[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, DAVIS]

A Study of the Proximity Effects of Substituents on the Dissociation of Iodobenzene Dichlorides

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The equilibrium and rate constants for the equilibration of a number of *o*-substituted iodobenzene dichlorides with the corresponding iodobenzenes and chlorine in acetic acid and in nitromethane have been determined. In general the constants are very similar to those for the corresponding *meta* or *para* isomers. The steric consequences of *o*-substitution on the course of the equilibration are, therefore, small or non-existent. Presumably a conformation in which the linear trihalide grouping is not coplanar with the aromatic nucleus provides for maximum dichloride stability. Even though there is strong evidence to indicate that the activated complexes are intensely solvated in the polar media, *o*-substituents apparently do not interfere with the solvation process. The instability of the dichloride prepared from *o*-iodobenzoic acid is discussed briefly. As has been reported previously this compound decomposes rapidly with gas evolution to form a heterocyclic product which has now been identified conclusively.

Attempts to prepare highly substituted derivatives of iodobenzene dichloride, such as the 2,3,4,6-tetrachloro and 2,5-dichloro-3,4,6-trimethyl derivatives, by gassing solutions of the iodobenzenes with chlorine have been unsuccessful.[1] Although these failures can be attributed to the unfavorable steric influences of substituents *ortho* to the potential reaction sites, this interpretation is questionable since the 2,4,6-trichloro[1] and tribromo[2] derivatives have been isolated. The fact that the solid dichlorides prepared from iodopentamethylbenzene[3] and related *o*-methyliodobenzenes[1] are unusually unstable may be cited as evidence of an *ortho* effect. However, this instability may be peculiar to the crystalline state and, as is the case for the pentamethyl derivative (which decomposes to a brown oil at room temperature[3]), may not necessarily measure the tendency for dissociation to the corresponding iodobenzene and chlorine.

The first evidence of a quantitative nature that steric factors might be of minor significance in controlling the stabilities of *o*-substituted dichlorides, relative to those of the component halobenzenes and halogen, was encountered in studying the equilibration process

$$ArICl_2 \underset{k_2}{\overset{k_1}{\rightleftarrows}} ArI + Cl_2;\ K = \frac{k_1}{k_2} = \frac{(ArI)(Cl_2)}{(ArICl_2)} \quad (1)$$

using nitromethane as the solvent.[1] The dissociation constants, K, at 25° for the *p*-methyl- and *m*-chloroiodobenzene dichlorides were not markedly larger than those for the corresponding *ortho* isomers. This observation seems reasonable provided a coplanar arrangement of the Cl–I–Cl grouping and the aromatic nucleus is not required for maximum dichloride stability. Actually in the crystalline state the linear trihalide function of the iodobenzene dichloride molecule has been found to lie at approximately right angles to the benzene ring.[5]

A more extensive investigation of the effects of substituents neighboring the reaction site on the equilibration process described in equation 1 has now been made through evaluation of k_1, k_2 and K for a number of appropriately constituted aromatic iodides in acetic acid or nitromethane at 25 and 45°. Although the experimental accuracy was in some instances discouragingly low, the results clearly establish that these particular reactions at aromatic side chains are, in their rates as well as in their equilibrium positions, relatively insensitive to proximity effects.

Experimental

Materials.—The procedure used in purifying the solvents and the sources of a number of the iodoaromatic compounds have been discussed previously.[3,4] Eastman Organic Chemicals *o*-iodobenzoic acid, m.p. 160–162°, and pentamethylbenzene were used without further purification. Samples of Eastman Organic Chemicals *o*-iodobiphenyl (b.p. 142° (3 mm.)), 1-iodonaphthalene (b.p. 186° (32 mm.)), 2-iodo-1,3-dimethylbenzene (b.p. 88° (7 mm.)) and 2-iodo-1,4-dimethylbenzene (b.p. 86° (8 mm.)) were distilled before use. The 2-iodonaphthalene, m.p. 53–54°, was prepared from β-naphthylamine[6] and was finally purified by repeated recrystallization from aqueous methanol using decolorizing carbon.

The Dichlorides.—The preparation and properties of several of these compounds have been described earlier.[3,4] Essentially the same preparative procedures, with acetic acid as the solvent, were used to obtain a number of dichlorides which have not been made previously in this Laboratory. These included the dichlorides of 1-iodonaphthalene,[7] 2-iodonaphthalene[7] (m.p. 48° dec.), *o*-iodobiphenyl (m.p. 115–116° dec.), 2-iodo-1,3-dimethylbenzene (m.p. 70–73° dec.) and 2-iodo-1,4-dimethylbenzene[8] (m.p. 78–80° dec.). The 1-iodonaphthalene dichloride was very unstable when dry and decomposed rapidly with gas evolution at room temperature to form a brown oil. No attempt was made to obtain an equivalent weight on this material. It was always dissolved in acetic acid immediately after its preparation, and the solutions were analyzed iodometrically. The other freshly prepared dichlorides generally had equivalent weights (as determined iodometrically) which agreed to within 1.5% of the theoretical value. Some difficulty was experienced in preparing samples of the 2-iodo-1,3-dimethylbenzene derivative which had acceptable equivalent weights.

