completely volatile under the conditions of distillation. As the data prove that the high molecular weight products are not formed exclusively through simple polysubstitution of biaryls, the above calculation of relative reactivities based entirely upon the yields of binuclear products seems the most logical method available.

The percentages of isomers in the biaryl fractions are listed in Table II. The accuracy of the analytical technique is indicated by the deviations shown.

TABLE II

	Ortho	Meta	Para
Chlorobiphenyl	54 ± 3.0	31 ± 2.0	15 ± 1.0
Bromobiphenyl	48.5 ± 3.0	33 ± 2.0	18.5 ± 1.0
Iodobiphenyl	55 ± 3.0	28 ± 2.0	16.5 ± 1.0
Phenylpyridine	58 ± 3.5	28 ± 3.0	14 ± 1.5
Methyl phenylbenzoates	49 ± 2.0	20 ± 3.0	31 ± 1.0

Since the reaction of benzoyl peroxide with isomer mixtures of the above percentages has been found to leave biaryl fractions of unchanged composition, the percentages of isomers shown are significant despite the accompanying formation of large quantities of tar. In other words, subsequent reactions of biaryls initially formed would not alter the percentage of isomers. Conversely it has been shown that the orientation of a single substituent in a substituted biphenyl does not appreciably affect the reactivity of the nuclei toward free radical substitution.

The isolation of phenylpyridine fractions of constant composition despite the variation of competitive phenyl halide solvent indicated that association of the phenyl halide and pyridine did not occur. However, since the completion of the major portion of this work, Hey[7] has reported that the reaction of benzoyl peroxide with chlorobenzene in the absence of a competitive solvent produces 62% *o*-, 24% *m*- and 14% *p*-chlorobiphenyl. This deviation from the values found in the present work indicates that association of the solvents in each competition reaction might have occurred but that the effect on the isomers produced from pyridine must be constant. Because of this possible association, the application of the relative reactivities determined in this paper to other systems of solvents may not be accurate.

The limited data available to date indicate that substitution by free radicals is properly described as invariably ortho, but that the ratio of meta to para substitution may be statistical with groups which are ortho para directing for the common ionic substitution reactions.

Acknowledgment.—We are indebted to the Research Corporation for financial aid to one of the authors, Mr. Robert E. Phelps, in the pursuance of this work.

CLEVELAND, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WESTERN AUSTRALIA]

The S_N Mechanism in Aromatic Compounds. VI. Carbonyl and Nitrile Substituents

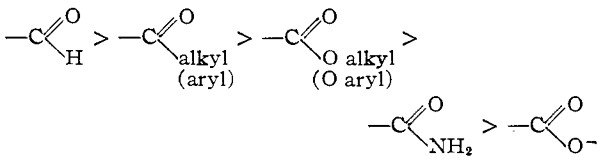
BY JOSEPH MILLER

RECEIVED MARCH 26, 1953

The activating power in aromatic S_N reactions of substituent groups containing C=O and C≡N bonds has been measured and discussed in terms of electronic effects. The Arrhenius parameters for the compounds containing the aldehyde and nitrile groups are abnormal and require either a special mechanism or the occurrence of side reactions which are reversible and do not affect the products.

In discussing a series of substituents of the general type $—C\begin{smallmatrix}\nearrow O\\ \searrow X\end{smallmatrix}$ Ingold[1] pointed out that as the electron donating power of X increases so the external effect of the whole group decreases.

In aromatic S_N reactions it has already been pointed out by the author[2] that these substituents are activating and that, following Ingold, one should then have the sequence of activating power

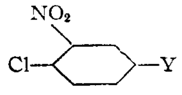


$$—C{\overset{O}{\underset{H}{}}} > —C{\overset{O}{\underset{\substack{alkyl\\(aryl)}}{}}} > —C{\overset{O}{\underset{\substack{O\ alkyl\\(O\ aryl)}}{}}} > —C{\overset{O}{\underset{NH_2}{}}} > —C{\overset{O}{\underset{O^-}{}}}$$

As is common, the C≡N group is to be included with this series.

It should be noted that only the permanent electron repulsion effects of X should operate.

These predictions have been tested by measuring the rate constants and Arrhenius parameters for the replacement of Cl by OMe^- in dry methanol, in the series



where Y = $—C\begin{smallmatrix}\nearrow O\\ \searrow X\end{smallmatrix}$, —C≡N or H. The compounds actually investigated were: (i) *o*-chloronitrobenzene, (ii) sodium 4-chloro-3-nitrobenzoate, (iii) 4-chloro-3-nitrobenzamide, (iv) methyl 4-chloro-3-nitrobenzoate, (v) 4-chloro-3-nitroacetophenone, (vi) 4-chloro-3-nitrobenzophenone, (vii) 4-chloro-3-nitrobenzaldehyde and (viii) 4-chloro-3-nitrobenzonitrile.

