Absorption Spectra in Relation to the Chemical Reactivity of Some Halogeno-aromatic Compounds.

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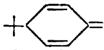
The ultra-violet light-absorption spectra of a number of chloro- and fluoro-aromatic compounds are described, and some correlation of the results with the degree of halogenation of the substances and their reactivity is attempted.

DURING studies on organic fluorides (*J.*, 1951, 1701 and others in the series), a number of chloro-aromatic compounds were obtained as intermediates (Harvey, Smith, Stacey, and Tatlow, *J. Appl. Chem.*, 1954, **4**, 319, 325). For many of these, no record of ultra-violet light absorption characteristics occurs in the literature and the relevant data are therefore tabulated below.

The spectra of *p*-xylene, benzene, benzyl fluoride, benzaldehyde, and benzoic acid have been compared by Ingold (*J.*, 1928, 2249), who observed a gradual displacement of wave-length of maximum absorption towards the blue which he correlated with the increasing tendency of the substituent groups to deactivate the aromatic nucleus. Conrad-Billroth (*Z. physikal. Chem.*, 1932, **19**, *B*, 83) made a comprehensive survey of the spectroscopic properties of nuclear-substituted chlorobenzenes, and Sponer (*Chem. Reviews*, 1947, **41**, 281) has compared, in some detail, the absorption characteristics of 1 : 2 : 3-, 1 : 2 : 4-, and 1 : 3 : 5-trichlorobenzenes with those of the corresponding trimethylbenzenes. Hamner and Matsen (*J. Amer. Chem. Soc.*, 1948, **70**, 2482) point out the resemblance between the spectra of toluene and benzyl chloride. Benzylidene chloride exhibits a slight shift of maximum absorption towards the red and benzotrichloride behaves similarly, although the $\varepsilon_{max.}$ value is higher (300 and 500 respectively). These authors suggest forms such as $=CH_2Cl^-$ (I) to account for the results. The greater the degree of side-chain chlorination, the more of such forms can be postulated.

Our measurements and the data for the hydrocarbons, taken from Conrad-Billroth (*Z. physikal. Chem.*, 1935, **29**, *B*, 170), permit the comparisons in Table 1, where the numbers at the head of columns denote positions in the benzene ring :

Table 1.

	1	2	3	4	5	6	
i	Me	Me	—	—	—	—	λ 2700, 2640; ε 390, 415
	$CHCl_2$	CCl_3	—	—	—	—	λ 2790; ε 750
ii	Me	—	—	Me	—	—	λ 2740, 2680, 2650, 2600, 2555, 2510; ε 960, 726, 780, 545, 400, 330
	CH_2Cl	—	—	CH_2Cl	—	—	λ 2680; ε 300
	CCl_3	—	—	CCl_3	—	—	No selective absorption at λ 2700—2500, *i.e.*, low-wave-length absorption is so intense as to mask completely the " benzene " band
iii	Et	—	—	—	—	—	λ 2610; ε 220
	$CCl_2{\cdot}CCl_3$	—	—	—	—	—	λ 2670, 2685; ε 800, 700
iv	Me	—	Me	—	Me	—	λ 2715, 2675, 2650, 2625, 2585, 2500; ε 266, 250, 303, 250, 273, 233
	CCl_3	Cl	CCl_3	—	CCl_3	—	No selective absorption at λ >2300

Some information about the effect of progressive halogen substitution in the side-chain of a nuclear chlorinated benzene derivative is afforded by the data in Table 2.

Except where the substituents are symmetrically placed (*e.g.*, the *p*-xylene and mesitylene derivatives with and without nuclear chlorine), these results support Hamner and Matsen's findings (*loc. cit.*) in that two or more side-chain chlorine atoms cause a considerable increase in the intensity of absorption. As is to be expected, the symmetrically substituted derivatives do not show the change, which is believed to be due to increase in the number of possible resonating forms.

Table 2.

