414. *The Halogenation of Phenolic Ethers and Anilides. Part VIII. Alkoxy- and Dialkoxy-benzophenones and Dialkoxydiphenylsulphones.*

By Brynmor Jones.

In continuation of previous work (Bradfield and B. Jones, J., 1928 *et seq.*; B. Jones, 1935, 1831, 1835), measurements have now been made of the velocities of chlorination in 99% acetic acid of a series of six symmetrical and seven unsymmetrical *pp'*-dialkoxybenzophenones, six symmetrical *pp'*-dialkoxydiphenylsulphones, and five *p*-alkoxy- and fifteen mono-substituted alkoxy-benzophenones. In the sulphone series only modifications of the group R of OR are considered, but in the benzophenones a study of the influence on the reaction velocity of polar groups in the nucleus not undergoing substitution has also been made.

Kinetic Aspects of the Measurements.—The measurements were carried out by the method employed in previous parts of this series, the velocity coefficients being calculated from the usual expressions for a bimolecular reaction. Since *pp'*-dialkoxy-benzophenones and -diphenylsulphones have four *o*-positions available for substitution, consecutive reactions must occur with all members of these series. Consideration of the possible reactions shows that, when substitution has occurred in the *o*-position to one group OR, then, in these series, as in most previous cases, substitution in the remaining *o*-position of the same nucleus will be so slow as to be entirely negligible. On the other hand, substitution ortho to the second alkoxy-group in the opposite nucleus will occur and, as anticipated, the velocity of this reaction is appreciable. Whereas, for instance, the velocity of chlorination of *p*-chlorophenetole to give 2 : 4-dichlorophenetole is 2·44 as compared with 0·0057 for the chlorination of the latter, direct measurement has shown that the velocities of chlorination of 4 : 4'-dimethoxybenzophenone and its 3-*chloro*-derivative are 4·64 and 1·54 respectively. In order to obtain true velocity values, therefore, the primary reaction has to be isolated and initial velocities studied. This was best achieved, and satisfactory coefficients obtained, by increasing the molecular ratio of ether to chlorine to 3 : 1 and confining the observations as far as possible to the first half of the reaction.

Substances of the types *p*-RO·C_6H_4·COPh and *p*-RO·C_6H_4·CO·C_6H_4X are of the simpler type investigated in earlier papers, substitution occurring only in the ortho-position to the group OR.

The mean velocity coefficients are given in Table I, in which concentrations are given in g.-mols./l.

Discussion of Results.—*Symmetrical* pp'*-dialkoxy-benzophenones and -diphenylsulphones.* The discovery of the same additive relationships for these series as for the simpler phenyl ethers of the type RO·C_6H_4X is a significant feature of the present data. The examination of such compounds would appear to involve a marked departure from the general type studied hitherto, in that two nuclei are available for substitution. Since the velocity coefficients recorded relate to chlorination in only one of the nuclei at a time, it is apparent that the series may be regarded as of the general type *p*-RO·C_6H_4X, where X, although not identical as in previous cases, is effectively the same in spite of the variation in the alkoxy-group within it. Consequently, by analogy with the expressions developed in previous parts, the following expressions may be set up : *

For RO·C_6H_4·CO·C_6H_4·OR,

$$k(\text{obs.}) = 4k^{\text{OR}}_{p\text{-CO}\cdot C_6H_4\cdot\text{OR}} = 4PZe^{-(E_{\text{OR}} + E_{p\text{-CO}\cdot C_6H_4\cdot\text{OR}})R/T}$$

Similarly, for R'O·C_6H_4·CO·C_6H_4·OR',

$$k'(\text{obs.}) = 4k^{\text{OR}'}_{p\text{-CO}\cdot C_6H_4\cdot\text{OR}'} = 4PZe^{-(E_{\text{OR}'} + E_{p\text{-CO}\cdot C_6H_4\cdot\text{OR}'})/RT}$$

Neglecting the small variations in Z due to differences in molecular weight, and, as in previous papers, assuming P (where $P = PS$ of earlier papers) constant for closely related ethers, then if $E_{p\text{-CO}\cdot C_6H_4\cdot\text{OR}} = E_{p\text{-CO}\cdot C_6H_4\cdot\text{OR}'}$, we have

$$k^{\text{OR}'}_{p\text{-CO}\cdot C_6H_4\cdot\text{OR}'}/k^{\text{OR}}_{p\text{-CO}\cdot C_6H_4\cdot\text{OR}} = e^{(E_{\text{OR}} - E_{\text{OR}'})/RT}$$

* For notation, see J., 1928. 1010.

TABLE I.

Velocity coefficients for the chlorination of substances of the types (a) (p)RO·C_6H_4·CO·C_6H_4·OR′(p) *and* (b) (p)RO·C_6H_4·SO_2·C_6H_4·OR′(p) *in* 99% *acetic acid, at* 20°.

$[Cl_2]$ = 0·0075; [HCl] = 0·0375.