The relevant results are given as Table I, which

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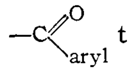
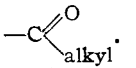
(1) C. K. Ingold, *Chem. Revs.*, **15**, 225 (1934).

(2) J. Miller, *Revs. Pure Appl. Chem. (Aust.)*, **1**, 171 (1951).

TABLE I

Compd.	Substituent	Rate constant: 10^5k_2 (l. moles^{-1} sec.$^{-1}$) Exptl. at temperatures shown in parentheses				Calcd. from the Arrhenius parameters			Substituent rate factor			Activation energy (E)	Frequency factor (log B)
						0°	50°	100°	0°	50°	100°		
i	H	...	3.62	6.82	37.4	0.0_3297	0.2515	34.95	1	1	1	23640	10.39
			(75.3)	(81.6)	(100.8)							±120	±0.07
ii	CO_2^-	4.85	20.45	36.4	165	0.0_2293	1.79	157.5	13.2	7.12	4.51	21460	9.77
		(59.9)	(75.3)	(81.6)	(100.6)							±120	±0.08
iii	$CONH_2$	...	12.95	40.3	178	0.152	65.8	5605	512	262	160	21300	11.21
			(35.2)	(45.3)	(60.2)							±190	±0.14
iv	CO_2CH_3	55.75	99.9	258	937	2.15	392.5	17700	7240	1560	506	18260	9.94
		(30.2)	(34.8)	(45.3)	(59.9)							±140	±0.09
v	$COCH_3$	48.2	76.2	117.3	325	2.40	500	24900	8080	1990	712	18730	10.37
		(26.1)	(30.2)	(35.0)	(45.3)							±240	±0.17
vi	COC_6H_5	...	170	442.5	1600	3.79	668	29500	12760	2655	844	18140	10.11
			(34.8)	(45.35)	(60.0)							±170	±0.11
vii	CHO	...	20.95	85.0	316	0.426	564	109000	1435	2240	3120	25210	14.81
			(25.0)	(35.2)	(45.3)							±80	±0.06
viii	CN	...	52.2	102	391.5	0.473	706	148500	1590	2810	4250	25630	15.19
			(30.2)	(35.0)	(45.3)							±100	±0.07

include the values of the substituent rate factors (S.R.F.'s[3]).

These results show clearly: (i) That CHO and CN groups appear to act by a different mechanism from the rest of the groups, which may be designated the main sequence. (ii) The S.R.F.'s of the main sequence groups are in the predicted order, with the additional information that  $-C\!\begin{smallmatrix}\nearrow O\\ \searrow aryl\end{smallmatrix}$ takes precedence over  $-C\!\begin{smallmatrix}\nearrow O\\ \searrow alkyl\end{smallmatrix}$. The order is thus COPh > $COCH_3$ > CO_2CH_3 > $CONH_2$ > CO_2^-. (iii) The activation by main sequence groups is almost wholly due to a considerable lowering of activation energy by up to 5500 cal., associated with a −I–T effect of considerable power. For comparison purposes, the NO_2 group which acts powerfully by −I–T effects, and also has a formal dipole, lowers E by 6210 cal. and raises log B by 0.87.[3] The S.R.F.'s of the NO_2 group are 673400, 114300 and 31300 at 0°, 50° and 100°, respectively. (iv) There is a large difference between CO_2^- and $CONH_2$, and a still considerable difference between the latter and the rest of the main sequence. This is due to the outstanding +M effect of the NH_2 and O^- groups, particularly O^-. The large differences are almost wholly energetic in character. The other groups are so close together that the small differences in E, and log B in particular are close to the experimental error. However, the difference of 590 cal. between COPh and COMe is a significant one and is associated with the Ph group being less electron repelling than Me, when electromeric effects are absent. The results also show that the +M effect of OMe is little different from that of the Me group, and that the large effects encountered in aromatic S_E reactions are mainly electromeric. (v) The CHO and CN groups are also powerfully activating, but act by a very large increase in the frequency factor (about 10^5) which more than outweighs a *rise* of about 2000 cal. in the activation energy. Either a different mode of activation or some reversible side-reaction not affecting the products, such as imino-ester or hemiacetal formation, must be occurring. Further investigation of these compounds is clearly necessary and this is being carried out in conjunction with the corresponding compounds having CHO and CN as ortho substituents. (vi) The position of the CHO and CN compounds with respect to the main sequence is markedly temperature dependent. At 0° they follow the CO_2Me compound; at 50° they bracket COPh at the top of the series; and at 100° they are the most activating. (vii) The CN group is a little more activating than the CHO group.

