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Raman Spectra. I. Benzoyl Chloride and Certain of its Substitution Products

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For a number of years the relative reactivities of certain bonds in organic compounds have been studied in this Laboratory. The determination of the rates at which a type substance and certain of its substitution products react with a definite compound under fixed conditions led to results that showed the effect of the nature of the substituent and its position on the reactivity of the bond under investigation. In certain cases the relative reactivities determined by rate measurements were compared, with striking results, with the temperatures at which the members of a series containing the same radicals first gave indication of the breaking of the bonds studied.

Among the series of reaction rate measurements was that of benzoyl chloride and its derivatives with methyl alcohol,[2] with ethyl alcohol[3] and with water in the presence of acetone.[4] Although interesting conclusions and comparisons were drawn from these data, no satisfactory interpretation of the results was reached since the mechanism of the reaction was not clearly understood. The differences in rate can be traced to the carbon–chlorine bond if the reaction is either one of simple substitution or one in which an unstable addition compound of the oxonium type is involved. If, however, an unstable compound is formed by the addition of alcohol across the carbonyl, the change in the carbon–oxygen bond is being measured. Or, if the intermediate compound of any type is formed rapidly and decomposed very slowly, the rates would be a measure of the relative reactivities of a bond in the intermediate.[3] Substitution of an atom in benzoyl chloride would alter both the carbon–chlorine and carbonyl bonds. It appeared, therefore, that an examination of the lines in the Raman spectra produced by these groups would add valuable information to this problem because of the following facts.

(1) Harkins and Haun[5] determined the Raman spectra of certain alkyl chlorides. When the positions of the intense lines which give the frequency of longitudinal vibration of the halogen atom with the adjacent $-CH_2-$ group are compared with the rates of hydrolysis of the corresponding halides, a striking relationship appears. In methyl chloride, which is hydrolyzed with difficulty, this line has a displacement of 712 cm.$^{-1}$; the other primary chlorides which hydrolyze more easily have a smaller displacement (around 650 cm.$^{-1}$), which corresponds to a smaller force of binding. The more easily hydrolyzed secondary chlorides have Raman frequencies around 610 cm.$^{-1}$, and the tertiary chlorides which hydrolyze still more readily have a still smaller displacement (560 cm.$^{-1}$). It seemed probable that a similar relationship would be found for the acyl chlorides.

(2) Bourguel[6] compared the effect of different groups in olefins on the strength of the double bonds by a comparison of the displacements of the lines characteristic of the carbon–carbon double bond. This bond is similar to the carbonyl in acyl chloride.

For these reasons measurements of the Raman spectra of a series of acyl chlorides were made and examined. In attempts to determine which lines were associated with the carbon–chlorine bond, the spectra were compared with each other and, in certain cases, with the corresponding ester and aldehyde. On account of the complexity of the problem we are not able, at this time, to identify with any certainty the lines sought.

It was possible to identify the lines produced by the carbonyl linking on account of their isolated position (around 1750 cm.$^{-1}$). There appeared to be no relation between the relative reactivities of the acyl chlorides and the position of these lines.

In order to find out more about any intermediate compound formed, the spectrum of a mixture of benzoyl chloride and ethyl alcohol was photographed as soon as possible after mixing and, later, after the reaction was complete. The first spectrum contained the lines due to the substances present—ethyl alcohol, benzoyl chloride and

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(1) From the thesis presented by Dorothy D. Thompson in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1935.

(2) James F. Norris and H. H. Young, Jr., THIS JOURNAL, **57**, 1420 (1935).

(3) Norris, Fasce and Staud, *ibid.*, **57**, 1415 (1935).

(4) Berger and Olivier, *Rec. trav. chim.*, **46**, 516 (1927).

(5) Harkins and Haun, THIS JOURNAL, **54**, 3920 (1932).

