[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF UTAH]

Ultraviolet Spectra of Substituted Acetophenones and Benzoic Acids

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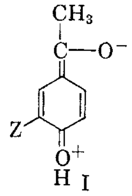
An empirical calculation of the maxima of 2,5-disubstituted acetophenones and benzoic acids is compared with the experimentally found values. A simple additive relationship holds since the steric factor of the substituent is contained in the constants used and since no strongly coupling (*ortho-para vs. meta*) substituents have been included.

In a previous article[2] the empirical method of Cram[3] was employed to calculate the maxima of the first primary and the secondary band of 2,3- and 2,5-hydroxy-, methoxy- or methyl-substituted acetophenones. In the present work these and similar calculations for other acetophenones are compared with the experimentally obtained values (Table I).

The excellent correlation between such calculated values and experimental values suggests a constant contribution by the substituents to each band, with the exception of two cases. Certain features inherent in the examples in Table I are responsible for such a simple treatment.

(a) No substituents are located at the position *para* to the electronegative acetyl group. Such *ortho-para vs. meta* directing groups are reported to couple strongly and give rise to $\Delta m\mu$'s which are products of the individual contributions rather than the sum.[4] Further, it has been proposed[5] that chromophores from strong coupling (I or II) explain the similarity of the trisubstituted benzene (I.Z = *ortho-para* directing group) spectra to that of the disubstituted benzene (I.Z = H).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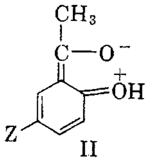
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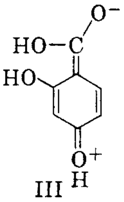
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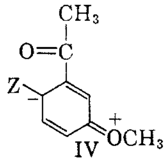
IV

(b) No examples in Table I involve 2,3-substituents. Such cases show hypsochromic effects due to distortion of the substituents out of the plane of the benzene ring.[2] The steric effects in the monosubstituted acetophenones (Table I) may be seen by comparing (in each band) the bathochromic shifts in the *meta* isomer relative to the *ortho* isomer. *o*-Hydroxyacetophenone is the exception and hydrogen bonding is no doubt responsible. Such steric effects in monosubstituted acetophenones are contained in the individual $\Delta m\mu$'s used to calculate the maxima of the 2,5-disubstituted acetophenones. It seems obvious from Table I that no interaction occurs between the 2- and 5-substituents so as to alter the steric portion of the increment ascribed to the *ortho* group. In the more widely deviating secondary band[6] of 2-halo-5-methyl- (or methoxy) acetophenones, the lack of agreement is directionally correct for an increased carbon-halogen bond distance due to the 5-substituent. Further, the deviation is greater with 2-halo-5-methoxy-[7] than with 2-halo-5-methylacetophenones. Such changes (III) in double bond character in the excited state resulting in changed steric conditions have been suggested.[8] A form such as IV (Z = halogen) might give rise to a greater carbon-halogen bond distance and a resulting hypsochromic effect.

(c) No 2,5-substituents are available in Table I which oppose *ortho-para-* and *meta*-directing groups. Such cases ought to give rise to strong coupling and nonadditivity of the individual contributions.[4]

An examination of the data in Table I suggests assignment, for these cases, of the first primary band to transitions to excited states analogous to I,[8] with the secondary band arising from transitions to states such as V. Substituent groups influence the positions of both bands by their influence on the π-electrons of the benzene ring. The *ortho* and *meta* halogens (Table I) raise the excited state

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(1) A part of the Doctoral Dissertation of Donald E. Robertson, 1959.

(2) W. J. Horton and J. T. Spence, *J. Am. Chem. Soc.*, **80**, 2453 (1958).

(3) D. J. Cram and F. W. Crantz, *J. Am. Chem. Soc.*, **72**, 595 (1950).

(4) L. Doub and J. M. Vandenbelt, *J. Am. Chem. Soc.*, **69**, 2714 (1947).

(5) L. Doub and J. M. Vandenbelt, *J. Am. Chem. Soc.*, **77**, 4535 (1955).

(6) In our hands, wide steric deviations in 2,3-disubstituted acetophenones are seen in the secondary band.[2]

(7) There is some uncertainty about the experimental values found for 2-bromo-5-methoxyacetophenone due to the lack of supporting analytical data. The identity of the compound is assured by the method of synthesis and an analysis of the crystalline oxime.

(8) W. F. Forbes and W. A. Mueller, *Can. J. Chem.*, **34**, 1340 (1956).