	Type (a).			Type (b).	
Concn. of ether	0·0225	0·0150	0·0075	0·0225	0·0150
Mol. propn.	3	2	1	3	2
R = R′ = CH_3	4·64	4·65	4·88	0·110	0·115
,, C_2H_5	9·40	—	—	0·223	0·231
,, *n*-C_3H_7	10·28	—	—	0·247	0·263
,, *iso*-C_3H_7	22·6	—	—	0·536	0·552
,, *n*-C_4H_9	10·48	—	—	0·247	0·255
,, *n*-C_5H_{11}	10·31	—	—	0·249	0·261
R = CH_3,R′ = C_2H_5	6·96	7·07	7·24		
,, *n*-C_3H_7	7·34	7·42	—		
,, *n*-C_4H_9	7·30	7·42	—		
,, *n*-C_5H_{11}	7·53	7·42	—		
,, $CH_2Cl·CH_2$	2·77	2·82	3·05		
R = C_2H_5,R′ = *n*-C_4H_9	9·83	—	—		
,, *n*-C_5H_{11}	9·74	—	—		

Type (a). $[Cl_2]$ = 0·0050; [ether] = 0·0150; [HCl] = 0·0250.

	k.		*k*.
R = CH_3,R′ = CH_3	4·53	R = CH_3,R′ = *n*-C_3H_7	7·18
,, C_2H_5	6·78	,, *n*-C_5H_{11}	7·33

Velocity coefficients for the chlorination of substances of the type (p)MeO·C_6H_4·CO·C_6H_3Cl(m)·OR(p) *in* 99% *acetic acid, at* 20°.

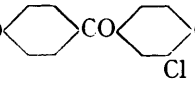
$[Cl_2]$ = 0·0075; [ether] = 0·0225; [HCl] = 0·0375.

R =	CH_3	C_2H_5	*n*-C_3H_7
k =	1·54	1·58	1·59

Velocity coefficients for the chlorination of substances of the type (p)RO·C_6H_4·CO·C_6H_4X *in* 99% *acetic acid, at* 20°.

$[Cl_2]$ = 0·0075; [ether] = 0·0225; [HCl] = 0·0375.

Group R.	Group X.	*k*.	Group R.	Group X.	*k*.
CH_3	H	1·26	CH_3	*o*-F	0·595
,,	*p*-CH_3	1·68	,,	*o*-Cl	0·47
,,	*p*-F	1·07	,,	*o*-Br	0·46
,,	*p*-Cl	0·87	C_2H_5	H	2·50
,,	*p*-Br	0·85	,,	*p*-Cl	1·73
,,	*p*-NO_2	0·385	*n*-C_4H_9	H	2·82
,,	*m*-CH_3	1·54	,,	*m*-NO_2	0·97
,,	*m*-F	0·78	*n*-C_5H_{11}	H	2·79
,,	*m*-Br	0·775	*n*-C_7H_{15}	H	2·69
,,	*m*-NO_2	0·44	$CH_2Cl·CH_2$	*o*-Cl	0·115

Justification for the view that the general polar influence of the *p*-substituents RO·C_6H_4·CO· in modifying the velocities of chlorination is virtually the same is provided by (1) the similarity of the dipole moments of anisole and phenetole, (2) the fact that the difference in the strengths of *p*-methoxy- and *p*-ethoxy-benzoic acids makes it probable that the small general field or inductive influence of these groups added to the much larger effects of the nearer carbonyl or sulphonyl group will be negligibly different. Direct evidence, which in this case is as near to experimental proof as can be obtained, is provided by the velocity coefficients for three ketones of the type  , where a change in R from methyl to *n*-propyl causes an increase of not more than 3% in the velocity of chlorination in the *o*-position to the methoxyl group. Clearly, the effect of a disparity of this order in the influence of the unsubstituted groups RO·C_6H_4·CO and MeO·C_6H_4·CO would be to increase the relative directive powers of all alkoxy-groups by an amount which

is within the limits of experimental error. The figures recorded in Table III, with the exception of the value for the *iso*propyl group, which is again anomalous (cf. J., 1935, 1833), show that the agreement with the previously observed values for the relative directive powers of alkoxy-groups which is to be expected on the basis of the foregoing assumption.

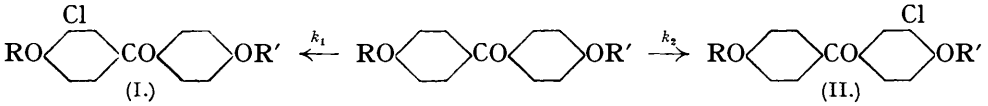
Comparison of the velocity coefficients for analogous dialkoxybenzophenones and diphenylsulphones (Table II) demonstrates the relative influence of the carbonyl and sulphonyl groups on nuclear reactivity. The greater electron-attracting influence of the sulphonyl group reduces the velocity of chlorination to approximately one-fortieth of that of the corresponding ketone.

TABLE II.

Relative velocities of chlorination of ketones and sulphones of the type (p)RO·C_6H_4·CO·C_6H_4·OR(p) *and* (p)RO·C_6H_4·SO_2·C_6H_4·OR(p). *Values of* $100k^{OR}_{p\text{-}SO_2\cdot C_6H_4\cdot OR}/k^{OR}_{p\text{-}CO\cdot C_6H_4\cdot OR}$.