(6) Bourguel, *Compt. rend.*, **194**, 1736 (1932).

ethyl benzoate; the second, the lines of ethyl benzoate and ethyl alcohol. If an intermediate compound had been formed in appreciable quantities as the result of an addition to the carbonyl group, the intensities of the lines corresponding to this group would have changed. This was found not to be the case. An experiment with a mixture of chloral and alcohol gave a spectrum in which lines due to the carbonyl in the aldehyde were not present—a fact which is optical evidence of the absence of a carbonyl linking in chloral alcoholate.

After the work described in this paper was completed, a paper was published by Kohlrausch, Pongratz and Stockmair[7] in which are reported the Raman spectra of a number of derivatives of benzoyl chloride. We had determined some of these and others not reported. In certain cases we found lines not observed by Kohlrausch and in other cases lines are missing in our spectra. It seems advisable to publish all our results so that the data will be available for future interpretation when Raman spectra are better understood.

Experimental

Apparatus.—A Hilger E-439 glass spectrograph was used for these determinations. Although the dispersion is small, the resolution is good and preliminary experiments with a Hilger "Constant Deviation" spectrograph of much higher dispersion showed that the use of fine-grained plates made possible by the large aperture of the former spectrograph gave greater precision than the coarse grained plates made necessary by the slower instrument. The time of exposure varied from one to four hours. Usually both long and short exposures were taken to give the best conditions for reading both the strong and weak lines.

In order to make certain the correct assignment of exciting line to a given Raman line, an efficient system of filters was worked out. Since benzoyl chloride and some of its derivatives are decomposed by ultraviolet light, the compound being investigated was always protected by either Corning "Greenish Nultra" glass (4 mm.) or by a saturated solution of sodium nitrite (2 mm.). These filters also, of course, prevented any Raman lines from being excited by the mercury lines in the ultraviolet. For every compound at least one plate was taken with radiation by both blue and violet mercury light, another with blue light only—the violet light being removed by a solution of quinine sulfate in dilute sulfuric acid. Although this filter was protected from ultraviolet light, there was some yellowing, so the solution was changed every hour. A third plate was taken with light filtered by Corning "Red Purple Ultra" glass (2 mm.) to weaken the blue light.[8] It was found much more efficient for this purpose than iodine in carbon tetrachloride usually recommended.

The photographs were made with Eastman Spectrographic plates—"III-O" for excitation by both blue and violet light, "III-G" for blue radiation alone, "I-O" (because of the density of the filter) for excitation by violet light, and "I-G" for photographs of the nitro compounds.

A Wood's type Raman tube was used with a cooling jacket and an extra jacket for liquid filters. The light source consisted of three Pyrex mercury arcs constructed according to High and Pool running vertically on 110 d. c. at a steady current of 3.5 to 4 amperes, and cooled by an electric fan.

Accuracy.—The accuracy of measuring the plates depends on the intensity and on the sharpness of the lines. The sharp, relatively strong lines were measured with an error of less than ±1 cm.$^{-1}$, while the error in reading the weak, diffuse lines was sometimes as great as ±3 cm.$^{-1}$. The values in the tables are weighted averages of at least three values (usually five or six) with the following exceptions: (1) the very weak lines which are not strong enough to appear on the plate when excited by the 4047 Å. line; (2) those in the region 1650–1800 cm.$^{-1}$, which when excited by the 4047 Å. line fall on the plate on top of the very much over-exposed mercury line (4358 Å. group); and (3) those of high frequency, above 2000 cm.$^{-1}$, which when excited by 4358 Å. fall below 4916 Å. where the dispersion is very poor.

The lines on the plate were measured to 0.001 mm. by a Hilger comparator. The wave lengths were determined by reference to three dispersion curves made from the spectrum of an iron arc and the wave numbers were determined (corrected to vacuum) by reference to Kayser's "Tabelle der Schwingungszahlen."[9]

Purification of Compounds.—With the exception of benzoyl chloride, *m*-chloro, *m*-nitro and *p*-nitrobenzoyl chloride which were purchased from Eastman Kodak Company and then highly purified, all of the compounds were prepared by the action of thionyl chloride on the purified acid according to the method previously described.[2] They were distilled under reduced pressure at least three times using a still-head provided with ground-glass joints, and large quantities were prepared, so that only constant boiling middle fractions need be used, thus avoiding the possibility of contamination by thionyl chloride or polymerization compounds.