TABLE I

ULTRAVIOLET ABSORPTION MAXIMA OF SUBSTITUTED ACETOPHENONES[a]

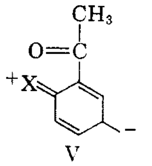
	Primary Band			Secondary Band		
	mμ	$\epsilon \times 10^{-3}$	Δmμ[b]	mμ	$\epsilon \times 10^{-3}$	Δmμ[b]
Acetophenone[c]	244	12.0	...	278	1.15	..
2-Fluoro	237	9.72	−7	282.5	1.55	4
3-Fluoro	238.5	8.91	−5	283.5	1.45	5
4-Fluoro[d]	242	11.5	−2	...		..
2-Chloro	239	5.65	−5	284	0.802	6
3-Chloro	239	4.98	−5	288	0.605	10
4-Chloro[d]	249	16.0	5	...		..
2-Bromo	~235.5[e]	4.61	−8	285	0.844	7
3-Bromo	242.5	9.02	−1	289.5	1.08	11
4-Bromo[d]	253	16.0	9	...		..
2-Iodo	~245[e]	4.79	1	294.5	1.02	16
4-Iodo[d]	262	16.0	18	...		..
2-Methyl[f]	242	8.5	−2	283	1.25	5
3-Methyl[c]	249	10.0	5	289	1.20	11
4-Methyl[f]	252	15.0	8	~278[e]	0.850	0
2-Methoxy[g]	246	11.0	2	305	3.8	27
3-Methoxy[c]	249	7.9	5	307	2.4	29
4-Methoxy[h]	276.5	15.5	33	...		..
2-Hydroxy[g]	251.5	9.3	7	327	3.2	49
3-Hydroxy[i]	252.5	10.0	8	311	5.0	33
4-Hydroxy[g]	276	13.0	32	...		..

2,5-DISUBSTITUTED ACETOPHENONES

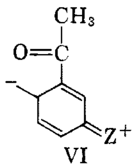
	Calcd. mμ	Experimental, mμ	$\epsilon \times 10^{-3}$	Deviation, mμ	Calcd. mμ	Experimental mμ	$\epsilon \times 10^{-3}$	Deviation, mμ
2-Cl-5-CH_3	244	243	5.25	−1	295	290	0.904	−5
2-Cl-5-CH_3O[j]	244	~240.5	4.97	−4	313	302.5	1.80	−11
2-Br-5-CH_3	240	~239	5.25	−1	296	291	0.10	−5
2-Br-5-CH_3O[k]	241	~242	5.26	1	314	298	1.63	−16
2,5-$(CH_3)_2$[l]	247	245	9.90		294	296	1.80	2
		251	8.70	−1 (mean)				
2-CH_3O-5-F	241	243	7.09	2	310	315	4.20	5
2-CH_3O-5-Cl	241	244	7.25	3	315	317	3.28	2
2-CH_3O-5-Br	243	239	7.59	−4	316	316	2.87	0
2-CH_3O-5-CH_3[c]	251	251	7.80	0	316	318	3.50	2
2,5-$(CH_3O)_2$[c]	251	250	6.30	−1	334	336	3.90	2
2-HO-5-F	246	248.5	8.44	2	332	335	4.20	3
2-HO-5-Cl	246	248	6.94	3	337	338	3.49	1
2-HO-5-Br	250	246	7.45	−4	338	339.5	3.30	1
2-HO-5-CH_3[c]	256	255	11.0	−1	338	338	3.50	0
2-HO-5-CH_3O[c]	256	256	7.4	0	356	355	3.8	−1
2,5-$(HO)_2$	259	256.5	6.88	−2	360	364	3.92	4

[a] The solvent was 95% ethanol unless otherwise noted. Other ultraviolet data on these acetophenones appears in the literature. Attention is directed here only to the Ref. under d below. [b] Δmμ = wave length of substituted acetophenone − corresponding wave length of acetophenone (244 or 278 mμ). Half mμ have been dropped. [c] Ref. 2, in 1:1 (vol.) ethanol-water; the acetophenone values 243 and 279 mμ (ethanol) are given by E. A. Braude and F. Sondheimer, *J. Chem. Soc.*, 3757 (1955). [d] W. F. Forbes and W. A. Mueller, *Can. J. Chem.*, **35**, 488 (1957). [e] Indicates an inflection. [f] In hexane or ethanol, E. A. Braude, F. Sondheimer, and W. F. Forbes, *Nature*, **173**, 117 (1954). [g] R. A. Morton and A. L. Stubbs, *J. Chem. Soc.*, 1347 (1940). [h] In 0.1*N* hydrochloric acid, maximum 2% methanol; band also at 219.5 mμ (ε, 1060). [i] N. A. Valyashko and A. E. Lutsky, *J. Gen. Chem. U.S.S.R.*, **21**, 1029 (1951). [j] Also λ_{max} 219 mμ, ε, 18500. [k] Repeated attempts failed to yield acceptable analytical values for carbon, hydrogen, and bromine. [l] E. A. Braude and F. Sondheimer, Ref. c.