R =	CH_3.	C_2H_5.	$C_3H_7^{\alpha}$.	$C_3H_7^{\beta}$.	$C_4H_9^{\alpha}$.	$C_5H_{11}^{\alpha}$.
Ketones	100	100	100	100	100	100
Sulphones	2·37	2·37	2·40	2·37	2·36	2·41

Unsymmetrical pp'-*dialkoxybenzophenones.* In compounds of this type, with alkoxy-groups of similar directive power the simultaneous reactions occurring will be of the same order of velocity but distinct; consequently, the observed velocity coefficient may be analysed as the sum of two independent velocities which may be represented as follows :



(I.) (II.)

Now suppose E_1 and E_2 are the activation energies corresponding to the formation of the products (I) and (II) respectively, and that $E_1 > E_2$. If it is assumed that collisions at which energy greater than E_1 is available, and for which some combination of conditions represented by the factor p_1 is satisfied, give product (I) only, and the formation of product (II) is similarly governed by activation energy E_2 and factor p_2, the two conditions represented by p_1 and p_2 being mutually exclusive, then

$$k_1 = \pi p_1 Z e^{-E_1/RT},\ k_2 = \pi p_2 Z e^{-E_2/RT} \text{ and } k'(\text{obs.}) = k_1 + k_2$$

where π represents any other conditions of a general type, such as those determined by the solvent or by the chlorine molecule.

It seems most likely that p_1 and p_2 may be regarded as the probabilities that several conditions are simultaneously satisfied; such as, that the molecules are suitably oriented at the moment of collision, and that the energy is correctly located in the molecule.

Owing to the almost complete symmetry of such a molecule, it is not unreasonable to assume that numerically the two factors p_1 and p_2 are equal. Hence we may write

$$k'(\text{obs.}) = \text{constant} \times (e^{-E_1/RT} + e^{-E_2/RT})$$

For the symmetrical ketone $CO(C_6H_4\cdot OR)_2$, where $p_1 = p_2$,

$$k(\text{obs.}) = 2 \times \text{constant} \times (e^{-E_1/RT})$$

Combining these two expressions, we have

$$k'(\text{obs.}) - \tfrac{1}{2}k(\text{obs.}) = \text{constant} \times (e^{-E_2/RT})$$

$$\text{and } [k'(\text{obs.}) - \tfrac{1}{2}k(\text{obs.})]/\tfrac{1}{2}k(\text{obs.}) = e^{(E_1 - E_2)/RT}$$

The relative directive powers of alkoxy-groups, calculated from the velocity coefficients for unsymmetrical benzophenones by employing the expression $[k'(\text{obs.}) - \frac{1}{2}k(\text{obs.})]/\frac{1}{2}k(\text{obs.})$, are in good agreement with those obtaining in other series (cf. Table III).

In the absence of the p terms, no simple relationship of the above type can be deduced. It being assumed that the additive relationships hitherto found in all cases hold in this new

class, the agreement in Table III may be regarded as providing evidence of the existence of one or more terms, of the nature suggested above, in the factor P of the expression $P.Z.e^{-E/RT}$. The minimum condition which would logically suffice here would be $P = 1/2$, which can be seen to represent the simple probability of a fruitful collision of the reagent molecule with either end of a symmetrical molecule.

TABLE III.*

Relative directive powers of the groups OR *in ketones and sulphones (molecular ratio, ether : chlorine = 3 : 1). Values of* $100k_{p-X}^{OR}/k_{p-X}^{OMe}$.

Type. R =	CH_3.	C_2H_5.	$C_3H_7{}^{\alpha}$.	$C_3H_7{}^{\beta}$.	$C_4H_9{}^{\alpha}$.	$C_5H_{11}{}^{\alpha}$.	$C_7H_{15}{}^{\alpha}$.	$CH_2Cl{\cdot}CH_2$.
(p)RO·C_6H_4·COPh	100	199	—	—	224	221	214	—
(p)MeO·C_6H_4·CO·C_6H_4·OR(p)	100	200	217	—	215	224	—	19·3
(p)RO·C_6H_4·CO·C_6H_4·OR(p)	100	203	222	489	226	222	—	—
(p)RO·C_6H_4·SO_2·C_6H_4·OR(p)	100	202	225	487	225	226	—	—
Phenyl ethers (mean)	100	199	223	440	223	221	219	—

* Ratios of velocities have been calculated from the original figures and not from the values now recorded where these have been rounded to three significant figures.

For the unsymmetrical ketone p-*methoxy*-p'-β-*chloroethoxybenzophenone*, where the velocity of chlorination in one nucleus is of a somewhat lower order than in the other and the adherence to the type of the group X (cf. p. 1854) is a little less strict, the error in the value of the velocity obtained by subtraction, as above, must be appreciably multiplied. Consequently, the relative directive power of such a group as $CH_2Cl{\cdot}CH_2{\cdot}O$– obtained by a difference method of the present type can only be approximate. This is apparent from the values 19·3, 21·2, and 25 obtained from the velocity coefficients for the above benzophenone with three different molecular ratios of ketone and chlorine. The probable correct value obtained in a different series is 24·6.