	1	2	3	4	5	6	
i	Me	Cl	Cl	Cl	Cl	Cl	λ 2800; ε 240
	$CHCl_2$	Cl	Cl	Cl	Cl	Cl	λ 3070, 2920—3050; ε 885, 575
	CCl_3	Cl	Cl	Cl	Cl	—	λ 2920, 3000; ε 900 (approx.)
ii	Et	Cl	Cl	Cl	Cl	Cl	λ 2900; ε 195
	$CH_2{\cdot}CCl_3$	Cl	Cl	Cl	Cl	Cl	λ 3070; ε 1170
	$CCl_2{\cdot}CCl_3$	Cl	Cl	Cl	Cl	—	λ 3030, 2940; ε 1260, 1160
iii	Me	Me	Cl	Cl	Cl	Cl	λ 2800; ε 230
	$CHCl_2$	$CHCl_2$	Cl	Cl	Cl	Cl	λ 2900, 3105; ε 1060, 1280
iv	Me	Cl	Cl	Me	Cl	Cl	λ 2810; ε 260
	$CHCl_2$	Cl	Cl	$CHCl_2$	Cl	Cl	λ 3160; ε 2760
	CCl_3	Cl	Cl	CCl_3	Cl	Cl	λ 2900, 2930—3020; ε 300, 255
v	Me	Cl	Me	Cl	Me	Cl	λ 2780; ε 150
	$CHCl_2$	Cl	$CHCl_2$	Cl	$CHCl_2$	Cl	λ 2900 (" step out "); ε 400
	CCl_3	Cl	CCl_3	Cl	CCl_3	Cl	λ 2750—2850 (" step out "); ε 250 approx.

It was found that there is a relation between the type of spectrum a chloro-compound possesses and the ease with which the compound can be changed into the corresponding fluoro-compound by reaction with anhydrous hydrogen fluoride. When the spectrum of the chloro-compound resembles that of benzoic acid (λ 2270 Å, ε 14,000; with a shallow band at λ 2670 Å, ε *ca.* 1000; cf. Waljascko and Bottino, *Centralbl.*, 1915, **11**, 463), the conversion is relatively easy; if, however, the spectrum resembles that of the analogous hydrocarbon or fluorocarbon, the reaction is difficult, if not impossible, as the following examples show :

(i) Anhydrous hydrogen fluoride cannot replace nuclear-substituted chlorine by fluorine, but trichloromethyl groups attached to nuclear carbon atoms are fluorinated easily. Fluorination of pentachloroethylbenzene in this way is difficult. It has been reported that the reaction $C_6H_5{\cdot}CCl_2{\cdot}CCl_3 \xrightarrow[\text{HF}]{\text{Anhyd.}} C_6H_5{\cdot}CF_2{\cdot}CCl_3$ occurs only at 200° and a hydrogen fluoride pressure of 3000 lb./sq. in., and Simons *et al.* (*J. Amer. Chem. Soc.*, 1921, **43**, 2064) record that vigorous fluorinating agents such as silver fluoride or antimony pentafluoride are necessary to introduce three or more fluorine atoms into its side-chain. The absorption spectrum of chlorobenzene closely resembles that of toluene and is similar to that of fluorobenzene. Fig. 1 illustrates the similarity in spectrum type between 1 : 4-bistrifluoromethylbenzene and pentachloroethylbenzene. 1-Dichloromethyl-2-trichloromethylbenzene is likewise not easily fluorinated by anhydrous hydrogen fluoride and again its spectrum is of the toluene type. 1 : 4-Bischloromethylbenzene (Fig. 1) should be easily fluorinated by anhydrous hydrogen fluoride.

FIG. 1.

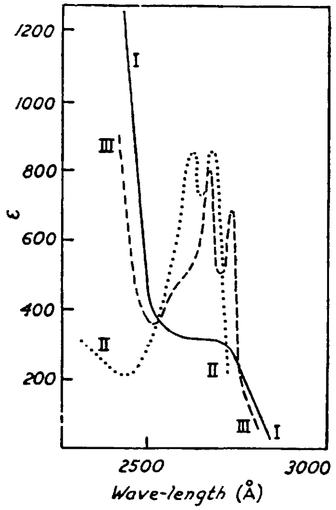


FIG. 2.

