar (Table 1, cols. 10 and 11; Table 2, cols. 7 and 8).

(i) Compounds  $\text{X}\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{R}$  ( $\text{R} = \text{Et}$  and  $\text{Me}$ ) show one band at  $1184\text{--}1161\text{ cm}^{-1}$  ( $170\text{--}310$ ) [ $1174 \pm 7\text{ cm}^{-1}$  ( $240 \pm 50$ )]. A band at  $1200\text{--}1100\text{ cm}^{-1}$  has been reported for unsaturated esters.<sup>5e</sup>

(ii) Compounds  $\text{X}\cdot\text{CH}_2\cdot\text{CO}_2\text{R}$  ( $\text{R} = \text{Et}$  and  $\text{Me}$ ) show a band at  $1158\text{--}1153\text{ cm}^{-1}$  ( $95\text{--}130$ ) [ $1155 \pm 2\text{ cm}^{-1}$  ( $110 \pm 15$ )] which has a shoulder at  $1140^*\text{--}1136^*\text{ cm}^{-1}$  ( $80\text{--}130$ ).

(iii) Compounds  $\text{X}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$  show two bands at  $1183\text{--}1180\text{ cm}^{-1}$  ( $125\text{--}150$ )

<sup>19</sup> Sheppard and Simpson, *Quart. Rev.*, 1952, **6**, 1.



and 1159—1151  $\text{cm}^{-1}$  (90—125); these two bands are shown by the compounds  $\text{X}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$  at *ca.* 10  $\text{cm}^{-1}$  higher frequencies, but have very similar intensities.

(iv) Compounds  $\text{X}\cdot\text{CO}_2\text{Et}$  show a band at 1175—1170  $\text{cm}^{-1}$  (20—70) [ $1172 \pm 3 \text{ cm}^{-1}$  ( $40 \pm 20$ )] which is at higher frequencies ( $\geq 1188$ ) in compounds  $\text{X}\cdot\text{CO}_2\text{Me}$  and is partly obscured by solvent absorption. Compounds  $\text{X}\cdot\text{CO}_2\text{Me}$  and  $\text{X}\cdot\text{CO}_2\text{Et}$  absorb at 1136—1108  $\text{cm}^{-1}$  (100—275) [ $1123 \pm 10 \text{ cm}^{-1}$  ( $180 \pm 55$ )]; the peak for the former is at 0—4  $\text{cm}^{-1}$  above that for the latter and has 0.80—1.30 [ $1.07 \pm 0.17$ ] times the intensity. The peaks for these ethyl esters often show a shoulder.

*The 1100—1080  $\text{cm}^{-1}$  Region.*—In this region (Tables 1—3, cols. 12, 9, and 7 respectively), all the ethyl esters and ketones show a peak at respectively 1095—1077  $\text{cm}^{-1}$  (25—65) [ $1092 \pm 4 \text{ cm}^{-1}$  ( $35 \pm 10$ )] and 1089—1075  $\text{cm}^{-1}$  (15—30) [ $1082 \pm 5 \text{ cm}^{-1}$  ( $25 \pm 10$ )], which is present only for those methyl esters with the group directly attached to the ring, and not all of these. The band is possibly present in spectra of the other methyl esters at intensities too low to be distinguished. Ethyl acetate shows a band at 1097  $\text{cm}^{-1}$  (40).<sup>16</sup>

*The 1040—950  $\text{cm}^{-1}$  Region.*—(i) The *trans*-CH:CH CH deformation of compounds  $\text{X}\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{R}$  (R = Me and Et) occurs at 982—977  $\text{cm}^{-1}$  (90—165) [ $980 \pm 2 \text{ cm}^{-1}$  ( $130 \pm 25$ )] (Table 1, col. 14; Table 2, col. 11); in simple *trans*-olefins it occurs at 980—965  $\text{cm}^{-1}$  (50—150).<sup>4i</sup>

(ii) The ketones show a band at 968—954  $\text{cm}^{-1}$  (15—55) [ $959 \pm 5 \text{ cm}^{-1}$  ( $35 \pm 15$ )] (Table 3, col. 8).