The *o*-Iodobenzoic Acid Derivative.—A mixture of 1.0 g. of *o*-iodobenzoic acid and 20 ml. of nitromethane was saturated with chlorine. The white solid phase changed to yellow crystalline material overnight. The crystals were filtered, washed with carbon tetrachloride and air-dried. In air this dried solid evolved a noxious gas rapidly and faded to a light yellow powder (later described as compound II). This material melted from 168–171°, and the melting point was substantially depressed by added *o*-iodobenzoic acid. The equivalent weight, as determined by dissolving a weighed sample in acetic acid, adding aqueous potassium

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(1) (a) C. Willgerodt, "Organische Verbindungen mit Mehrwertigen Jod," Enke, Stuttgart, 1914; (b) N. V. Sidgwick, "Chemical Elements and Their Compounds," Vol. II, Oxford University Press, London, 1950, pp. 1246–1248.

(2) J. McCrae, *J. Chem. Soc.*, **73**, 691 (1898).

(3) R. M. Keefer and L. J. Andrews, THIS JOURNAL, **80**, 277 (1958).

(4) R. M. Keefer and L. J. Andrews, *ibid.*, **80**, 5350 (1958).

(5) E. M. Archer and T. G. D. Van Schalkwyk, *Acta Cryst.*, **6**, 88 (1953).

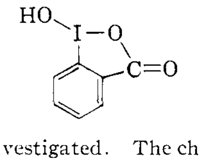
(6) J. Schmidlin and M. Huber, *Ber.*, **43**, 2829 (1910).

(7) C. Willgerodt, *ibid.*, **27**, 591 (1894).

(8) C. C. Nichol and R. B. Sandin, THIS JOURNAL, **67**, 1307 (1945).

iodide and titrating the liberated halogen with standard sodium thiosulfate, was 142.3; calcd. for $C_7H_4O_2ClI$: 141.2.

That II did not contain a free carboxyl group was established by treating a weighed sample with dilute aqueous potassium iodide. The material dissolved completely, whereas aromatic carboxylic acids are generally water insoluble. The resultant solution was decolorized by dropwise addition of dilute sodium thiosulfate solution and was then titrated with standard sodium hydroxide solution. The results indicated an experimental equivalent weight for the unknown as a carboxylic acid of about 7000. On acidification of the titrated solution *o*-iodobenzoic acid, m.p. and mixed m.p. with an authentic sample 162–163°, was precipitated. A weighed sample of II was dissolved in dilute potassium hydroxide solution to liberate chloride ion. The solution was acidified with dilute nitric acid. The white precipitate which formed was filtered and dried. It did not melt when heated to 210° and was undoubtedly the compound[9]



It was not further investigated. The chlorine content of the original sample was established by gravimetric analysis of the filtrate. Calcd. for $C_7H_4O_2ClI$: Cl, 12.54. Found: Cl, 12.49.

The Kinetic Measurements.—The general methods for establishing the equilibrium and rate constants (equation 1) by spectrophotometric methods have been described in detail in the previous publications.[3,4,10] A modification of earlier procedures, which proved useful in determining k_1-values in the present study, was based on the observation that pentamethylbenzene reacts very rapidly with free chlorine in acetic acid solution but does not react directly with iodobenzene dichloride.[11] Thus, although the degree of dissociation of some of the dichlorides under investigation is low in acetic acid solution, in the presence of an excess of pentamethylbenzene complete dissociation occurs since the chlorine is consumed as rapidly as it is formed.

For runs in which the dichloride in question and pentamethylbenzene were the starting materials, rate constants (k_1) were evaluated from optical densities measured during the course of the reactions assuming the rate law

$$-d[C_6H(CH_3)_5]/dt = -d(ArICl_2)/dt = k_1(ArICl_2) \quad (2)$$

In general these runs were conducted at concentration levels and at wave lengths such that the free iodo compounds and the pentamethylbenzene did not show appreciable light absorption. The reactions were carried to completion and the measured optical densities were corrected for small final readings, which presumably were characteristic of chlorine-containing reaction products, before rate constants were calculated. In a few cases in which the dichloride dissociated sufficiently so that k_1-values could be determined with reasonable accuracy without added pentamethylbenzene, rate constants were obtained both in the presence and absence of the aromatic hydrocarbon. The values obtained by the two procedures agreed reasonably well with each other.

As in the previous investigations the optical measurements to determine rate and equilibrium constants were made at wave lengths (360–420 mμ region) in which the dichlorides absorbed strongly. Typical extinction coefficients for the iodo compounds and for their dichlorides in acetic acid and in nitromethane which were found useful and which have not been reported earlier are given in Table I.

TABLE I

EXTINCTION COEFFICIENTS OF THE IODO COMPOUNDS AND THE DICHLORIDES

ArI[a]	λ, mμ	ϵ_{ArI}	ϵ_{ArICl_2}
o-Iodotoluene	380	0.05	74.3
o-Chloroiodobenzene	370	.15	107
o-Iodobiphenyl	370	.34	193
1-Iodonaphthalene	424	.13	85.6
2-Iodonaphthalene	410	.37	145
2-Iodo-1,3-dimethylbenzene	380	.80	85.1
2-Iodo-1,4-dimethylbenzene	380	.06	107.5
o-Iodobiphenyl[b]	380	.34	138

[a] Except as noted the solvent was acetic acid. [b] The solvent was nitromethane.