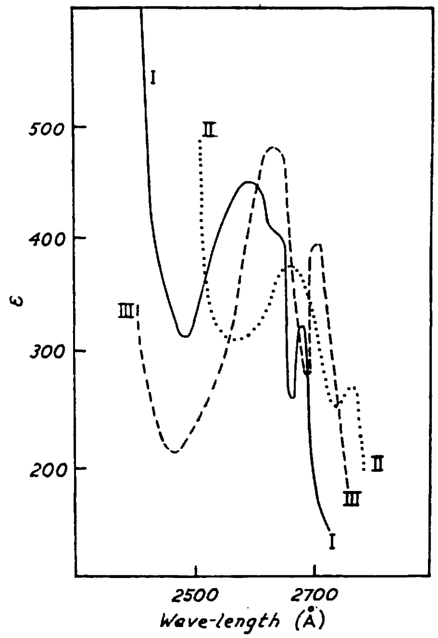


FIG. 1. *Absorption spectra of* (I) 1 : 4-*bischloromethylbenzene in* EtOH, (II) 1 : 4-*bistrifluoromethylbenzene in* cyclo*hexane, and* (III) *pentachloroethylbenzene in* cyclo*hexane.*

FIG. 2. *Absorption spectra of* (I) 1 : 1 : 1-*trichloro*-2 : 2-*diphenylethane,* (II) 1 : 1 : 1-*trichloro*-2 : 2-*di*-p-*chlorophenylethane, and* (III) 1 : 1 : 1-*trichloro*-2 : 2-*di*-p-*fluorophenylethane, all in* cyclo*hexane.*

(ii) Dichlorodiphenylmethane readily reacts with anhydrous hydrogen fluoride to give difluorodiphenylmethane, although the difluoro-compound tends to be hydrolysed to benzophenone on being kept.

The difficulty of the replacement of chlorine by fluorine follows approximately the same order as the amount of *meta*-direction of a nitro-group entering the ring (caused by the chlorine-containing substituent) (cf. Rice, " The Mechanism of Organic Reactions," McGraw-Hill, New York, p. 146; Hamner and Matsen, *loc. cit.*; Flürscheim and Holmes, *J.*, 1928, 1607).

It is well known that the halogens are capable not only of attracting electrons but also of donating them in suitable circumstances, *e.g.*, the relative strengths of the acids

$F{\cdot}CH_2{\cdot}CO_2H$, $Cl{\cdot}CH_2{\cdot}CO_2H$, $CH_3{\cdot}CO_2H$ decrease in the order given (inductive attraction of electrons by F > Cl > H), whereas a nuclear halogen atom is largely *ortho-para*-directing to an incoming electrophilic substituent (activation of *ortho*- and *para*-positions by the electromeric donor effects of halogens). The groups CH_2F and CH_2Cl are also largely *ortho-para*-directing, the inductive attraction of electrons not becoming marked until two side-chain halogen atoms are present. It should be noted that the resonance forms postulated by Hamner and Matsen would deactivate the *ortho*- and *para*-positions [see (I)]. The following experimental results suggest that successive nuclear chlorination makes the electromeric effect subsidiary to the inductive effect : (i) One chlorine atom in hexachlorobenzene is quite easily hydrolysed. (ii) The chlorine in *m*-dichlorobenzene is more reactive towards sodium methoxide than in the *o*- and *p*-isomers. (iii) The nuclear chlorine atoms in 1 : 3 : 5-trichlorobenzene are relatively reactive and resemble to some extent that in picryl chloride. In this, the three attractor groups present cause the nuclear chlorine to be labile as in an acid chloride group.

TABLE 3.