Explanation of Tables.—The values of the Raman spectra have been summarized in the usual way. The value of the Raman shift in cm.$^{-1}$ is followed by a number in parentheses indicating the relative intensity (estimated)—the large numbers indicating greater intensity and the letter "b" for broad. This is followed by letters indicating the exciting lines as follows: a = 4047 Å., b = 4078 Å., c = 4339 Å., d = 4348 Å. and e = 4358 Å., the symbols ± before a letter indicate that the line appeared both as Stokes and anti-Stokes line.

Preceding the summary of Raman values is a summary of experimental detail. The first

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[7] Kohlrausch, Pongratz and Stockmair, *Monatsh.*, **67**, 104 (1935–1936).

[8] Murray and Andrews, *J. Chem. Phys.*, 1, 406 (1933).

[9] Kayser, "Tabelle der Schwingungszahlen," Verlag S. Hirzel, Leipzig, 1925.

column gives the number of the plate which was measured. Roman numerals refer to earlier work. The second column gives the type of filter used: (G. N., Corning "Greenish Nultra" glass; Q. S., a saturated solution of quinine sulfate in dilute sulfuric acid; R. P. U., Corning "Red Purple Ultra" glass). The type of plate listed in the third column refers to those of Eastman Kodak Company. The fourth column gives the exposure time in hours. The strength of the continuous background was greatest between 4358 and 4916 Å. Column 5 refers to this region. "Very weak" indicates practically no background, and "very strong" that the plate had to be illuminated by a very strong light to see the Raman lines. The spectrograph used was, unless otherwise stated, the Hilger E-439 described above. Some of the earlier investigations, however, were carried out on a Zeiss of low dispersion and on a Hilger Constant Deviation all glass spectrograph having a dispersion two to three times that of the Hilger E-439. The employment of these instruments is indicated in the last column.

BENZOYL CHLORIDE

Previous investigators: Kohlrausch and Pongratz,[10] *Monatsh.*, **64,** 361 (1934), Thatte and Ganesan,[11] *Phil. Mag.*, **12,** 823 (1931), Matsuno-Han,[12] *Bull. Chem. Soc. Japan*, **9,** 88 (1935). Eastman White Label, distilled 4 times *in vacuo;* b. p. 67.6–67.8° at 7.5 mm.

Plate	Filter	Type	Time	Background	Spectrograph
97	G. N.	III-O	3	Weak	Hilger E-439
98	G. N.	III-O	5	Weak	Hilger E-439
5	Q. S.	I-G	21	Strong	Hilger C. D.
99	Q. S.	III-G	3	Medium	Hilger E-439

Δν = 164(1b)(e); 313(3)(a, e); 415(2b)(a, e);[a] 507(3)(a, e); 672[a](3)(a, e); 775(00)(e); (840)(00)(e); (873)[a](00)(e); 1002[a](5)(a, b, e); 1026(1)(a, e); 1164(2)(a, e); 1175(4)(a, b, e); 1205(4)(a, b, e); 1450(2)(a, e); 1490(0)(a, e); 1595(8)(a, c, e); 1738[a](2b)(b, c, e); 1780[a](4b)(b, c, e); 3074(6b)(a).

[a] Differ from Kohlrausch and Pongratz by more than 2 cm.$^{-1}$. None differ by more than 6 cm.$^{-1}$.