Results

The Equilibrium Constants.—Table II summarizes the results of experiments conducted to determine K-values. Except as noted, the reported constants were calculated from equilibrium concentrations, evaluated spectrophotometrically, of solutions which initially contained only the dichloride as a solute. The compounds for which data are reported include several *o*-substituted iodobenzene dichlorides and the corresponding *m*- or *p*-isomers as well 2-iodonaphthalene dichloride and its potentially hindered (by the peri hydrogen atom) isomer, 1-iodonaphthalene dichloride.

The electronic effects of methyl and chloro substituents on the stability of iodobenzene dichloride in acetic acid are opposite. The *p*-methyl derivative has a somewhat smaller and the *m*-chloro derivative a considerably larger dissociation constant than the parent compound. Since the degree of dichloride dissociation is enhanced as either *p*-methyl or *m*-chloro substituents are moved to *o*-positions (as is also the case when nitromethane is the solvent[4]), it would appear offhand that *o*-substituents have an unfavorable proximity effect. However the differences in K-values for the *o*- and *p*-methyl derivatives and for the *o*- and *m*-chloro isomers are much smaller than would be anticipated were it essential for maximum stabilization of the dichloride that the linear trihalide grouping lie parallel to the aromatic ring plane. A consideration of molecular models indicates that hindrance to such an arrangement by *o*-substituents would be intense. Furthermore *o*-iodobiphenyl dichloride in which the hindrance problem might be acute actually has a smaller dissociation constant in acetic acid than the *p*-isomer. In nitromethane the constants for the two substances are very similar in magnitude. The differences in K-values for the 1- and 2-iodonaphthalene derivatives in acetic acid are also minor. Perhaps most indicative of the intensity of dichloride stability to proximity effects is the fact that the dissociation constants of 2-iodo-1,3-dimethylbenzene dichloride and 2-iodo-1,4-dimethylbenzene dichloride in acetic acid are of the same general order of magnitude. For reactions which are subject to steric influences of *o*-substituents the effects generally are vastly magnified when the reaction site is flanked by ring substituents.[12]

The Rate Constants.—There is an abundance of evidence[3,4,10] which indicates that in a polar medium solvent molecules must make a significant structural contribution to the activated complex separating an iodobenzene dichloride and its dissociation products. Therefore a substituent neigh-

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(9) (a) C. Willgerodt, *J. prakt. Chem.*, **49**, 476 (1894); (b) V. Meyer and W. Wachter, *ibid.*, **25**, 2632 (1892); V. Meyer and P. Askenasy, *Ber.*, **26**, 1357 (1893).

(10) L. J. Andrews and R. M. Keefer, THIS JOURNAL, **80**, 1723 (1958).

(11) R. M. Keefer and L. J. Andrews, *ibid.*, **79**, 4348 (1957).

(12) (a) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 204; (b) see V. Meyer, *Ber.*, **27**, 519 (1894), for a specific illustration.

boring the reaction site might well serve as a substantial enough barrier to solvation, as required for activation, so that the rate of dichloride equilibration would be appreciably affected even though the equilibrium constant were not subject to steric influences.

In reality, however, there is little if any indication that such a hindrance problem exists. In general the k_1- and k_2-values for dissociation and formation of isomeric *o*- and *p*-substituted dichlorides in acetic acid are closely comparable (see Table III). The rate constants for formation and dissociation of 1-iodonaphthalene dichloride are actually slightly larger than those for the 2-iodonaphthalene derivative, and the differences in k_1- and k_2-values for the dichlorides of 2-iodo-1,3-dimethylbenzene and 2-iodo-1,4-dimethylbenzene are very small.

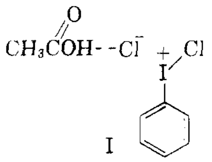
TABLE II

EQUILIBRIUM CONSTANTS FOR DICHLORIDE DISSOCIATION[a,b]