(primary band) relative to acetophenone itself but lower the excited state that is responsible for the secondary band. The inductive effect of the halogens, F>Cl>Br>I, is in the order of the Δmμ's (Table I) of the *ortho* increments for the primary band (-7, -5, -1, 1) and similarly of the *meta* increments (-5, -5, -1, --). Such an order is the inverse of that expected on the basis of size and consequent steric interaction with the acetyl group. The comparison of even *ortho*-fluoro- *vs.* *meta*-fluoroacetophenone indicates some steric effects in the *ortho*



V



VI

TABLE II[a]

ULTRAVIOLET ABSORPTION SPECTRA OF SUBSTITUTED BENZOIC ACIDS

	Primary Band				Secondary Band			
	mμ	$\epsilon \times 10^{-3}$	log ε	Δmμ	mμ	$\epsilon \times 10^{-3}$	log ε	Δmμ
Benzoic acid[b]	228		4.02	...	273		2.94	..
o-Fluoro	224	9.27		−4	275	1.51		2
m-Fluoro	225.5	10.4		−2	275.5	1.60		2
p-Fluoro	228.5	10.2		0	...			..
o-Chloro	~229	5.00[d]		1	278		2.88[c]	5
m-Chloro	229	8.98		1	280.5	0.975		7
p-Chloro[d]	234	15.0		6	...			..
o-Bromo	~222	7.61		−6	280	0.867		7
m-Bromo	222	9.11		−6	281	0.888		8
p-Bromo[d]	238.5	16.0		10	...			..
o-Iodo	233[d,e]	7.00		5	288	1.24		15
m-Iodo	...				286	1.09		13
p-Iodo	252[d]	17.0		24	...			..
o-Methyl[d]	228	5.00		0	279		2.86[c]	6
m-Methyl[d]	232	9.00		4	279		3.01[c]	6
p-Methyl[d]	236	14.0		8	...			..
o-Methoxy[d]	230	6.00		2	291		3.43[c]	18
m-Methoxy[d]	230	7.00		2	293		3.39[c]	20
p-Methoxy[d]	249	14.0		21	...			..
o-Hydroxy[d]	236	7.50		8	307		3.57[c]	34
m-Hydroxy[d]	236	6.00		8	301		3.39[c]	28
p-Hydroxy[d]	251	12.5		23	...			..

2,5-DISUBSTITUTED BENZOIC ACIDS

	Calcd.	Experimental	$\epsilon \times 10^{-3}$	Deviation	Calcd.	Experimental	$\epsilon \times 10^{-3}$	Deviation
2-F-5-CH_3O	...	...		...	295	299.5	2.99	4
2-Cl-5-CH_3	...	...		...	284	285	1.11	1
2-Cl-5-CH_3O	231	233	9.03	2	298	298.5	2.05	0
2-Br-5-CH_3	226	~228	8.26	2	286	287	1.12	1
2-Br-5-CH_3O	224	~232	8.84	8	300	298	1.93	−2
2-Br-5-HO	230	~230	7.81	0	308	300	1.96	−8
2-CH_3O-5-F	228	229	6.13	1	293	301	3.62	8
2-CH_3O-5-Cl	231	232	9.01	1	298	304	2.93	6
2-CH_3O-5-Br	224	231	9.64	7	299	304.5	2.66	5
2-HO-5-F	234	231	6.29	−3	309	312	4.39	3
2-HO-5-Cl	237	232.5	7.52	−4	314	314	3.64	0
2-HO-5-Br	230	230.5	8.05	0	315	314	3.40	−1

[a] The solvent was 95% ethanol unless otherwise noted. [b] H. E. Ungnade, E. E. Pickett, L. Rubin, and E. Youse, *J. Org. Chem.*, **16**, 1318 (1951). [c] C. M. Moser and A. T. Kohlenberg, *J. Chem. Soc.*, 804 (1951). [d] In absolute ethanol, W. F. Forbes and M. B. Sheratte, *Can. J. Chem.*, **33**, 1829 (1955). [e] Missing in our examination of the spectra.

compound. The primary band Δmμ's for the other substituents (Table I) at the *ortho* and *meta* positions reflect their influence on the π-electrons, giving rise to slightly bathochromic Δmμ's.

