further cooled in an ice bath to complete crystallization. The crystals were collected on a Büchner funnel, triturated with a 3:1 water–ethanol solution, and vacuum dried.

The product from one run was carried through 160 transfers in a 100-tube Craig countercurrent extractor using cyclohexene saturated with nitromethane as the upper moving phase and nitromethane saturated with cyclohexene as the lower stationary phase. The solvent system has been shown to have reasonable distribution coefficients for the desired separation but apparently caused side reactions which destroyed the identity of the anilino-ketones.

The product from a second run was submitted for mass spectral analysis.

Mass Spectrometric Analysis.[12]—The mass spectra were determined for separate samples of the two pure dihalo-α-anilino-ketones, a mechanical mixture of the two, and the product isolated from the competitive rearrangement. In all cases the

(12) The mass spectrometric analyses were run by Dr. Don Schissler of Shell Development Laboratories, Emeryville, Calif.

parent peaks differed from the expected values by the mass of water (not surprising in view of the synthetic conversion of α-anilinoketones to indoles).

The mass spectrum of the dibromo-α-anilinoketone shows ion currents at 455, 457, 459 (loss of water); 304, 306 (loss of the p-bromoanilino group); 171, 173 (the p-bromoanilino group); 440, 442, 444 (loss of the methoxyl group from the ketone or the methyl group from the indole); 155, 157 (the bromophenyl group); 135 (loss of both the p-bromobenzoyl group and the the bromophenyl group); and 121 (the p-methoxybenzal group). Peak heights and positions corresponded to expected relationships for relative isotope abundances.

The spectrum of the dichloro-α-anilinoketone was exactly analogous.

The spectrum for the mechanical mixture was an exact superposition of the spectra for the separate components.

The spectrum from the competitive rearrangement product shows all of the ion currents found in the spectra of the pure dibromo- and dichloro-α-anilinoketones and, in addition, ion currents corresponding to fragments containing both bromine and chlorine atoms in the same fragment.

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

Ester, Ether, and Carbonyl Functions as *ortho* Participants in the Dissociation of Iodobenzene Dichloride

BY L. J. ANDREWS, L. J. SPEARS, AND R. M. KEEFER

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The rates of dissociation of a series of o- and p-isomers of iodobenzene dichloride ($XC_6H_4ICl_2$) in acetic acid have been determined ($X = CH_2COCH_3$, $CH_2COC_6H_5$, $COCH_3$, COC_6H_5, and CH_2COOCH_3). The capacities of various o-substituents to promote the dissociation reaction by electron release to iodine in the transition

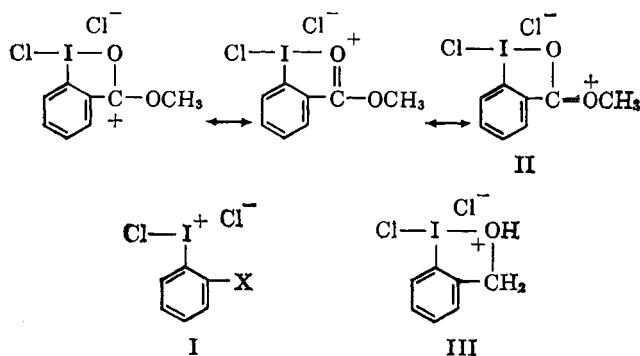state varies in the order $CH_2OC_6H_5 < CH_2COOCH_3 < CH_2OCH_3 <$

The mechanistic implications of these observations are discussed.

The rate of dissociation of iodobenzene dichloride (eq. 1) in acetic acid ordinarily is not strongly influenced by the introduction of ring substituents.[1] The k_1 values
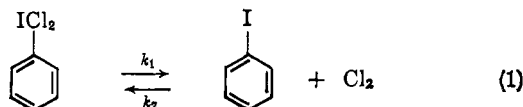
for isomeric o- and p-substituted dichlorides are generally about the same. Certain of the o-isomers—in particular those in which the substituents can function as nucleophiles—are, however, much more reactive than the corresponding p-derivatives.[2,3] The carbomethoxy- and hydroxymethyliodobenzene dichlorides, among others, fall into this exceptional reactivity class. Presumably when the –COOCH$_3$ and –CH$_2$OH groups are located *ortho* to the reaction center, they contribute to the transition state (which is considered to be polarized as indicated in formula I) by release of electrons to the iodine atom (II, III).