<table>
<tr><th>10^3-(ArI)$_T$, moles/l.</th><th>10^3-(Cl$_2$)$_T$, moles/l.</th><th>10^3K, moles/l.</th><th>10^3-(ArI)$_T$, moles/l.</th><th>10^3-(Cl$_2$)$_T$, moles/l.</th><th>10^3K, moles/l.</th></tr>
<tr><td colspan="6">Acetic acid solvent</td></tr>
<tr><td colspan="3">*p*-Iodotoluene, 25.2°</td><td colspan="3">*o*-Iodotoluene, 25.2°</td></tr>
<tr><td colspan="2">8.61</td><td>0.78</td><td colspan="2">13.87</td><td>1.15</td></tr>
<tr><td colspan="2">5.74</td><td>.75</td><td colspan="2">9.28</td><td>1.15</td></tr>
<tr><td colspan="2">2.83</td><td>.72</td><td colspan="2">4.59</td><td>0.97</td></tr>
<tr><td colspan="3">Av. 0.75 ± 0.02</td><td colspan="3">Av. 1.09 ± 0.08</td></tr>
<tr><td colspan="3">45.4°</td><td colspan="3">45.6°</td></tr>
<tr><td colspan="2">8.45</td><td>1.65</td><td colspan="2">7.75</td><td>1.73</td></tr>
<tr><td colspan="2">5.62</td><td>1.77</td><td colspan="2">5.17</td><td>2.29</td></tr>
<tr><td colspan="2">2.78</td><td>1.91</td><td colspan="2">2.58</td><td>2.29</td></tr>
<tr><td colspan="3">Av. 1.77 ± 0.09</td><td colspan="3">Av. 2.10 ± 0.25</td></tr>
<tr><td colspan="3">2-Iodo-1,4-dimethylbenzene, 25.0°</td><td colspan="3">2-Iodo-1,3-dimethylbenzene, 25.0</td></tr>
<tr><td colspan="2">10.45</td><td>0.82</td><td colspan="2">10.25</td><td>1.0</td></tr>
<tr><td colspan="2">6.99</td><td>.82</td><td colspan="2">6.79</td><td>0.8</td></tr>
<tr><td colspan="2">3.46</td><td>.74</td><td colspan="2">3.37</td><td>.6</td></tr>
<tr><td></td><td></td><td></td><td>7.60</td><td>8.04</td><td>.7</td></tr>
<tr><td></td><td></td><td></td><td>3.80</td><td>3.59</td><td>.5</td></tr>
<tr><td colspan="3">Av. 0.79 ± 0.04</td><td colspan="3">Av. 0.7 ± 0.14</td></tr>
<tr><td colspan="3">45.6°</td><td colspan="3">45.6°</td></tr>
<tr><td colspan="2">10.05</td><td>1.54</td><td colspan="2">11.21</td><td>1.36</td></tr>
<tr><td colspan="2">6.77</td><td>1.76</td><td colspan="2">7.48</td><td>1.39</td></tr>
<tr><td colspan="2">3.40</td><td>1.88</td><td colspan="2">3.77</td><td>1.42</td></tr>
<tr><td colspan="3">Av. 1.73 ± 0.12</td><td colspan="3">Av. 1.39 ± 0.02</td></tr>
<tr><td colspan="3">2-Iodonaphthalene, 25.1°</td><td colspan="3">1-Iodonaphthalene, 25.1°</td></tr>
<tr><td colspan="2">6.00</td><td>2.46</td><td colspan="2">10.90</td><td>2.75</td></tr>
<tr><td colspan="2">4.12</td><td>2.40</td><td colspan="2">7.34</td><td>2.79</td></tr>
<tr><td colspan="2">2.08</td><td>2.02</td><td colspan="2">3.77</td><td>2.94</td></tr>
<tr><td colspan="3">Av. 2.29 ± 0.18</td><td colspan="3">Av. 2.83 ± 0.08</td></tr>
<tr><td colspan="3">45.4°</td><td colspan="3">45.6°</td></tr>
<tr><td colspan="2">6.88</td><td>5.7</td><td colspan="2">9.72</td><td>7.1</td></tr>
<tr><td colspan="2">4.54</td><td>5.4</td><td colspan="2">6.75</td><td>7.4</td></tr>
<tr><td colspan="2">2.37</td><td>5.1</td><td colspan="2">3.74</td><td>7.6</td></tr>
<tr><td colspan="3">Av. 5.4 ± 0.2</td><td colspan="3">Av. 7.4 ± 0.2</td></tr>
<tr><td colspan="3">*o*-Iodobiphenyl,[c] 25.2°</td><td colspan="3">*o*-Chloroiodobenzene,[d] 25.2°</td></tr>
<tr><td>8.50</td><td>6.85</td><td>0.98</td><td>54.7</td><td>6.64</td><td>21</td></tr>
<tr><td>8.50</td><td>3.30</td><td>1.12</td><td>27.3</td><td>13.42</td><td>25</td></tr>
<tr><td>9.25</td><td>3.10</td><td>1.02</td><td>27.3</td><td>6.54</td><td>24</td></tr>
<tr><td colspan="2">4.28</td><td>1.19</td><td>27.3</td><td>5.65</td><td>24</td></tr>
<tr><td colspan="2">2.14</td><td>1.23</td><td colspan="2">10.4</td><td>20</td></tr>
<tr><td colspan="3">Av. 1.11 ± 0.09</td><td colspan="3">Av. 23 ± 2</td></tr>
<tr><td colspan="3">45.5°</td><td colspan="3">45.6°</td></tr>
<tr><td>8.33</td><td>5.90</td><td>2.6</td><td>54.8</td><td>6.36</td><td>50</td></tr>
<tr><td>8.33</td><td>2.82</td><td>2.8</td><td>27.4</td><td>13.11</td><td>55</td></tr>
<tr><td>4.17</td><td>3.02</td><td>2.9</td><td>27.4</td><td>6.31</td><td>54</td></tr>
<tr><td colspan="2">4.10</td><td>2.9</td><td>13.7</td><td>6.20</td><td>49</td></tr>
<tr><td></td><td></td><td></td><td colspan="2">9.96</td><td>52</td></tr>
<tr><td colspan="3">Av. 2.8 ± 0.1</td><td colspan="2">6.72</td><td>49</td></tr>
<tr><td></td><td></td><td></td><td colspan="3">Av. 51.5 ± 2</td></tr>
<tr><td colspan="6">Nitromethane solvent</td></tr>
<tr><td colspan="3">*p*-Iodobiphenyl[e]</td><td colspan="3">*o*-Iodobiphenyl, 25.1°</td></tr>
<tr><td colspan="2">..</td><td></td><td colspan="2">7.47</td><td>0.50</td></tr>
<tr><td colspan="2">..</td><td></td><td colspan="2">4.98</td><td>.44</td></tr>
<tr><td colspan="2">..</td><td></td><td colspan="2">2.49</td><td>.43</td></tr>
<tr><td></td><td></td><td></td><td colspan="3">Av. 0.46 ± 0.03</td></tr>
<tr><td colspan="3">45.6°</td><td colspan="3">45.6°</td></tr>
<tr><td colspan="2">3.31</td><td>0.89</td><td colspan="2">7.59</td><td>1.17</td></tr>
<tr><td colspan="2">1.65</td><td>.95</td><td colspan="2">5.09</td><td>1.16</td></tr>
<tr><td></td><td></td><td></td><td colspan="2">2.51</td><td>1.13</td></tr>
<tr><td colspan="3">Av. 0.92 ± 0.03</td><td colspan="3">Av. 1.15 ± 0.02</td></tr>
</table>