Lines reported by Kohlrausch and Pongratz not found here 1317($^1/_2$); 2610(3b); 2649(2b); 3012(1b). Lines not reported by Kohlrausch and Pongratz and found here 840(00); two lines at 1164(2) and 1175(4), where Kohlrausch and Pongratz report only one 1170(11b).

o-METHYLBENZOYL CHLORIDE

Previous investigators: Kohlrausch, Pongratz and Stockmair,[7] *Monatsh.*, **67,** 104 (1935–1936). Prepared from synthetic *o*-methylbenzoic acid and thionyl chloride. Distilled 3 times; b. p. 75.6 ± 0.05° at 5.5 mm.

Plate	Filter	Type plate	Time	Background
38	G. N.	III-O	3.5 hrs.	Weak
39	G. N.	III-O	3.5	Very weak
35	Q. S.	III-G	3	Weak
57	R. P. U.	I-O	4	Weak
42	R. P. U. (Satd. NaNO$_2$)	I-O	4	Medium

Δν = 126[a](6b)(a, ±e); 220[a](2)(a, e); 286[b](4)(a, b, e); 382(2)(a, ±e); 436[b](2)(a, d, e); 477(2b)(a, c, e); 568(7)(a, e); 648(0)(a, e); 665(4)(a, e); 714(00)(a, e); 768(2)(a, e); 864(1)(a, e); 1053[b](6)(a, b, e); 1121(1)(a, e); 1164(3)(a, b, e); 1186(2)(a, e); 1204(6)(a, b, e); 1296[b](0)(a, e); 1382(2)(a, e); 1436(00)(a, e); 1476[b](4)(a, e); 1567[b](6)(a, e); 1599(6)(a, e); 1770(7b)(b, e); 2936[b](3)(a, b); 3070[b](5b)(a).

[a] Differ by more than ±6 cm.$^{-1}$. [b] Differ from Kohlrausch, Pongratz and Stockmair by more than 2 cm.$^{-1}$. Av. dev. of at least 7 readings < ±1 cm.$^{-1}$.

Kohlrausch, Pongratz and Stockmair report, also, 89(4); 1725(2b); 2975(5). Not reported by Kohlrausch, Pongratz and Stockmair 714(00) (found 5 times); 1436(00).

m-METHYLBENZOYL CHLORIDE

Previous investigators: Kohlrausch, Pongratz and Stockmair.[7] Prepared from synthetic *m*-methylbenzoic acid by SOCl$_2$. Distilled 2 times *in vacuo;* b. p. 71.2 ± 0.05° at 4 mm.

Plate	Filter	Type plate	Time	Background
80	G. N.	III-O	2.75	Weak
81	Q. S.	III-G	3	Dark
82	Q. S.	III-G	1.75	Medium
83	R. P. U.	I-O	2	Weak

Δν = 155(7b)(±a, e); 222(4)(±e); 270(3)(a, ±e); 304(1)(a, ±e); 350(1)(a, ±e); 375(00)(e); 421(3b)(a, e); 505[a](2)(a, e); 524(1)(a, e); 537[a](2)(a, e); 668(5)(a, b, e); 768(1)(a, e); 948(0)(a, e); 1003(5)(a, b, e); 1094[b](00)(a, e); 1152(2)(a, b, e); 1174(1)(a, e); 1244(5)(a, b, e); 1380(1)(a, e); 1586[a](7)(a, e); 1606[b](7)(a, e); 1769[b](7b)(e); 2925(2b)(a); 3066[a](4b)(a).

[a] Differ from Kohlrausch, Pongratz and Stockmair by more than 2 cm.$^{-1}$. [b] Differ by more than 6 cm.$^{-1}$.

Reported by Kohlrausch, Pongratz and Stockmair and not found; 480($^1/_2$); 802(1); 892(2); 927(2); 1410($^1/_2$); 1481(0); 1719($^1/_2$); 2964(1). Not reported by Kohlrausch, Pongratz and Stockmair 375(0).

p-METHYLBENZOYL CHLORIDE

Previous investigators: Kohlrausch, Pongratz and Stockmair.[7] Prepared from synthetic *p*-methylbenzoic acid + SOCl$_2$. Distilled 8 times *in vacuo;* b. p. 72.8–73.0° at 4.5 mm.