(iii) All the ethyl esters have a band at 1035—1010  $\text{cm}^{-1}$  (45—145) (Table 1, col. 13), but the position and intensity is more exactly defined for each type; thus compounds  $\text{X}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$  and  $\text{X}\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{Et}$  have the band at 1028—1027  $\text{cm}^{-1}$  (100—145) and 1033—1027  $\text{cm}^{-1}$  (95—115) [ $1029 \pm 3 \text{ cm}^{-1}$  ( $105 \pm 10$ )] respectively; and for compounds  $\text{X}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$  a main band is found at 1035—1034  $\text{cm}^{-1}$  (60—85) and a subsidiary one at 1018—1015  $\text{cm}^{-1}$  (40—50). The relative positions of the band for compounds  $\text{X}\cdot\text{CO}_2\text{Et}$  are Ph (1028  $\text{cm}^{-1}$ ) > 3- > 4- > 2-pyridyl ~ 4- > 3- > 2-pyridyl 1-oxide ~ 3- ~ 4-pyridyl-boron trichloride (1010  $\text{cm}^{-1}$ ), which is the order of electron-withdrawing ability of the ring; <sup>2,3</sup> the intensity is (45—95) [(70  $\pm$  15)].

(iv) The corresponding band for the methyl esters is presumably that in Table 2, col. 10. For compounds  $\text{X}\cdot\text{CO}_2\text{Me}$  it appears at 983—958  $\text{cm}^{-1}$  (20—85) [ $965 \pm 8 \text{ cm}^{-1}$  ( $45 \pm 25$ )]; there is no simple dependence of position on the electron-withdrawing ability of the ring. The band occurs at considerably higher frequencies in spectra of the other compounds, and as a doublet for  $\text{X}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$  (cf.  $\text{X}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ ). A band at 980  $\text{cm}^{-1}$  (20) has been reported<sup>15</sup> for methyl acetate.

*The 900—800  $\text{cm}^{-1}$  Region.*—(i) The aldehydes show the CH out-of-plane deformation band at 835—828  $\text{cm}^{-1}$  (50—120) (Table 4, col. 8), in the range 975—825  $\text{cm}^{-1}$  given by Colthup.<sup>20</sup>

(ii) One or two weak bands of unknown origin are found for many ethyl (Table 1, col. 15) and some methyl esters (Table 2, col. 12) at 880—850  $\text{cm}^{-1}$  ( $\leq 65$ ).

*Conclusions.*—The 1400—800  $\text{cm}^{-1}$  region of the spectrum has been shown to be much more amenable to quantitative treatment than was previously suspected. Apparent extinction coefficients are reproducible and comparable when measured under standard conditions, and are shown to be of great value to the interpretation of the spectrum in terms of structural groups.

#### EXPERIMENTAL

*Preparation of Compounds.*—The pyridine-aldehydes and most of the benzenoid compounds were redistilled commercial products; the others were prepared by standard methods. The

<sup>20</sup> Colthup, *J. Opt. Soc. Amer.*, 1950, **40**, 379.

preparations of most of the pyridines and 1-oxides have already been reported;<sup>3, 6, 21</sup> compounds were recrystallised or redistilled before measurement.

*2-Ethoxycarbonylpyridine 1-Oxide*.—Hydrogen chloride was passed 6 hr. through picolinic acid 1-oxide (4.5 g.) in boiling ethanol [100 c.c.; dried over  $\text{Mg}(\text{OEt})_2$ ]. Volatile material was removed at  $100^\circ/15$  mm., the residue added to water (50 c.c.) at  $0^\circ$ , and the whole basified with aqueous sodium carbonate and extracted with chloroform ( $5 \times 30$  c.c.). Distillation of the dried extracts gave the *ester oxide* (0.15 g., 3%), b. p.  $170\text{--}180^\circ$  (bath)/0.4 mm. (Found: C, 57.6; H, 5.7.  $\text{C}_8\text{H}_9\text{O}_3\text{N}$  requires C, 57.5; H, 5.4%).

The *methyl ester oxide* was similarly prepared (3%, but 60% of acid recovered), b. p.  $175\text{--}180^\circ$  (bath)/0.1 mm. (Found: C, 54.8; H, 4.7.  $\text{C}_7\text{H}_7\text{O}_3\text{N}$  requires C, 54.9; H, 4.6%). The compound has been reported<sup>22, 23</sup> as an intermediate, but not characterised.