[a] Where the dichloride, rather than its components, was the starting material its concentration is shown between the (ArI) and (Cl_2) columns. [b] The K-values in acetic acid for iodobenzene are 1.9×10^{-3} and 4.2×10^{-3} moles/l. at 25.0 and 45.4°, respectively; in nitromethane they are 0.42×10^{-3} and 1.21×10^{-3} at 25.0 and 45.4°, respectively.[4] [c] The K-values in acetic acid for *p*-iodobiphenyl are 2.10×10^{-3} and 5.3×10^{-3} mole/l. at 25.2 and 45.4° respectively.[3] [d] The K-values in acetic acid for *m*-chloroiodobenzene are 13.2×10^{-3} and 29.6×10^{-3} mole/l. at 25.2 and 45.4°, respectively.[3] [e] The K-value for *p*-iodobiphenyl at 25.0° in nitromethane is $0.30 \pm 0.04 \times 10^{-3}$ mole/l.[4]

It has been proposed previously[3,4] that the effectiveness of acetic acid as a medium for dichloride equilibration lies primarily in its capacity for solvation through hydrogen bond formation. A crude attempt to describe the role played by the acid in forming the activated complex has been made (structure I).



I

Actually both chlorine atoms may be solvated. Certainly the major function of acetic acid in the solvation process is to assist in the polarization of the I–Cl bond. Apparently it can serve this purpose without encountering undue steric interference from nearby ring substituents. Very likely a perpendicular arrangement of the aromatic ring and the plane described by the three halogen atoms is an energetically acceptable (or preferred) arrangement for the activated state as well as for the ground state of the dichloride.

The energy of activation for dichloride dissociation in nitromethane is much lower than in acetic acid.[4] This fact suggests that a very close affiliation of the solute and solvent is established when activation occurs in this medium. Yet in nitromethane, as in acetic acid, the rate constants (k_2) for *o*- and *p*-iodobiphenyl dichlorides are closely similar, even though the phenyl group has large space requirements. The severe entropy losses[4] which attend activation in this highly polar medium must reflect a high degree of solvent orientation, but the clustering of solvent molecules about the centers

TABLE III

RATE CONSTANTS FOR FORMATION AND DISSOCIATION OF THE DICHLORIDES[a,b]