Monoalkoxybenzophenones. Comparison of the velocity ratios given in Table III for *p*-alkoxybenzophenones with the mean values for phenyl ethers shows that the new values support the views previously expressed (cf. Part V). The new data, moreover, provide a further illustration of the influence of changes in the nature of the *p*-substituent X on the velocity of chlorination. The relative effects of COPh, CO_2H, and Cl as *p*-substituents are compared in the following table.

Relative effects of the groups CO_2H, COPh, *and* Cl *in compounds of the type p*-RO·C_6H_4X. *Values of* $100k_{p-X}^{OR}/k_{p-CO_2H}^{OR}$.

X.	R = CH_3.	C_2H_5.	$C_4H_9{}^{\alpha}$.	$C_5H_{11}{}^{\alpha}$.	$C_7H_{15}{}^{\alpha}$.
p-CO_2H	100	100	100	100	100
p-COPh	284	286	293	288	285
p-Cl	276	278	283	285	290

The influence of polar substituents in the nucleus not undergoing substitution is in the expected order, the reactivity being increased by the introduction of a methyl group and decreased by that of a halogen or nitro-group in the order $CH_3 > H >$ Halogens $> NO_2$.

TABLE IV.

Relative influences of the groups X *in compounds of the type* (p)RO·C_6H_4·CO·C_6H_4X.

R.	X = H.	*p*-CH_3.	*p*-F.	*p*-Cl.	*p*-Br.	*p*-NO_2.	*m*-CH_3.	*m*-F.	*m*-Br.	*m*-NO_2.	*o*-F.	*o*-Cl.	*o*-Br.
Me	100	133	85	69	67·5	30·4	122	61·7	61·5	34·2	47·1	37·3	36·5
Et	100	—	—	69	—	—	—	—	—	—	—	—	—
Bu$^{\alpha}$	100	—	—	—	—	—	—	—	—	34·5	—	—	—

In accordance with general experience the influence of the methyl and the nitro-group is greater in the *o*- than in the *m*-position, whilst the deactivating field or inductive effects

is reflected in the identical reactivity of 3′-*fluoro*- and 3′-*bromo*-4-*methoxybenzophenones* (see also Dippy and Lewis, this vol., p. 644). Similarly, the order of strengths Br>Cl>F of the *p*-halogenobenzoic acids (Dippy, Watson, and Williams, J., 1935, 346) corresponds with the order F>Cl>Br for the reactivities of the 4′-halogeno-4-methoxybenzophenones. The same order is observed for the 2′-halogeno-4-methoxy-isomerides. The new data in general agree with the views put forward from this laboratory relating to the polar effects of halogens in aromatic compounds (Bennett, J., 1933, 1112; Baddeley, Bennett, Glasstone, and B. Jones, J., 1935, 1827).

No extensive study of the influence of changes in the group OR on the reactivity has been made in this series, but from the two cases investigated (cf. Table IV) the additive relationships are found to hold.

The main results of this investigation may be summarised as follows : (1) For series of symmetrical *pp*′-dialkoxy-benzophenones and -diphenylsulphones the same additive relationships are observed as for the simpler phenyl ethers of the type *p*-RO·C_6H_4X examined in earlier papers. (2) In these new series the reactivities of analogous ketones and sulphones are in the ratio 100 : 2·38. (3) For a series of unsymmetrical *pp*′-dialkoxybenzophenones, relative directive powers of alkoxy-groups are observed which are in good agreement with those found in other series. This agreement is regarded as providing evidence of the existence of the factor P in the expression $P . Z . e^{-E/RT}$. (4) Comparison of the velocities of chlorination of *p*-alkoxybenzophenones with those determined previously for the corresponding *p*-alkoxybenzoic acids shows that the ketones are 2·87 times as reactive as the acids. (5) For polar groups X in ketones of the type *p*-RO·C_6H_4·CO·C_6H_4X, the order of reactivity for *p*-substituents is CH_3>H>F>Cl>Br>NO_2; in the *m*-position fluorine and bromine exert identical influences, but in the *o*-position the order of reactivity is again F>Br. In general, the stronger the acid $C_6H_4X·CO_2H$ the lower the reactivity of the corresponding ketone.

Experimental.

Velocity Measurements.—Reference may be made to the earlier parts of this series for details of the measurements not now specifically mentioned.

The presence of consecutive reactions in the chlorination of *pp*′-dialkoxy-benzophenones and -diphenylsulphones discussed above was apparent from the steady rise in the velocity coefficient that was observed when equimolecular proportions of ether and chlorine were employed. Over the usual range of 35—60% change, the velocity coefficients rose by approximately 10% but this discrepancy in the measurements was largely eliminated by investigating only the first third of the reaction. To minimise the effect still further, most of the measurements were carried out with two or three molecular proportions of ether, and the observations, as far as possible, limited to the first 50% change. With 2 mols. of ether a steady rise of 2—3% was still noticeable in the velocity coefficients, but with 3 mols. satisfactory coefficients were obtained. Comparison of the velocity ratios at the different concentrations (Table V) shows that when these precautions are taken the values obtained at the two lower concentrations are not seriously vitiated.