Plate	Filter	Type plate	Time	Background
70	G. N.	III-O	3	Dark
71	G. N.	III-O	1	Medium
72	Q. S.	III-G	1	Dark
74	R. P. U.	I-O	1	Weak
75	Q. S.	III-G	2	Medium

Δν = 170(2)(+b, e); 264(4)(a, ±e); 290(4)(a, ±e); 413(5b)(a, d, e); 484(4)(a, ±e); 614(3)(a, e); 640(3)(a, b, e); 715(00)(a, e); 781[a](6)(a, b, e); 827(0)(a, e); 875(0)(a, e); 1122(0)(a, e); 1173[a](8)(a, b, c, e); 1207[a](4)(a, b, e); 1306(3)(a, e); 1380[a](1)(a, b, e); 1503(1)(a, d, e); 1606[a](10b)(a, e); 1744[b](5b)(b, e); 1777[b](6b)(b, e); 2927[a](4)(a); 3072(3)(a).

[a] Differ from Kohlrausch, Pongratz and Stockmair by more than 2 cm.$^{-1}$. [b] By more than 6 cm.$^{-1}$.

Lines reported by Kohlrausch, Pongratz and Stockmair not found: 355(2); 1027($^1/_2$); 1443(1); 2873(2). Lines not reported by Kohlrausch, Pongratz and Stockmair but found: 1122(0)(a, e).

o-METHOXYBENZOYL CHLORIDE

Previous investigators: None. Prepared from methylsalicylic acid + $SOCl_2$. Distilled 4 times *in vacuo;* b. p. 119.6 ± 0.05° at 1 mm.

Plate	Filter	Type plate	Time	Background	Spectrograph
115	G. N.	III-O	4	Weak	Hilger E-439
116	Q. S.	III-G	4	Weak	Hilger E-439
116(a)	R. P. U.	I-O	1.5	Weak	Hilger E-439
12	Q. S.	I-G	14	Medium	Hilger C. D.

$\Delta\nu$ = 125(4b)(a, ±e); 249(00)(e); 377(1)(d, e); 426(0)(e); 449(a, e); 535(0)(e); 574(3)(a, e); 651(1b)(e); 743(1)(e); 776(1)(e); 857(00)(e); 1052(6)(a, e); 1126(1)(a, c, e); 1166(7)(a, e); 1189(6)(a, e); 1258(6)(a, e); 1284(0)(a, e); 1481(6)(a, e); 1574(6)(a, e); 1600(6)(a, e); 1778(7b)(b, e); 2841(0)(a); 2943(00)(a); 3080(2)(a).

m-METHOXYBENZOYL CHLORIDE

Previous investigators: None. Prepared from *m*-methoxybenzoic acid (Eastman White Label) + $SOCl_2$. Distilled 3 times *in vacuo;* b. p. 110.8–111.0° at 8.5 mm.

Plate	Filter	Type plate	Time	Background
109	G. N.	III-O	4	Medium
110	G. N.	III-O	2	Weak
118	G. N.	III-O	6	Medium
111	Q. S.	III-G	3	Weak
112	R. P. U.	I-O	2	Weak

$\Delta\nu$ = 155(3b)(±e); 260(0b)(e); 327(2)(e); 369(1)(e); 415(1b)(e); 452(2)(a, e); 502(2)(a, e); 567(1)(a, e); 667(8)(a, b, e); 770(0)(a, e); 996(10)(a, e); 1154(2)(a, b, e); 1190(2)(a, e); 1261(10)(a, b, e); 1289(2)(a, b, e); 1319(0b)(a, e); 1341(1)(a, e); 1587(8)(a, e); 1602(5)(a, e); 1736(1)(b, e); 1771(8)(e); 2839(1)(a); 2922(1)(a); 3085(4)(a).

p-METHOXYBENZOYL CHLORIDE

Previous investigators: Kohlrausch, Pongratz and Stockmair.[7] Prepared from *p*-methoxybenzoyl chloride (Eastman White Label) + $SOCl_2$. Distilled 5 times *in vacuo;* b. p. 90.8 ± 0.05° at 1 mm.; d^{20}_4 1.2609; n^{20} 1.5802.