10^3-(ArI)$_T$, moles/l.	10^3(Cl$_2$)$_T$, moles/l.	10^4k_1, sec.$^{-1}$	10^2k_2, l. mole^{-1} sec.$^{-1}$	10^3(ArI)$_T$, moles/l.	10^3(Cl$_2$)$_T$, moles/l.	10^4k_1, sec.$^{-1}$	10^2k_2, l. mole^{-1} sec.$^{-1}$
Acetic acid solvent							
p-Iodotoluene, 25.2°				*o*-Iodotoluene, 25.2°			
5.28		2.71		7.75		2.65	
3.52		2.67		5.17		2.60	
1.76		2.56		2.58		2.35	
		Av. 2.65 ± 0.06				Av. 2.53 ± 0.12	
16.57	8.73		26.7	62.0	6.05		17
8.28	8.38		27.2	31.0	11.48		18
8.28	4.36		25.8	31.0	6.00		16
				15.5	5.88		17
			Av. 26.6 ± 0.5				Av. 17 ± 0.5
45.6°				45.6°			
7.98		25		7.39		21.2	
5.32		24		4.92		21.1	
2.66		23		2.46		19.9	
		Av. 24 ± 1				Av. 20.7 ± 0.6	
2-Iodo-1,4-dimethylbenzene, 25.0°				2-Iodo-1,3-dimethylbenzene, 25.1°			
3.71		1.78		3.67		1.17	
2.47		1.73		2.45		1.15	
1.24		1.66		1.22		1.16	
		Av. 1.72 ± 0.04				Av. 1.15 ± 0.01	
17.0	9.52		21.6	18.9	7.06		21
8.50	4.71		22.6	9.45	3.57		22
				7.60	8.04		23
				3.80	3.59		25
							Av. 23 ± 1
45.5°				45.6°			
3.75		16.1		3.37		11.2	
2.50		16.3		2.24		10.9	
1.25		15.9		1.12		10.5	
		Av. 16.1 ± 0.1				Av. 10.9 ± 0.2	
2-Iodonaphthalene, 25.0°				1-Iodonaphthalene, 25.0°			
2.20		2.28		6.30		4.07	
1.46		2.25		4.20		3.88	
0.73		2.18		2.10		3.64	
		Av. 2.24 ± 0.04				Av. 3.86 ± 0.15	
45.4°				45.4°			
2.46		19.7		6.36		30.2	
1.64		20.0		4.24		30.0	
0.84		19.4		2.12		28.7	
		Av. 19.7 ± 0.2				Av 29.6 ± 0.6	
o-Iodobiphenyl,[c] 25.2°				*o*-Iodochlorobenzene,[d] 25.2°			
8.50	6.85		21.8	54.7	6.64		0.84
8.50	3.30		21.0	27.3	13.42		.85
4.25	3.10		22.6	27.3	6.54		.82
4.28			21.6	10.4			.84
2.14			22.3	6.95			.84
3.09		1.63		3.47			.82
2.06		1.64					
1.03		1.55					
		Av. 1.61 ± 0.04	21.9 ± 0.5				Av. 0.83 ± 0.01
45.5°				45.6°			
4.10			64	9.96			3.0
2.05			58	6.72			3.0
				3.40			2.8
							Av. 2.9 ± 0.1

TABLE III (*continued*)

10^3-$(ArI)_T$ moles/l.	$10^4(Cl_2)_T$, moles/l.	10^4k_1 sec.$^{-1}$	10^2k_2 l. mole^{-1} sec.$^{-1}$	$10^3(ArI)_T$, moles/l.	$10^4(Cl_2)_T$, moles/l.	10^4k_1, sec.$^{-1}$	10^2k_2, l. mole^{-1} sec.$^{-1}$
Nitromethane solvent							
p-Iodobiphenyl, 25.1°				*o*-Iodobiphenyl, 25.1°			
40.8	3.75		15	30.65	3.20		29
20.4	6.40		10	16.3	8.6		20
20.4	3.60		12	16.3	4.14		26
10.1	3.38		14	15.3	1.60		32
				8.68	4.25		27
				7.66	4.01		36
		Av.	13 ± 2			Av.	28 ± 4

[a] Where the dichloride rather than the iodine compound and chlorine were the starting materials, the initial reactant concentration is listed between the $(ArI)_T$ and $(Cl_2)_T$ columns. Except for *o*-chloroiodobenzene and for those compounds investigated in nitromethane, all k_1-values reported in the body of the table were determined from runs in which pentamethylbenzene (initially about 18×10^{-3} *M*) was present in excess of the dichloride. [b] For iodobenzene in acetic acid the k_1-values at 25.0 and 45.4° are, respectively, 1.7×10^{-4} and 14.1×10^{-4} sec.$^{-1}$, and the corresponding k_2-values are 9×10^{-2} and 34×10^{-2} l. mole^{-1} sec.$^{-1}$. In nitromethane the k_1-values at 25.0 and 45.4° are, respectively, 0.18×10^{-4} and 0.7×10^{-4} sec.$^{-1}$, and the corresponding k_2-values are 4.4×10^{-2} and 5.9×10^{-2} l. mole^{-1} sec.$^{-1}$ (ref. 4). [c] For *p*-iodobiphenyl in acetic acid the k_1-values at 25.2 and 45.4° are 2.35×10^{-4} and 17×10^{-4} sec.$^{-1}$, respectively, and the corresponding k_2-values are 11.0×10^{-2} and 32×10^{-2} l. mole^{-1} sec.$^{-1}$ (ref. 3). [d] From *m*-iodochlorobenzene in acetic acid the k_1-values at 25.2 and 45.4° are 1.48×10^{-4} and 11.5×10^{-4} sec.$^{-1}$, respectively, and the corresponding k_2-values are 1.13×10^{-2} and 3.9×10^{-2} l. mole^{-1} sec.$^{-1}$ (ref. 3).

of polarization at the reaction site apparently can be accomplished without interference from neighboring substituents. This conclusion calls to mind the observation that steric hindrance to carbonium ion solvation is not a dominant factor in determining the rates of hydrolysis of tertiary halides in which the α-alkyl substituents are bulky.[13] Neither is it a critical factor in controlling the hydrolysis rates of *o*-substituted benzyl halides.[14] It is probable, however, that in some cases abnormal reactivity (*e.g.*, the high acid strength of 2,6-di-*t*-butylanilinium ion)[15] correctly may be attributed to a steric hindrance to solvation.