Table V.

Effect of relative concentrations of ether to chlorine on the directive powers of the groups OR *in* (a) *ketones of the type* (p)MeO·C_6H_4·CO·C_6H_4·OR(p) *and sulphones of the type* (p)RO·C_6H_4·SO_2·C_6H_4·OR(p).

Mol. proptn., ether : Cl_2.	R = CH_3.	C_2H_5.	$C_3H_7{}^{\alpha}$.	$C_3H_7{}^{\beta}$.	$C_4H_9{}^{\alpha}$.	$C_5H_{11}{}^{\alpha}$.	$CH_2Cl·CH_2$.
(*a*) 3 : 1	100	200	217	—	215	225	19·3
3 : 1	100	199	217	—	—	223	—
2 : 1	100	204	219	—	219	219	21·2
1 : 1	100	197	—	—	—	—	25·0
(*b*) 3 : 1	100	202	225	487	225	226	—
2 : 1	100	201	228	479	221	226	—

The high reactivity of the dialkoxybenzophenones on the one hand, and the low solubility of the dialkoxydiphenylsulphones on the other, precluded a further increase in the molecular ratio of ether to chlorine at the above selected concentrations.

Careful standardisation of procedure was necessary in all measurements, particularly in those

on the dialkoxybenzophenones, since here accidental errors of measurement affect the value of the velocity coefficients to a greater extent than with less reactive ethers. The variations observed in the value of the velocity coefficients in individual experiments, and the variations of the mean values of single experiments for fast and slow chlorinations of the type discussed are shown by the data in Table VI.

TABLE VI.

pp'-Dimethoxybenzophenone.
(5 C.c. burette graduated in 0·01 c.c.)
$[Cl_2] = 0·0075$; [ether] = 0·0225; [HCl] = 0·0375.

Time, mins.	Titre, c.c.	*k*.
0	4·77	
4·667	3·03	4·627
7·60	2·33	4·644
9·92	1·92	4·623
	Mean	4·631

p-Methoxy-*p'*-*n*-propoxybenzophenone.
(10 C.c. burette graduated in 0·02 c.c.)
$[Cl_2] = 0·0075$; [ether] = 0·0150; [HCl] = 0·0375.

Time, mins.	Titre, c.c.	*k*.
0	9·94	
5·00	6·07	7·38
8·33	4·60	7·42
11·00	3·68	7·46
	Mean	7·42

pp'-Di-*n*-propoxydiphenylsulphone.
(10 C.c. burette graduated in 0·02 c.c.)
$[Cl_2] = 0·0075$; [ether] = 0·0225; [HCl] = 0·0375.

Time, mins.	Titre, c.c.	*k*.
0	9·12	
52·08	6·93	0·2447
83·00	5·90	0·2489
119·0	4·97	0·2477
	Mean	0·2471

3'-Chloro-4-methoxy-4'-ethoxybenzophenone.
(10 C.c. burette graduated in 0·02 c.c.)
$[Cl_2] = 0·0075$; [ether] = 0·0225; [HCl] = 0·0375.

Time, mins.	Titre, c.c.	*k*.
0	9·12	
12·20	6·07	1·578
19·60	4·83	1·581
26·00	4·00	1·582
	Mean	1·580

Mean values of *k* for individual experiments (molecular ratio, ether : $Cl_2 = 3 : 1$).

p-Ethoxy-*p'*-*n*-butoxybenzophenone	9·80, 9·77, 9·90, 9·84
p-Methoxy-*p'*-*n*-propoxybenzophenone	7·33, 7·35
pp'-Dimethoxybenzophenone	4·631, 4·696, 4·582, 4·637
p-Methoxy-*p'*-β-chloroethoxybenzophenone	2·763, 2·769
pp'-Dimethoxydiphenylsulphone	0·1114, 0·1085

Materials.—Carefully purified materials were employed throughout, special care being taken to ensure freedom of the medium and of the ethers from trace of impurities reactive towards chlorine. Three crystallisations of the ethers, usually from alcohol or glacial acetic acid, were necessary to ensure pure specimens. The constancy of the velocity coefficients after further crystallisations is illustrated by the following mean values for (*a*) 3'-bromo-4-methoxybenzophenone and (*b*) *p*-*n*-amyloxybenzophenone : (*a*) After two crystallisations from ethyl alcohol and one from glacial acetic acid, $k = 0·778$; after two further crystallisations from alcohol, $k = 0·773$ and 0·776. (*b*) After distillation under reduced pressure, two crystallisations from ligroin and one from alcohol, $k = 2·783$; after a further crystallisation from alcohol, $k = 2·790$.