Plate	Filter	Type plate	Time	Background	Spectrograph
XV	None	50	1	Medium	Zeiss
3	G. N.	Hyperpress	30	Strong	Hilger C. D.
8	Q. S.	I-G	21.5	Strong	Hilger C. D.
119	G. N.	III-O	4.5	Medium	Hilger E-439
120	R. P. U.	I-O	2	Weak	Hilger E-439

$\Delta\nu$ = 247(2)(d, e); 288(4b)(a, ±e); 410[a](2)(a, e); 454[b](3)(a, d, e); 470[a](2)(a, e); 612[b](6)(a, c, e); 635(1)(a, e); 650[b](5)(a, b, e); 735[b](0)(a, e); 783[b](b)(a, b, e); 879[b](2b)(a, e); 1007[b](2)(a, e); 1123(1)(a, b, e); 1165[b](20b)(a, b, e); 1212(4)(a, b, e); 1230(0)(a, e); 1270[b](2)(a, b, e); 1322[a](2)(a, e); 1423(1)(a, b, e); 1444(0)(a, e); 1465[b](0)(a, e); 1506[b](1)(a, e); 1579[b](4)(a, e); 1599(20b)(a, e); 1736[b](4b)(a, b, e); 1770[b](5b)(b, e); 2844(2)(a); 2938(0)(a); 3083(3b)(a).

[a] By more than 6 cm.$^{-1}$. [b] Differ from Kohlrausch, Pongratz and Stockmair by more than 2 cm.$^{-1}$.

Reported by Kohlrausch, Pongratz and Stockmair, not found: 148(6); 223(3); 1022($^1/_2$); 1059($^1/_2$); 1104(3). Not reported by Kohlrausch, Pongratz and Stockmair: 247(2); 635(1); 1123(1); 1230(0); 1444(0); 2844(2); 2938(0); 3083(3b).

o-CHLOROBENZOYL CHLORIDE

Previous investigators: Kohlrausch, Pongratz and Stockmair.[7] Prepared from *o*-chlorobenzoic acid + $SOCl_2$. Distilled 3 times *in vacuo;* b. p. 78.9–79.2° at 2 mm.

Plate	Filter	Type plate	Time	Background
87	G. N.	II-O	4	Weak
89	Q. S.	III-G	2	Weak
91	R. P. U.	I-O	2	Weak

$\Delta\nu$ = 125(4)(±a, ±e); 201[a](1)(a, ±e); 252[a](2b)(a, ±e); 356(1)(e); 423[a](1)(a, e); 447[a](4)(a, d, e); 482[a](1)(a, e); 540[a](4)(a, b, e); 643[a](3)(a, e); 659[a](3)(a, e); 727[a](0)(a, e); 767[b](00)(a, e); 1044[b](5)(a, b, e); 1138[b](1)(a, e); 1168[b](2)(a, b, e); 1194[b](4)(a, b, c, e); 1266(1)(a, b, e); 1287[a](0)(a, e); 1406(00)(a, e); 1437(00)(a); 1464[a](1)(a, c, e); 1569(0)(a); 1589[b](6)(a, e); 1790[b](4b)(b, d, e); 3074(5)(a).

[a] Differ from Kohlrausch, Pongratz and Stockmair by more than 2 cm.$^{-1}$. [b] By more than 6 cm.$^{-1}$.

Lines reported by Kohlrausch, Pongratz and Stockmair not found: 176(4); 860(1b); 1725(1). Lines not reported by Kohlrausch, Pongratz and Stockmair but found: 1406(00); 1437(00); 1569(0).

m-CHLOROBENZOYL CHLORIDE

Previous investigators: Kohlrausch, Pongratz and Stockmair.[7] Eastman White Label, distilled 4 times *in vacuo;* b. p. 103.4 ± 0.05° at 12.5 mm.