Compound	Yield of mononitro-compound (%) *o*-	*m*-	*p*-
Chlorobenzene	30·1	—	69·9
Toluene	61·5—62·5	4·5—4·2	33·5—32
Benzyl chloride	40·9	4·2 *	54·9
Benzylidene chloride	23·3	33·8	42·9
Benzotrichloride	6·8	64·5 *	28·7
Benzoic acid	18·5	80·2	1·3

* Flürscheim and Holmes, *loc. cit.*, give 11·2 and 48·3—48·6%, respectively.

In this connection, Fig. 2 is of interest. The fluoro-substituted compound has a band of slightly higher intensity than the unsubstituted molecule; the chloro-substituted compound is of very slightly lower intensity; the orders of magnitude, however, are the same in each case. The shift towards the red is greatest in the case of the nuclear chloro-substituted derivative. The relative intensities are such as to suggest that fluorine is a better donor than chlorine, which is in agreement with the finding by Kharasch *et al.* (*J. Org. Chem.*, 1938, **3**, 347) that the ease of cleavage in the reaction $R{\cdot}Hg{\cdot}R' + HCl \longrightarrow R{\cdot}Hg{\cdot}Cl + R'H$ (R′ is the more electronegative) decreases in the order *p*-fluorophenyl > phenyl > *p*-chlorophenyl.

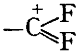
A correlation of the directive effects of a number of groups on substituents entering a benzene ring to which they are attached with their dipole moments in aromatic (ar) and aliphatic (al) combination, made by Sutton (*Proc. Roy. Soc.*, **1931**, **133**, 686), affords a preliminary unification of these various data. He showed that when $\mu_{al} > \mu_{ar}$ the group deactivates the nucleus and is *meta*-directing. Some values of the difference ($\mu_{ar} - \mu_{al}$) are given in Table 4.

TABLE 4. *Dipole moments of some organic groups.*

(Unless stated otherwise the following data are due to Sutton, *loc. cit.*)

Group	μ_{ar}	μ_{al}	Diff.	Group	μ_{ar}	μ_{al}	Diff.
Cl	−1·56	−2·15	+0·59	CCl_3	−2·07	−1·57	−0·50
F[1]	−1·57	−1·92	+0·35[1]	CH_3	+0·45	0·0	+0·45
CH_2Cl	−1·82	−2·03	+0·21	CO_2Et	−1·95	−1·77	−0·18
$CHCl_2$	−2·03	−2·06	+0·03	CO_2H[2]	−0·56	—	—

[1] Groves and Sugden, *J.*, 1935, 972. [2] Conrad-Billroth, *Z. physikal. Chem.*, 1934, **25**, *B*, 139.

Both CCl_3 and CO_2Et deactivate the benzene nucleus, and it was noted above that the spectra of benzotrichloride and of ethyl benzoate are similar. It will be seen that μ_{al} is more negative for CO_2Et than for CCl_3, while μ_{ar} is approximately the same. Trichloromethyl groups directly attached to the benzene nucleus are readily fluorinated, whereas the CCl_3 group in ethyl trichloroacetate does not react with anhydrous hydrogen fluoride under the same conditions (Amphlett, Musgrave, and Smith, unpublished results). This would follow if the reaction depended on electrons' being drawn into the CCl_3 group from the rest of the molecule. If the spectrum type is governed by the same consideration, then the values of dipole moments of the CF_3 group in aliphatic and aromatic combination will prove of interest, in that μ_{ar} and μ_{al} for this group should both be smaller than the corresponding values for CCl_3. ($\mu_{ar} - \mu_{al}$) must be negative to fall into line with the known *meta*-directing properties, while to account for the difference in spectrum between CF_3 and corresponding CCl_3 derivative, μ_{ar} must have a smaller negative value for the fluoro- than for the chloro-compound. This would be expected if resonance forms of the type  $-\overset{+}{C}\begin{smallmatrix}\diagup F\\ \diagdown F\end{smallmatrix}\ F^-$ are prominent (see Smith and Turton, *J.*, 1951, 1701). All the available information appears to support this view.

Experimental.—The spectrophotometric measurements were carried out as described by Smith and Turton (*loc. cit.*).

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