Experimental

Thermostats were of standard type accurate to better than 0.02°. Runs were followed by back-titration of standard dilute acid used to stop the reaction. Dilute acetic acid was used for the nitrile to avoid possible formation of imino-ester and also hydrolysis of the nitrile group. Later tests with the amide and ester showed hydrolysis reactions to be negligible and dilute HCl was used for the other compounds. Runs at each temperature were in duplicate.

Products.—The sole products obtained direct from surplus reaction mixtures were found to be the expected and

TYPICAL RUNS

Titration values	Log term	Time, sec.	Titration values	Log term	Time, sec.
4-Chloro-3-nitrobenzonitrile at 45.3°			4-Chloro-3-nitrobenzaldehyde at 45.3°		
6.97	0.2627	0	3.62	0.4392	0
8.06	2925	480	4.02	4628	300
8.10	2938	540	4.34	4835	620
8.95	3226	1050	4.63	5042	900
9.02	3252	1080	4.88	5238	1200
9.65	3512	1620	5.36	5665	1800
9.75	3558	1680	5.76	6088	2400
10.41	3893	2280	6.11	6529	3000
10.49	3937	2340	6.47	7058	3900
11.01	4260	2880	7.02	8123	5400
11.02	4267	2940	8.61	..	Inf.
11.50	4621	3480			
11.50	4621	3540			
12.04	5106	4320			
15.03	..	Inf.			
Expected infinity reading 14.95			Expected infinity reading 8.55		
Initial concn.: ArCN = 0.0505 M, OMe = 0.0840 M			Initial concn.: ArCHO = 0.050 M, OMe = 0.102 M		

These lead to values of k, nitrile, 3.930 ± 0.021 l. moles^{-1} sec.$^{-1}$; aldehyde, 3.077 ± 0.015 l. moles^{-1} sec.$^{-1}$.

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(3) J. Miller, *J. Chem. Soc.*, 3550 (1952).

known 4-methoxy-3-nitro compounds, *e.g.*, from the ester on pouring into cold water containing excess acid a white crystalline precipitate was obtained which melted sharply at 108°. On recrystallization from methanol the melting point was raised to 109° (lit. 108°, 109–110°).

Preparation of Materials. *o*-Chloronitrobenzene: the commercial product was recrystallized from ethanol; m.p. 32.5° (lit. 32°).

4-Chloro-3-nitrobenzoic Acid: from *p*-chlorobenzoic acid by the outline procedure of King and Murch.[4] The nitration was carried out at 65° then the mixture heated for a few minutes at 90° until all material went into solution; yield 90%, m.p. 183° (lit. 182.5°).

4-Chloro-3-nitrobenzamide: from the acid *via* the acid chloride according to the method of Montagne[5]; m.p. 156° (lit. 156°).

Methyl 4-chloro-3-nitrobenzoate: from the acid *via* the acid chloride by a standard procedure; yield 84%, m.p. 83° (lit. 83°).

4-Chloro-3-nitroacetophenone: from *p*-chloroacetophenone by the method of LeFèvre and LeFèvre[6]; m.p. 99–101° (lit. 99–101°).

4-Chloro-3-nitrobenzophenone: from the benzoyl chloride and benzene by the method of Montagne[7]; m.p. 104–105° (lit. 104–105°, 105.5°).

4-Chloro-3-nitrobenzaldehyde: from *p*-chlorobenzaldehyde by the method of Van der Lee[8]; m.p. 63° (lit. 61.5–62°, 64.5°).

4-Chloro-3-nitrobenzonitrile: from *p*-chlorobenzonitrile by the method of Mattaar[7]; m.p. 101° (lit. 101°).

Solvent: The solvent dried as in previous papers was shown by the method of Weaver[9] to contain not more than 0.001% water.

The author acknowledges financial assistance from the research grant to Australian Universities.

NEDLANDS, WESTERN AUSTRALIA

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(4) H. King and W. O. Murch, *J. Chem. Soc.*, **127**, 2646 (1925).

(5) P. J. Montagne, *Rec. trav. chim.*, **19**, 55 (1900).

(6) C. G. LeFèvre and R. J. W. LeFèvre, *J. Chem. Soc.*, 1988 (1932).