pp'-*Dihydroxydiphenyl sulphoxide and sulphone.* The sulphoxide, m.p. 194°, prepared from phenol and thionyl chloride by the method of Smiles and Bain (J., 1907, **91**, 1118), was converted into the sulphone by treating a solution in glacial acetic acid with the calculated amount of hydrogen peroxide. On careful evaporation of the mother-liquor, the sulphone was isolated as a pale brown solid, m. p. 239° after one crystallisation. The dialkoxydiphenylsulphones, with one exception, were then prepared by heating under reflux 1 mol. of the sulphone, 2 mols. of sodium ethoxide in alcohol, and 2·1 mols. of the appropriate alkyl bromide or iodide. The resulting solution was poured into dilute aqueous sodium hydroxide, whereupon the dialkoxysulphone crystallised. Each sulphone was recrystallised thrice from ethyl alcohol before being used in velocity measurements. All members of the series now investigated are only sparingly soluble in cold alcohol and glacial acetic acid, the dimethoxy-compound appearing from qualitative observations to have the greatest solubility.

4 : 4'-*Dialkoxydiphenylsulphones.* The dimethoxy-sulphone was obtained as a white crystalline solid, m. p. 129—130° (Found : * C, 60·4; H, 5·5. Calc. : C, 60·4; H, 5·1%). The n- and the iso-*dipropoxy-sulphones* had m. p. 142—143° and 157° respectively (Found for both compounds : C, 64·7; H, 6·5. $C_{18}H_{22}O_4S$ requires C, 64·7; H, 6·6%). The *di*-n-*butoxy-sulphone* had m. p. 92·5° (Found : C; C, 66·4; H, 7·2. $C_{20}H_{26}O_4S$ requires C, 66·3; H, 7·2%),

* Micro-determinations by Dr. A. Schoeller or Dr. G. Weiler.

and the *di*-n-*amyloxy*-compound m. p. 86·5° (Found : C, 67·4; H, 7·7. $C_{22}H_{30}O_4S$ requires C, 67·7; H, 7·75%).

The diethoxydiphenyl sulphoxide was prepared by Smiles and Le Rossignol's method (J., 1906, **89**, 707), and converted into the sulphone by treatment with hydrogen peroxide; after three crystallisations from alcohol the sulphone had m. p. 164° (Found : C, 62·8; H, 5·8. Calc. : C, 62·7; H, 5·9%).

The symmetrical *pp'*-dialkoxybenzophenones were obtained from *pp'*-dihydroxybenzophenone, prepared from the corresponding dimethoxy-compound by dealkylation with anhydrous aluminium chloride. *pp'*-Dimethoxybenzophenone was prepared in quantity, and in good yield, by the Friedel–Crafts condensation of anisoyl chloride and anisole, the use of an inert solvent being avoided by employing 2—3 mols. of anisole. When the addition of the aluminium chloride was completed, the mixture was heated on a steam-bath for 10—15 minutes. If the heating is prolonged at this stage, dealkylation is liable to occur. The product was purified in the usual manner, the excess anisole being first removed by steam-distillation. The cooled product solidified, and was crystallised from alcohol and acetic acid; m. p. 143—144° (Found : C, 74·3; H, 5·9. Calc. : C, 74·35; H, 5·8%).

pp'-Dihydroxybenzophenone was prepared by heating the dimethoxy-compound with 2 mols. of finely powdered anhydrous aluminium chloride until the evolution of methyl chloride ceased. Addition of excess of dilute hydrochloric acid to the cooled mass liberated the free dihydroxy-compound which, after crystallisation from alcohol, had m. p. 206°. The following dialkoxybenzophenones, prepared by standard methods from the above and commercially pure specimens of the alkyl bromides or iodides, crystallised from alcohol in flat glistening plates.

pp'-Diethoxybenzophenone, m. p. 130—131° (Found : C, 75·3; H, 6·5. Calc. : C, 75·5; H, 6·7%). pp'-*Di*-n-*propoxybenzophenone*, m. p. 127° (Found : C, 76·7; H, 7·4. $C_{19}H_{22}O_3$ requires C, 76·5; H, 7·4%). pp'-*Di*iso*propoxybenzophenone*, m. p. 72·5° (Found : C, 76·3; H, 7·5%). pp'-*Di*-n-*butoxybenzophenone*, m. p. 118° (Found : C, 77·3; H, 8·1. $C_{21}H_{25}O_3$ requires C, 77·5; H, 7·8%). pp'-*Di*-n-*amyloxybenzophenone*, m. p. 108° (Found : C, 77·9; H, 8·5. $C_{23}H_{29}O_3$ requires C, 78·1; H, 8·3%).