Thermodynamic Data.—The heats and entropies of dissociation and the entropies and energies of activation for dissociation of the several dichlorides which have been investigated are reported in Table IV. The energies and entropies (E_2 and $\Delta S_2^{\ddagger}$) of activation for formation of the dichloride from its components readily can be derived from the figures in the table. The reported values of $\Delta H°$ and $\Delta S°$ were calculated from the constants K, at 25 and 45° (Table II). The constants E_1 and $\Delta S_1^{\ddagger}$ were calculated, where it was possible, from experimentally measured values of k_1 (Table III). Where a directly measured value of k_1 was unavailable, it was derived from k_2 and K. The tabulated errors were calculated by taking into account the average deviations of several measured values of the rate or equilibrium constant (see Tables II and III) from the average value. Unfortunately the errors, particularly in the entropy values, are large enough so that the data are of only semi-quantitative significance.

The observation, made earlier,[3,4] that E_1 and $\Delta S_1^{\ddagger}$ are considerably larger than E_2 and $\Delta S_2^{\ddagger}$ is upheld by the results of this investigation. Because equilibration of the *o*- and *p*-iodobiphenyl derivatives in nitromethane occurs rather rapidly at 45°, rate constants for reactions of these compounds at this temperature are not reported in Table III; however, crude estimates of the k_2-values at 45° were made. Comparison of these values with those at 25° leads to the conclusion that in nitromethane the activation energies for the reactions of of the two iodobiphenyls, like those for other iodo compounds, are much smaller than in acetic acid.

TABLE IV

THERMODYNAMIC CONSTANTS FOR FORMATION AND DISSOCIATION PROCESSES

Iodo compound	$\Delta H°$, kcal./mole	$\Delta S°$, e.u.	E_1, kcal./mole	$-\Delta S_1^{\ddagger}$, e.u.
Acetic acid solvent				
Iodobenzene[a]	7.0	11	19.6	12
p-Iodotoluene	8.1 ± 0.5	13 ± 2	20.4 ± 0.4	8.5 ± 1.7
o-Iodotoluene	6.2 ± 1.3	7 ± 5	19.5 ± .5	11.6 ± 1.7
2-Iodo-1,4-dimethylbenzene	7.1 ± 0.8	10 ± 3	20.6 ± .2	8.7 ± 0.7
2-Iodo-1,3-dimethylbenzene	6.4 ± 1.2	7 ± 4	20.8 ± .2	8.7 ± 0.7
p-Iodobiphenyl[b]	9.0	17.7	18.6	14.8
o-Iodobiphenyl	8.6 ± 0.8	15 ± 3	18 ± 1[c]	14 ± 3[c]
2-Iodonaphthalene	8.0 ± .8	15 ± 3	20.2 ± 0.2	9.6 ± 0.7
1-Iodonaphthalene	8.9 ± .3	18 ± 1	18.9 ± 0.4	12.8 ± 1.3
m-Chloroiodobenzene[b]	7.6	17	19.1	13.1
o-Chloroiodobenzene	7.8 ± 0.8	18.5 ± 3	20 ± 1[c]	11 ± 3[c]
Nitromethane solvent				
Iodobenzene[a]	9.8	17	12.5	40
p-Iodobiphenyl[d]	10.3 ± 1.2	18 ± 5	....	....
o-Iodobiphenyl	8.5 ± 0.6	13 ± 2	....	....

[a] From ref. 4. [b] From ref. 3. [c] The values of E_1 and $\Delta S_1^{\ddagger}$ are estimated from k_1-values determined from the known values of K and k_2. [d] Values calculated using the equilibrium constant at 25.0° reported in ref. 4 and that at 45.6° reported in Table III.

The Product of Reaction of *o*-Iodobenzoic Acid and Chlorine.—In connection with the current investigation an attempt to prepare *o*-iodobenzoic acid dichloride was made. The product of reaction of the iodo acid with chlorine in nitromethane

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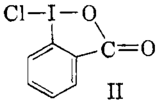
(13) (a) H. C. Brown and R. S. Fletcher, THIS JOURNAL, **71**, 1845 (1949); (b) F. Brown, T. D. Davis, I. Dostrovsky and E. D. Hughes, *Nature*, **167**, 987 (1951).

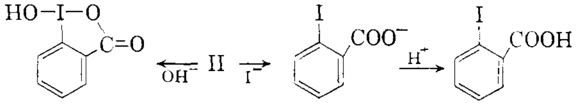
(14) (a) S. C. J. Olivier, *Rec. trav. chim.*, **45**, 296 (1926); (b) G. N. Burkhardt, W. G. K. Ford and E. Singleton, *J. Chem. Soc.*, **17** (1936).

(15) P. D. Bartlett, M. Roha and R. M. Stiles, THIS JOURNAL, **76**, 2349 (1954).

(presumed to be the dichloride) rapidly evolved a gas in the dry state and changed in crystalline character to form a product which, although it oxidized iodide ion, had a lower iodometric equivalent weight than the theoretical value for iodobenzoic acid dichloride. Because of the instability of the dichloride, plans to study its equilibration with its components were abandoned.