Plate	Filter	Type plate	Time	Background
46	G. N.	III-G	6	Weak
45	Q. S.	III-G	6	Medium
84	R. P. U.	I-O	2	Very weak
117	G. N.	III-O	8	Weak

$\Delta\nu$ = 149[a](8)(±a, ±e); 205(3)(±a, ±e); 241[a](3)(±e); 289(2)(a, ±e); 328(2)(a, e); 352(2)(a, e); 443[b](4)(a, d, e); 479[a](0)(e); 515[b](4)(a, c, e); 555(0)(a); 657(8)(a, b, e); 718[b](1)(a, e); 798(0)(a, e); 1000(12)(a, e); 1039(1)(a, e); 1086(2)(a, e); 1164[a](3)(a, e); 1191(15)(a, b, e); 1415[b](2)(a, e); 1588[a](10)(a, e); 1754[a](8)(e); 3074(8)(a).

[a] Differ from Kohlrausch, Pongratz and Stockmair by more than 2 cm.$^{-1}$. [b] By more than 6 cm.$^{-1}$.

Lines reported by Kohlrausch, Pongratz and Stockmair not found: 312(2); 387(2); 406(2); 613(1); 1385(0). Lines not reported by Kohlrausch, Pongratz and Stockmair but found: 555(0); 1039(1).

p-CHLOROBENZOYL CHLORIDE

Previous investigators: Kohlrausch, Pongratz and Stockmair.[7] Prepared from *p*-chlorobenzoic acid + $SOCl_2$. Distilled 3 times *in vacuo;* b. p. 93.6–93.9° at 9 mm.

Plate	Filter	Type plate	Time	Background
92	G. N.	III-O	4	Medium
93	G. N.	III-O	2	Medium
94	Q. S.	III-G	4	Very strong
95	Q. S.	III-G	2	Medium
96	R. P. U.	I-O	1	Medium

$\Delta\nu$ = 115(0b)(±a); 150[a](3b)(+a, ±e); 262[a](8b)(a, ±e); 311[a](2)(a, e); 402(4)(a, b, e); 455[a](4)(a, ±e); 562(4)(a, b, e); 628(3)(a, b, e); 723[a](10)(a, b, ±e); 875[a]-

(0b)(a, e); 1015[a](0)(a, e); 1091(15)(a, b, e); 1172(15)(a, b, e); 1203(15)(a, b, e); 1398(1)(a, e); 1589[a](20)(a, c, e); 1739[b](8b)(b, e); 1780[b](6b)(b, e); 3075[a](12)(a).

[a] Differ from Kohlrausch, Pongratz and Stockmair by more than 2 cm.$^{-1}$. [b] By more than 6 cm.$^{-1}$.

Lines reported by Kohlrausch, Pongratz and Stockmair not found: 1295($^1/_2$). Lines not reported by Kohlrausch, Pongratz and Stockmair but found: 115(0b).

o-NITROBENZOYL CHLORIDE

Previous investigators: None. Prepared from *o*-nitrobenzoic acid + $SOCl_2$. Distilled 4 times *in vacuo;* b. p. 128.2 ± 0.05° at 5 mm. [Excitation by blue light only. Violet light completely absorbed. No Raman lines of longer wave length than 4916 Å. measured because of low dispersion and large number of weak Hg lines there.]