The increments in the secondary band (a) are positive with respect to acetophenone itself (b) increase when the substituent is shifted from the *ortho* to the *meta* position (c) are large, relative to the corresponding Δmμ for the primary band and (d) appear, in the case of the *para* isomer to be shifted onto the primary band. A comparison of the respective *meta*-secondary-Δmμ's *vs.* *para*-primary-Δmμ's (F, 5, −2; Cl, 10, 5; Br, 11, 9; CH_3, 11, 8; CH_3O, 29, 33; HO, 33, 32) seems to indicate that the chromophore to which the secondary band is mainly ascribed (such as VI) has been shifted onto the 1,4-axis (such as I.Z = H) to which the primary band is assigned. The zero increment in the secondary band for *p*-methylacetophenone is similarly accounted for on this basis. It should also be noted that a secondary band reappears in 4-methoxyacetophenones which contain an additional methoxy group (2,4-dimethoxy-, 302.5 mμ, ε-8190; 3,4-dimethoxy-, 302.5 mμ, ε, 8100 and 2,4,5, trimethoxyacetophenone, 327 mμ, ε, 8380).[9]

In a similar treatment of benzoic acids (Table II) several divergent cases arise. These cases of non-additivity of the 2- and 5-substituent -Δmμ's (such as 2-bromo-5-hydroxybenzoic acid) give rise to large negative deviations in the secondary band which suggest the similar behavior of this type of compound in the acetophenone (secondary band).

The secondary band positive deviations in the case of 2-methoxy-5-halobenzoic acids have their

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(9) Unpublished data by W. J Horton.

TABLE III

ACETOPHENONES

		B.P. °(mm.)			Analyses, %			
					Calcd.		Found	
Acetophenone	Yield, %[a]	Found	Reported	Formula	C	H	C	H
2-F	41	94.5 (34.5)	80–85 (16)[b]					
3-F	40	190 (630.0)	81 (9)[c]					
Oxime, m.p.	43.6–44.5			C_8H_8NOF	62.74	5.27	62.98	5.31
2-Cl	71	119–120 (26)	85–87.5 (5.5)[d]					
Oxime, m.p.	104–105		105–106[d]					
3-Cl	37	120 (27)	80 (2.5)[e]					
Oxime, m.p.	85.5–88		88–89[f]					
2-Br	54	136 (28)	131–135 (20)[g]					
Oxime, m.p.	127.5–129		129[h]					
3-Br	49	155 (47)	102–106 (4)[g]					
Oxime, m.p.	100.6–101.6			C_8H_8NOBr	44.88	3.77	44.87	3.85
2-I	70	103 (1.5)	112 (4)[i]					
Oxime, m.p.	129.5–136		130–132[i]					
2-Cl-5-CH_3	42	67 (0.65)	245.8–246 (760.1)[j]					
Oxime, m.p.	115.8–117.4		100–101[k]	$C_9H_{10}NOCl$	58.86	5.49	59.13	5.48
2-Cl-5-CH_3O	63	116 (3)		$C_9H_9O_2Cl$	58.55	4.91	58.61	4.99
Oxime, m.p.	114.4–117.2			$C_9H_{10}NO_2Cl$	54.14	5.05	54.26	5.08
2-Br-5-CH_3	54	83 (0.45)		C_9H_9OBr	50.73	4.26	51.24	4.48
Oxime, m.p.	128.8–131.5			$C_9H_{10}NOBr$	47.39	4.42	47.38	4.58
2-Br-5-CH_3O	60	105 (0.65)		$C_9H_9O_2Br$	47.19	3.96	47.49	4.16
Oxime, m.p.	130.8–132.2			$C_9H_{10}NO_2Br$	44.28	4.13	44.38	4.17
2-CH_3O-5-F	30[l]	135 (23.5)	128 (15)[m]					
2-CH_3O-5-Cl	67[l]	162 (25)	108 (2)[n]					
Oxime, m.p.	157.9–159.3			$C_9H_{10}NO_2Cl$	54.14	5.05	54.16	5.05
2-CH_3O-5-Br	44	128.5 (2.2)		$C_9H_9O_2Br$	47.18	3.96	46.10	4.06
Oxime, m.p.	159.6–161.8			$C_9H_{10}NO_2Br$	44.28	4.13	43.98	4.22
2-HO-5-F	59[m] m.p.	56.4–57.6	57[m]					
2-HO-5-Cl	96[o] m.p.	52.2–53.6	54[p]					
2-HO-5-Br	44[q] m.p.	57.4–59.2	56[p]					
2,5-$(HO)_2$	59 m.p.	204.6–205.4	202–203[r]					