Similarly, the unsymmetrical *pp'*-dialkoxybenzophenones were prepared by condensing, at room temperature, *p*-anisoyl or *p*-ethoxybenzoyl chloride and the appropriate phenyl ether. The procedure was the same as that for *pp'*-dimethoxybenzophenone except that now only 1·5—2 mols. of the phenyl ether were used. Consequently, when the product was added to dilute hydrochloric acid and cooled, it partly solidified. After decantation of the aqueous layer, the oily product was washed with water and cooled in a freezing mixture. The adhering excess phenyl ether was removed by rapid filtration through a well-cooled funnel, and the product purified by decolorisation (charcoal) and crystallisation from ethyl alcohol.

p-*Methoxy*-p'-*ethoxybenzophenone*, m. p. 111° (Found : C, 74·6; H, 6·1. $C_{16}H_{16}O_3$ requires C, 75·0; H, 6·3%). p-*Methoxy*-p'-n-*propoxybenzophenone*, m. p. 111° (Found : C, 75·4; H, 6·7. $C_{17}H_{18}O_3$ requires C, 75·5; H, 6·7%). p-*Methoxy*-p'-n-*butoxybenzophenone*, m. p. 105—106° (Found : C, 75·9; H, 7·0. $C_{18}H_{20}O_3$ requires C, 76·0; H, 7·1%). p-*Methoxy*-p'-n-*amyloxybenzophenone*, m. p. 101° (Found : C, 76·7; H, 7·3. $C_{19}H_{22}O_3$ requires C, 76·5; H, 7·4%). p-*Methoxy*-p'-β-*chloroethoxybenzophenone*, m. p. 106° (Found : C, 65·9; H, 5·2. $C_{16}H_{15}O_3Cl$ requires C, 66·1; H, 5·2%). p-*Ethoxy*-p'-n-*butoxybenzophenone*, m. p. 103° (Found : C, 76·2; H, 7·4. $C_{19}H_{22}O_3$ requires C, 76·5; H, 7·4%). p-*Ethoxy*-p'-n-*amyloxybenzophenone*, m. p. 95° (Found : C, 76·6; H, 7·7. $C_{20}H_{24}O_3$ requires C, 76·9; H, 7·7%).

3'-*Chloro*-4-*methoxy*-4'-*ethoxybenzophenone*, m. p. 108° (Found : C, 66·2; H, 5·2. $C_{20}H_{15}O_3Cl$ requires C, 66·1; H, 5·2%), 3'-*chloro*-4 : 4'-*dimethoxybenzophenone*, m. p. 97·5° (Found : C, 64·9; H, 5·0. $C_{19}H_{13}O_3Cl$ requires C, 65·1; H, 4·8%), and 3'-*chloro*-4-*methoxy*-4'-n-*propoxybenzophenone*, m. p. 77° (Found : C, 66·7; H, 5·7. $C_{21}H_{17}O_3Cl$ requires C, 67·0; H, 5·6%), were prepared in a similar manner from *p*-anisoyl chloride and *o*-chlorophenetole, *o*-chloroanisole, and *o*-chlorophenyl *n*-propyl ether respectively.

Monoalkoxybenzophenones. With the exception of *p*-methoxy- and *p*-ethoxy-benzophenones, the monoalkoxybenzophenones were prepared by standard methods from a commercially pure sample of the parent hydroxy-compound. *p*-Methoxy- and *p*-ethoxy-benzophenones were obtained by the condensation of benzoyl chloride and anisole or phenetole, by means of anhydrous aluminium chloride. The use of an inert solvent was again dispensed with by employing an excess of the phenyl ether, which was later removed by steam-distillation. The *o*-isomeride formed in these condensations was removed by crystallisation, and *o*-methoxybenzophenone could only be eliminated by repeated crystallisation from ligroin (b. p. 40—60°) and alcohol. The product, m. p. 61—62°, was freely soluble in alcohol and crystallised only with difficulty.

p-Ethoxybenzophenone, on the other hand, was readily purified, since the *o*-isomeride is a liquid at room temperature. The initial product was dissolved in warm ligroin (b. p. 40—60°) and frozen; the *p*-isomeride crystallised, leaving the *o*-compound as an oily layer. After further crystallisations from ligroin and alcohol, the former melted at 47° (previously recorded value 38—39°) (Found: C, 79·6; H, 6·2. Calc.: C, 79·6; H, 6·4%).

p-n-*Butoxybenzophenone*, prepared from *p*-hydroxybenzophenone and commercially pure *n*-butyl bromide, is a white crystalline solid, m. p. 37° (Found: C, 80·6; H, 7·0. $C_{17}H_{18}O_2$ requires C, 80·3; H, 7·1%). p-n-*Amyloxybenzophenone*, prepared similarly, was first obtained as a colourless liquid, b. p. 238°/14 mm., which on standing crystallised to a white solid; after two crystallisations from ligroin (b. p. 40—60°) and one from alcohol, it had m. p. 41° (Found: C, 80·6; H, 7·4. $C_{18}H_{20}O_2$ requires C, 80·6; H, 7·5%).

A commercially pure specimen of *n*-heptyl alcohol was converted into the chloride by the action of thionyl chloride and pyridine, chloroform being used as a diluent. Condensation of this with *p*-hydroxybenzophenone in the usual manner afforded p-n-*heptoxybenzophenone* as a colourless liquid, b. p. 255/15 mm., and m. p. 47° after crystallisations from ligroin (b. p. 40—60°) and alcohol (Found: C, 80·8; H, 8·1. $C_{20}H_{24}O_2$ requires C, 81·0; H, 8·2%).