Plate	Filter	Type plate	Time	Continuous Background	Spectrograph
14	Q. S.	I-G	20	Weak	Hilger C.D.
XXI	None	"Gaevaert Sensima"	4	Strong	Zeiss
77	Q. S.	I-G	2	Strong	Hilger E-439
85	Q. S.	I-G	1.25	Medium	Hilger E-439
126	Satd. $NaNO_2$	I-G	4	Faint	Hilger E-439

$\Delta\nu$ = 49(1)(e); 98(1)(e); 125(0)(e); 168(1)(e); 474(2)(e); 552(0)(e); 646(2b)(e); 854(2)(e); 1043(5)(e); 1085(1)(e); 1152(1)(e); 1170(2)(e); 1205(4)(e); 1352(20b)(e); 1449(1)(e); 1540(2)(d, e); 1581(5)(c, e); 1608(1)(e); 1800(1)(e).

m-NITROBENZOYL CHLORIDE

Previous investigators: None. Eastman "White Label," crystallized from carbon tetrachloride and petroleum ether. Distilled *in vacuo* 4 times; b. p. 120.2–120.4° at 2.5 mm. [Absorbed violet light completely treated as *o*-nitro-.]

Plate	Filter	Type plate	Time	Background
78	Q. S.	I-G	1	Dark
79	Q. S.	I-G	2	Very dark
124	Satd. $NaNO_2$	I-G	4	Weak

$\Delta\nu$ = 48(1)(e); 192(0)(d, e); 387(1)(e); 437(1)(e); 491(0)(e); 518(0)(e); 656(2)(e); 700(0)(e); 843(0)(e); 928(00)(e); 1005(5)(e); 1091(1)(e); 1203(6)(e); 1284(0)(e); 1352(10)(e); 1437(1)(e); 1540(2)(e); 1586(2)(e); 1618(1)(e); 1760(3)(e); 2500(0)(e).

p-NITROBENZOYL CHLORIDE

Previous investigators: None. Eastman "White Label," crystallized from carbon tetrachloride 4 times, but still yellow. [Dissolved in acetone. Absorbed all Raman light of shorter wave length than 4579 Å.]

$\Delta\nu$ = 1109(1)(e); 1353(6)(e); 1534(0)(e); 1601(6)(e); 1772(1)(d, e).

Summary

The Raman spectra of the monomethoxy and mononitro (incomplete) substitution products of benzoyl chloride have been determined for the first time. The spectra of benzoyl chloride, its monomethyl and monochloro derivatives have been determined and compared with the data of Kohlrausch, Pongratz and Stockmair.

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Alkyl Phenols. I. The 4-*n*-Alkylpyrogallols[1]

BY MERRILL C. HART AND E. H. WOODRUFF

Since Johnson and Lane[2] demonstrated that the introduction of an alkyl group into resorcinol increased its germicidal activity, a vast amount of work has been done on the alkyl mono- and dihydroxy phenols and their derivatives. The literature of the past fifteen years is so voluminous in this respect that no attempt will be made to list it here.

However, during this time the alkylated trihydroxyphenols have received only a haphazard attention. Hurd and Parrish[3] recently reported the phenol coefficients of dihexenyl (2 forms), heptenyl and diheptenylpyrogallol, using *S. Aureus* as the test organism, to be 20 and 250, 120 and 20, respectively. Niederl, Natelson and Beekman[4] prepared diisobutylpyrogallol but have not reported its phenol coefficient. Klarmann[5] gives the phenol coefficients of *n*-hexyl, phenylmethyl, phenethyl and phenylpropyl phloroglucinol as 8 by the Hygienic Laboratory test.

In view of the wide divergence of the phenol coefficients as well as the lack of definite information concerning the variation of activity with structure in the trihydroxy phenols, it was thought to be of interest to prepare a homologous series of alkylpyrogallols and determine their activity as germicides. As is readily seen from Fig. 1, the phenol coefficients vary regularly with increasing length of the alkyl group attached in a manner quite similar to those series already investigated.

Since the maximum germicidal activity against

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[1] Presented at the Pittsburgh meeting of The American Chemical Society, September, 1936.

[2] Johnson and Lane, THIS JOURNAL, **43**, 348 (1921).

[3] Hurd and Parrish, *ibid.*, **57**, 1731 (1935).

[4] Niederl, Natelson and Beekman, *ibid.*, **55**, 2571 (1933).

[5] Klarmann, *ibid.*, **48**, 2359 (1926).