[a] From the benzoic acid according to Ref. 11. [b] W. Borsche and M. Wagner-Roemmich, *Ann.*, **546,** 273 (1941). [c] D. P. Evans, V. G. Morgan, and H. B. Watson, *J. Chem. Soc.*, 1167 (1935). [d] H. G. Walker and C. R. Hauser, *J. Am. Chem. Soc.*, **68,** 1386 (1946). [e] N. J. Leonard and J. N. Boyd, Jr., *J. Org. Chem.*, **11,** 405 (1946). [f] A. B. Sen and D. D. Mukerji, *J. Indian Chem. Soc.*, **28,** 161 (1951); *Chem. Abstr.*, **46,** 935a (1952). [g] R. L. Lutz *et al.*, *J. Org. Chem.* **12,** 617 (1947). [h] W. Borsche and W. Scriba, *Ann.*, **541,** 283 (1939). [i] W. S. Rapson and R. G. Shuttleworth, *J. Chem. Soc.*, 487 (1941). [j] C. F. H. Allen and M. P. Bridgess, *J. Am. Chem. Soc.*, **49,** 1846 (1927). [k] F. Mayer and W. Freund *Ber.* **55,** 2049 (1922). [l] By methylation (methyl sulfate) of the corresponding hydroxy compound. [m] Ng. Ph. Buu-Hoï, D. Levit and Ng. D. Xuong. *J. Org. Chem.*, **19,** 1617 (1954). [n] A. B. Sen and P. M. Bhargava. *J. Indian Chem. Soc.*, **26,** 287 (1949), *Chem. Abstr.*, **44,** 3197i (1950). [o] By Fries Rearrangement of the corresponding phenol acetate. [p] K. Kindley and H. Oelschlager, *Chem. Ber.*, **87,** 194 (1954). [q] By bromination of *o*-hydroxyacetophenone. [r] G. C. Amin and N. M. Shah, *Org. Syntheses*, **Coll. Vol. III,** 280 (1955).

counterpart in 2-methoxy-5-fluoroacetophenone (and decrease in 2-methoxy-5-chloro- or 2-methoxy-5-bromoacetophenone so as to be inconspicuous). All of these secondary band deviations suggest interaction between 2,5-substituents resulting in changed bond distances and consequent nonadditivity due particularly to the group at the 2-position.

In the primary band, the positive deviation of 2-methoxy-5-bromobenzoic acid is consistent with the above discussion; however, the positive primary deviation of 2-bromo-5-methoxybenzoic acid is not explained.

In summary, the benzoic acids follow the pattern of the acetophenones but are less regular in their agreement with prediction.

EXPERIMENTAL[10]

The ultraviolet absorption maxima were obtained on a Beckman Model DU Spectrophotometer: the material used was that submitted for analysis for carbon and hydrogen in the case of unreported compounds or material submitted to a similar regimen in the case of a known compound. The acetophenones were obtained from the corresponding benzoic acid *via* the acid chloride and sodio malonic ester[11] except for several cases, noted in Table III.

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(10) The melting points of materials prepared for the determination of spectra or for ultimate analysis are corrected.

(11) A. L. Wilds and L. W. Beck, *J. Am. Chem. Soc.*, **66,** 1692 (1944).