All the above monoalkoxybenzophenones are freely soluble in ethyl alcohol, acetone, and acetic acid.

Monosubstituted alkoxybenzophenones. The methoxybenzophenones of the type *p*-MeO·C_6H_4·CO·C_6H_4X were, with one exception, prepared by the Friedel–Crafts method from the chloride C_6H_4X·COCl and anisole. The precautions mentioned above were again observed.

2′-, 3′-, *and* 4′-*Fluoro*-4-*methoxybenzophenones.* Pure specimens of the *o*-, *m*-, and *p*-fluorobenzoic acids required for these preparations were obtained by oxidation with aqueous potassium permanganate of the corresponding fluorotoluenes, prepared from the toluidines by Balz and Schiemann's method (*Ber.*, 1927, **60**, 1186). Distillation of the acids with phosphorus pentachloride gave the chlorides, which were immediately condensed with anisole to give the three fluoromethoxybenzophenones. All three ketones are white crystalline solids, soluble in alcohol and glacial acetic acid, and freely soluble in acetone. The following are the m. p.'s and analyses: 2′-*Fluoro*-compound, m. p. 49° (Found: C, 72·8; H, 4·7. $C_{14}H_{11}O_2F$ requires C, 73·0; H, 4·8%); 3′-*isomeride*, m. p. 72° (Found: C, 72·7; H, 4·8%); 4′-*isomeride*, m. p. 95° (Found: C, 73·0; H, 4·8%).

2′- *and* 4′-*Chloro*-4-*methoxybenzophenones.* Commercially pure specimens of *o*- and *p*-chlorobenzoic acids were converted into the chlorides, and these, immediately after distillation, condensed with anisole as above. The 4′-*chloro*-compound had m. p. 125·5° (Found: C, 67·8; H, 4·4. $C_{14}H_{11}O_2Cl$ requires C, 68·2; H, 4·5%), and the 2′-*isomeride* had m. p. 80° (Found: C, 68·3; H, 4·5%).

4′-*Chloro*-4-*ethoxybenzophenone*, prepared similarly from phenetole and *p*-chlorobenzoyl chloride, had m. p. 121° (Found: C, 69·1; H, 5·0. $C_{15}H_{13}O_2Cl$ requires C, 69·4; H, 5·0%).

2′-*Chloro*-4-β-*chloroethoxybenzophenone.* β-Phenoxyethyl alcohol, prepared from phenol, sodium ethoxide, and ethylene chlorohydrin, was converted by the action of thionyl chloride and pyridine into phenyl β-chloroethyl ether which, after distillation, solidified in a freezing mixture into a white crystalline solid, m. p. 25°. Condensation of this with *o*-chlorobenzoyl chloride gave 2′-*chloro*-4-β-*chloroethoxybenzophenone* as a white crystalline solid, m. p. 65° after three crystallisations from alcohol (Found: C, 60·8; H, 4·35. $C_{15}H_{12}O_2Cl_2$ requires C, 61·0; H, 4·1%).

2′-, 3′-, and 4′-Bromo-4-methoxybenzophenones, m. p.'s 96° (previous value 95·5°), 80°, and 154° respectively, were prepared in a similar manner from purchased specimens of the three monobromobenzoic acids (Found: for 2′-bromo-compound, C, 58·5; H, 4·0; for 3′-*bromo*-compound, C, 58·3; H, 3·9; for 4′-*bromo*-compound, C, 57·8; H, 4·0. $C_{14}H_{11}O_2Br$ requires C, 57·8; H, 3·8%).

4-*Methoxy*-2′-, -3′-, *and* -4′-*methylbenzophenones.* The 3′-*methyl* compound (Found: C, 79·6; H, 6·1. $C_{15}H_{14}O_2$ requires C, 79·6; H, 6·2%), m. p. 56°, was obtained from anisole and *m*-toluoyl chloride, and the 4′-*isomeride*, m. p. 90—91° (Found: C, 79·5; H, 6·0%), was prepared by the condensation of *p*-anisoyl chloride and toluene. The 2′-methyl isomeride, from anisole and *o*-toluoyl chloride is a liquid, b. p. 220°/23 mm., and was not obtained in a sufficiently pure state for velocity measurements.

3′- and 4′-Nitro-4-methoxybenzophenones were prepared from commercially pure specimens of *m*- and *p*-nitrobenzoyl chloride and anisole. The 4′-nitro-compound had m. p. 123° (cf. 121° previously recorded) (Found: C, 65·0; H, 4·2%). The 3′-*nitro*-isomeride had m. p. 93° (Found: C, 65·5; H, 4·4. $C_{14}H_{11}O_4N$ requires C, 65·4; H, 4·3%).

3′-*Nitro*-4-n-*butoxybenzophenone*, from *m*-nitrobenzoyl chloride and phenyl *n*-butyl ether, crystallises from glacial acetic acid in soft pale yellow crystals, m. p. 73° (Found : C, 67·8; H, 5·6. $C_{17}H_{17}O_4N$ requires C, 68·2; H, 5·7%).

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