(7) P. J. Montagne, *Ber.*, **49**, 2262 (1926).

(8) J. Van der Lee, *Rec. trav. chim.*, **45**, 686 (1926).

(9) E. R. Weaver, THIS JOURNAL, **26**, 2463 (1914).

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

The Peroxide- and Light-induced Additions of Alcohols to Olefins[1]

BY W. H. URRY, F. W. STACEY, E. S. HUYSER AND O. O. JUVELAND

RECEIVED JULY 24, 1953

α-C-Alkylation of primary and secondary alcohols results from their peroxide- and light-induced reactions with olefins. For example, this reaction with ethanol and ethene gives butanol-2, hexanol-2, octanol-2 and decanol-2 while that with propanol-2 and ethene yields 2-methylbutanol-2, 2-methylhexanol-2, 2-methyloctanol-2 and 2-methyldecanol-2. In each case, higher telomers also are formed. The peroxide initiation of these reactions shows an interesting specificity since alkyl peroxides are effective inducing agents while acyl peroxides are ineffective. The evidence suggests a free-radical, chain mechanism.

The peroxide- and light-induced additions of primary and secondary alcohols to olefins result in the replacement of a hydrogen atom attached to the hydroxyl-bearing carbon atom by an alkyl group to give secondary and tertiary alcohols, respectively. The free radical, chain mechanism in each such reaction leads to the formation of products (telomers: with 1:1, 2:1, 3:1 and higher whole number ratios of olefin to alcohol) of differing complexity in the alkyl group substituted. High yields of lower addition products (1:1 and 2:1) are favored by high alcohol to olefin concentration ratios.

In addition to the practical result that a variety of alcohols may be prepared conveniently from homologs of lower molecular weight, this work confirms two previous observations of theoretical importance in free radical chemistry. First, it clearly indicates that free radicals attack these alcohols to remove α-hydrogen atoms.[2] Second, it was predicted and then confirmed that in these reactions *t*-butyl peroxide is an effective initiator while benzoyl peroxide is not, in contrast to other addition reactions previously studied where either peroxide can be used. Previous work which suggested this outcome has shown that the former peroxide shows first-order kinetics with approximately the same rates of decomposition[3,4] in a wide range of organic solvents while the latter undergoes rapid chain decomposition in alcohols[5,6] (see Discussion).

The reactions of alcohols with olefins studied (induced by *t*-butyl peroxide at 125–130°) are summarized in Table I. The products listed were iden-

TABLE I

PRODUCTS IDENTIFIED IN PEROXIDE-INDUCED ADDITIONS OF ALCOHOLS TO OLEFINS[a]

Alcohol	Olefin	Products
Methanol	Octene-1	Nonanol-1
Ethanol	Ethene	Butanol-2, hexanol-2, octanol-2, decanol-2
Ethanol	Hexene-1	Octanol-2
Ethanol	Octene-1	Decanol-2
Propanol-2	Ethene	2-Methylbutanol-2, 2-methylhexanol-2, 2-methyloctanol-2, 2-methyldecanol-2
Propanol-2	Propene	2-Methylpentanol-2
Propanol-2	3-Hydroxypropene	4-Methylpentanediol-1,4
Propanol-2	Octene-1	2-Methyldecanol-2
Propanol-2	Dodecene-1	2-Methyltetradecanol-2
Butanol-1	Octene-1	Dodecanol-4
Butanol-2	Octene-1	3-Methylhendecanol-3
Cyclohexanol	Hexene-1	1-*n*-Hexylcyclohexanol
Cyclohexanol[b]	Octene-1	1-*n*-Octylcyclohexanol

[a] All reactions represented were obtained with *t*-butyl peroxide. [b] Induced by *t*-butyl peroxide, *t*-amyl peroxide and 2,2-bis-(*t*-butylperoxy)-butane.

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(1) Previous communication, W. H. Urry, F. W. Stacey, O. O. Juveland and C. H. McDonnell, THIS JOURNAL, **75**, 250 (1953).

(2) *Cf.* M. S. Kharasch, J. L. Rowe and W. H. Urry, *J. Org. Chem.*, **16**, 905 (1951).

(3) J. H. Raley, F. F. Rust and W. E. Vaughan, THIS JOURNAL, **70**, 1336 (1948).

(4) W. H. Urry and E. M. Amir, unpublished work.

(5) P. D. Bartlett and K. Nozaki, *ibid.*, **68**, 1686 (1946); **69**, 2299 (1947).

(6) W. E. Cass, *ibid.*, **68**, 1976 (1946); **69**, 500 (1947), **72**, 4915 (1950).