Attempts to prepare the above compounds by oxidation of the pyridine esters by peracetic acid failed.

*Boron Halide Complexes*.—The following were made by the method given in Part VIII:<sup>3</sup> *4-ethoxycarbonylpyridine-boron tribromide*, prisms, m. p.  $97\text{--}98^\circ$ , from ethanol (Found: N, 3.5; Br, 59.7.  $\text{C}_8\text{H}_9\text{O}_2\text{NBr}_3\text{B}$  requires N, 3.5; Br, 59.7%); *3-ethoxycarbonyl-*, m. p.  $64\text{--}65^\circ$ , from ethanol (Found: C, 36.0; H, 3.8.  $\text{C}_8\text{H}_9\text{O}_2\text{NCl}_3\text{B}$  requires C, 35.8; H, 3.4%); *4-(2-ethoxycarbonylvinyl)-*, rhombs, m. p.  $202\text{--}204^\circ$ , from ethanol (Found: C, 40.4; H, 4.2.  $\text{C}_{10}\text{H}_{11}\text{O}_2\text{NCl}_3\text{B}$  requires C, 40.8; H, 3.8%); *4-methoxycarbonyl-* (87%), prisms, m. p.  $115\text{--}117^\circ$ , from ethanol (Found: C, 32.9; H, 2.8; N, 5.3.  $\text{C}_7\text{H}_7\text{O}_2\text{NCl}_3\text{B}$  requires C, 33.1; H, 2.8; N, 5.5%); *3-methoxycarbonyl-pyridine-boron trichloride* (54%), prisms, m. p.  $113\text{--}114^\circ$ , from ethanol (Found: C, 33.1; H, 2.8; N, 5.5%).

*Preparation of Oxides*.—Oxidation of the corresponding pyridine with peracetic acid gave: *4-methoxycarbonyl-*, m. p.  $116.5\text{--}118.5^\circ$ , from ethyl acetate (lit.,<sup>24</sup>  $118\text{--}119^\circ$ ); *3-methoxycarbonyl-*, m. p.  $97\text{--}98^\circ$ , from ethyl acetate (lit.,<sup>25</sup> m. p.  $97^\circ$ ; <sup>23</sup> m. p.  $101\text{--}102^\circ$ ), and *2-acetylpyridine 1-oxide*, b. p.  $82^\circ$  (bath)/0.3 mm. (Found: C, 61.6; H, 5.3.  $\text{C}_7\text{H}_7\text{O}_2\text{N}$  requires C, 61.3; H, 5.2%) [*picrolonate*, prisms (from ethanol), changing to needles at  $109^\circ$ , then melting at  $157^\circ$  (Found: C, 50.4; H, 3.9.  $\text{C}_{17}\text{H}_{15}\text{O}_7\text{N}_5$  requires C, 50.9; H, 3.8%)].

*Measurement of Spectra*.—A Perkin-Elmer model 21 instrument was used with the following settings: gearing 2" per micron; mechanical speed belt at bottom but one position; electrical speed 4; no auto-suppression (*i.e.*, speed 20 min. per run); gain 7.7; mechanical response 1; electrical response 1; light source 0.34 amp.; slit programme 4 (*i.e.*, resolution at 1600, 1400, 1250, 1100, and 850  $\text{cm}^{-1}$  was respectively 8.0, 5.5, 4.7, 3.8, 2.6 wave numbers). A sodium chloride prism was used.

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<sup>21</sup> (a) Part II, Katritzky, *J.*, 1956, 2404; (b) Parts VII and X, Katritzky and Monro, *J.*, 1958, 150, 1263; (c) Katritzky, *J.*, 1955, 2581, 2586.

<sup>22</sup> Newbold and Spring, *J.*, 1949, S 133.

<sup>23</sup> Shimizu, Naito, Ohta, Yoshikawa, and Dohmori, *J. Pharm. Soc. Japan*, 1952, 72, 1474; *Chem. Abs.*, 1953, 47, 8077.

<sup>24</sup> Yale, Losee, Martins, Holsing, Perry, and Berstein, *J. Amer. Chem. Soc.*, 1953, 75, 1933.

<sup>25</sup> Clemo and Koenig, *J.*, 1949, S231.