II

The behavior which has been described was noted many years ago and explained without confirming evidence, on the assumption that the dichloride evolved hydrogen chloride to produce II.[9a] Confirmation of this lactone structure has been obtained through study of the reactions, described below, of II in dilute solutions of potassium iodide and sodium hydroxide. Complete details are given in the Experimental section.



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DAVIS, CALIF.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

The Stereoisomers of 10-Methyl-2-decalol[1,2]

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An improved synthesis of *cis*-10-methyl-2-*trans*-decalol (I) and the synthesis of the *trans-trans* isomer (II) of the *cis-cis* isomer (III) and of the *trans-cis* isomer (IV) by procedures which permit assignment of configuration are reported. Absorption bands in the infrared spectra of these and related compounds appear to be diagnostic of the nature of the ring fusion geometry.

Two of the four isomers of 10-methyl-2-decalol have been described previously.[3–7] Both of these isomers melt in the region of 65–70° at very nearly the same temperature. The *p*-nitrobenzoate of one has been reported to melt at 65–67°,[5,7] the 3,5-dinitrobenzoates to melt at 110.6–111.2° and at 97.5–98.5°.[4] The isomer which forms the higher melting 3,5-dinitrobenzoate has been synthesized from a 10-carboxy-2-decalol which forms a lactone.[4] Also, when oxidized with chromic anhydride, this isomer has furnished 10-methyl-2-*trans*-decalone.[6] It is therefore *cis*-10-methyl-2-*trans*-decalol (I). We have found the *p*-nitrobenzoate derivative to melt at 71–73°; hence it would appear to be identical with that described by Yanagita and coworkers.[5,7]

While compound I can be prepared in three steps from 2-methylcyclohexanone by way of 10-methyl-$\Delta^{1,9}$-octal-2-one,[3,4,7,8] we have come to prefer the synthetic sequence to 10-methyl-2-*trans*-decalone, as developed by Dreiding,[9] followed by reduction with lithium aluminum hydride. In spite of the nine steps involved, the over-all yield of I is 35–40% and the product is much less subject to contamination by isomeric impurities.

When compound I, prepared in this way, was converted to its *p*-toluenesulfonate and the latter was refluxed with potassium acetate in acetic acid –acetic anhydride solvent, the epimeric acetate was formed in 25–30% yield. Considerable (*ca.* 30%) elimination accompanied the displacement reaction. Saponification and a chromatographic procedure on alumina led to the isolation of *trans*-10-methyl-2-*trans*-decalol (II) m.p. 89.5–90.5°. The *p*-nitrobenzoate and the 3,5-dinitrobenzoate of II melted at 153–154° and 122–123°, respectively. Therefore the second isomer previously reported[4] is not the *trans-trans* isomer II.

The synthesis of *cis*-10-methyl-2-*cis*-decalol (III) and of *trans*-10-methyl-2-*cis*-decalol (IV) involved the common starting material, 10-hydroxymethyl-2 *cis*-decalone (V)[10] as follows: V was converted to its *p*-toluenesulfonate VI and the latter was reduced with sodium borohydride to a mixture of the epimeric 10-[*p*-toluenesulfonoxymethyl]-2-*cis*-decalol isomers. By way of a fractional crystallization procedure, the epimeric *p*-nitrobenzoates were separated to furnish 17% of the *cis-cis* isomer VII and 71% of the *trans-cis* isomer VIII. The former melted at 114–116° and showed no depression of melting point when mixed with an authentic sample of VII, m.p. 115–116°, from *cis*-10-hydroxymethyl-2-*cis*-decalol.[10] Similarly VIII, m.p. 161–162°, did not depress the melting point of an authentic sample, m.p. 161–163°, prepared from *trans*-10- hydroxymethyl-2-*cis*-decalol.[10]

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[2] A grant from the Research Corporation assisted the carrying out of this research.

[3] E. C. du Feu, F. J. McQuillen and R. Robinson, *J. Chem. Soc.*, 53 (1937).

[4] A. S. Hussey, H. P. Liao and R. H. Baker, THIS JOURNAL, **75**, 4727 (1953). See footnote 3 for the naming convention used to designate the geometry of these isomers.

[5] M. Yanagita and A. Tahara, *J. Org. Chem.*, **18**, 792 (1953).

[6] A. S. Dreiding and A. J. Tomasewski, THIS JOURNAL, **77**, 168 (1955).

[7] M. Yanagita, K. Kamakawa and A. Tahara, *J. Org. Chem.*, **20**, 1767 (1955).

[8] See F. D. Gunstone and R. M. Heggie, *J. Chem. Soc.*, 1437 (1952); A. L. Wilds, C. H. Hoffman and T. H. Pearson, THIS JOURNAL, **77**, 647 (1955); and F. Sondheimer and D. Russell, *ibid.*, **80**, 3995 (1958), for variations in the preparation of this intermediate.

[9] A. S. Dreiding and A. J. Tomasewski, *ibid.*, **77**, 411 (1955).

[10] L. S. Minckler, A. S. Hussey and Robert H. Baker, *ibid.*, **78**, 1009 (1956).