TABLE IV

BENZOIC ACIDS

Benzoic Acid	Yield,[a] %	Melting Point		Formula	Analyses			
		Found (corrected)	Reported		Calcd.		Found	
					C	H	C	H
o-F	55[b]	124.4–126.3	126.5[c]					
m-F	55[b]	122.4–124.4	124[c]					
p-F	50	185.4–187.2	186[d]					
m-Cl	46	155.8–156.8	154.25[e]					
o-Br	32	149.1–150.3	148[f]					
m-Br	50	154.9–157.3	152–153[g]					
o-I	[h]	161.6–163.0	162.5–163[i]					
m-I	15[j]	186.8–188.4	187–188[k]					
2-F-5-CH_3O	36[l]	146.3–148.3		$C_8H_7O_3F$	56.47	4.15	56.56	4.18
Amide		122.4–125.0		$C_8H_8NO_2F$	56.80	4.77	56.96	4.66
2-Cl-5-CH_3	75[m]	148.5–149.7		$C_8H_7O_2Cl$	56.32	4.14	56.88	4.06
Amide		186.8–187.6		C_8H_8NOCl	56.65	4.75	56.95	4.85
2-Cl-5-CH_3O	21	173.4–174.9	172.5–173[n]					
2-Br-5-CH_3	81[m]	137.6–139	135[o]					
Amide		197.9–198.5		C_8H_8NOBr	44.88	3.77	45.09	3.84
2-Br5-CH_3O	89[p]	159.4–160.1	160[n]					
2-Br-5-HO	[q]	184.2–185.6	185 (dec.)[r]					
Benzoate		198.7–199.9		$C_{14}H_9O_4Br$	52.36	2.83	52.67	3.08
2-CH_3O-5-F	78[s]	88.0–89.0	89[s]					
2-CH_3O-5-Cl	36[t]	97.6–98.8	96.2–97.2[u]					
2-CH_3O-5-Br	72[v]	119.8–121	120.0–120.8[u]					
2-HO-5-F	83[w]	178.8–180.4	180[v]					
2-HO-5-Cl	[h]	173.8–175.1	173–174[x]					
2-HO-5-Br	[h]	167.5–169.5	165.4–166.2[u]					

[a] By potassium permanganate oxidation of the appropriate methyl compound, except for those cases which are noted.
[b] By Schiemann reaction from the ethyl aminobenzoate.
[c] J. F. J. Dippy and F. R. Williams, *J. Chem. Soc.*, 1466 (1934).
[d] G. Schiemann and W. Winkelmüller, *Org. Syntheses*, **Coll. Vol. II,** 299 (1943).
[e] D. H. Andrews, G. Lynn, and J. Johnston. *J. Am. Chem. Soc.*, **48,** 1286 (1926).
[f] J. Meisenheimer, P. Zimmermann, and U. V. Kummer, *Ann.*, **446,** 213 (1926).
[g] B. Flürscheim and E. L. Holmes, *J. Chem. Soc.*, **131,** 474 (1928).
[h] Eastman Kodak Company material recrystallized repeatedly.
[i] H. G. Rule, W. Hay, A. N. Numbers, and T. R. Paterson, *J. Chem. Soc.*, **131,** 183 (1928).
[j] Overall, by diazotization of *m*-toluidine and permanganate oxidation.
[k] V. H. Wallingford and P. A. Krueger, *Org. Syntheses*, **Coll. Vol. II,** 353 (1943).
[l] The necessary *4-fluoro-3-methylanisole*, b.p. 169.5–170° (633.3 mm.), *Anal.* Calcd. for C_8H_9OF: C, 68.55; H, 6.47. Found: C, 68.71; H, 6.53, was prepared in 30% yield *via* the Schiemann reaction from 4-methoxy-2-methylaniline.
[m] By diazotization of 2-amino-5-methylbenzoic acid.
[n] G. B. Bachman and G. M. Picha, *J. Am. Chem. Soc.*, **68,** 1599 (1946).
[o] W. Borsche and A. Herbert, *Ann.*, **546,** 277 (1941).
[p] By permanganate oxidation of the corresponding aldehyde.
[q] By chromic acid–acetic acid oxidation (25% yield) of the benzoate of the aldehyde followed by saponification (75% yield).
[r] P. H. Beyer, *Rec. trav. chim.*, **40,** 621 (1921).
[s] By sodium hypobromite oxidation of the corresponding acetophenone as reported; Ng. Ph. Buu-Hoï, D. Levit, and Ng. D. Xuong, *J. Org. Chem.*, **19,** 1617 (1954).
[t] By permanganate oxidation of the corresponding acetophenone.
[u] A. S. Hussey and I. J. Wilk, *J. Am. Chem. Soc.*, **72,** 830 (1950).
[v] By permanganate oxidation of the corresponding aldehyde.
[w] By demethylation as in footnote s.
[x] G. Wittig, *Ber.*, **57,** 88 (1924).

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