The capacities of several more o-substituents to participate in the iodobenzene dichloride dissociation reaction in acetic acid have now been investigated. The relative effectiveness of ether and of carbonyl oxygen, as compared with the previously investigated ester oxygen, in acting a scenters of nucleophilicity has been assessed through a comparative rate study of the o- and p-CH_2OCH_3, –$CH_2OC_6H_5$, –$COCH_3$, and –CO-C_6H_5 iodobenzene dichloride derivatives. To determine whether a five- or six-ring cycle provides for greater transition state stabilization by the –COOCH$_3$ group, the relative reactivities of the o- and p-CH_2-$COOCH_3$ substituted dichlorides have been compared

(1) R. M. Keefer and L. J. Andrews, *J. Am. Chem. Soc.*, **80**, 277 (1958).
(2) L. J. Andrews and R. M. Keefer, *ibid.*, **81**, 4218 (1959).
(3) R. M. Keefer and L. J. Andrews, *ibid.*, **81**, 5329 (1959).

with those of the o- and p-carbomethoxy substituted dichlorides.

Experimental

The Iodo Compounds. (a) **Methyl o-Iodophenylacetate.**—A sample of o-iodobenzyl alcohol was prepared by reduction of o-iodobenzoyl chloride (Eastman Organic Chemicals) with lithium aluminum hydride.[4] The alcohol was converted to the corresponding bromide.[5] This was converted, *via* the cyanide, to o-iodo-phenylacetic acid (m.p. 112–114°) by the procedure of Rapson and Shuttleworth.[6] A mixture of 18 g. of the acid, 13 g. of methanol, 250 ml. of methylene chloride, and 7 ml. of concentrated sulfuric acid was refluxed for 24 hr. The ester was isolated from the crude product by standard procedures in 8.6 g. (45%) yield, b.p. 138° (5 mm.), lit.[7] b.p. 114° (1 mm.).

(b) **Methyl p-Iodophenylacetate.**—A sample of p-iodophenyl-acetic acid was prepared by reaction of the diazonium salt of p-aminophenylacetic acid (Eastman Organic Chemicals) with potassium iodide.[8] A 10.7-g. sample of the acid was refluxed with thionyl chloride for 3 hr. The excess thionyl chloride was

(4) B. O. Field and J. Grundy, *J. Chem. Soc.*, 983 (1927).
(5) W. Raum, *Ber.*, **27**, 3233 (1894).
(6) W. S. Rapson and R. G. Shuttleworth, *J. Chem. Soc.*, 489 (1941).
(7) J. E. Leffler and A. F. Wilson, *J. Org. Chem.*, **25**, 424 (1960).
(8) A. I. Vogel, "A Textbook of Practical Organic Chemistry," Longmans, Green and Co., London, 1956, p. 599.

removed by distillation, and the residue was refluxed for 6 hr. with 250 ml. of methanol. The ester was recovered from the crude product in 2.0 g. (17%) yield, b.p. 135–136° (2 mm.).

Anal. Calcd. for $C_9H_9O_2I$: C, 39.13; H, 3.26; I, 46.01. Found: C, 39.13; H, 3.32; I, 45.82.

(c) **Methyl o-Iodobenzyl Ether.**—A 16.5-g. sample of o-iodobenzyl bromide was refluxed for 1 hr. with a solution of 4.0 g. of sodium in 200 ml. of absolute methanol. The bulk of the methanol was removed by distillation, and the pot residue was diluted with water and ether extracted several times. From the extracts 6.5 g. (47% yield) of methyl o-iodobenzyl ether was obtained, b.p. 99–103° (4 mm.).

Anal. Calcd. for C_8H_9OI: C, 38.71; H, 3.63; I, 51.21. Found: C, 38.94; H, 3.65; I, 51.02.

(d) **Methyl p-iodobenzyl ether** was prepared by Mr. Craig Asmundson using p-iodobenzoic acid (Eastman Organic Chemicals) as starting material. A 15.5-g. sample of the acid was refluxed with thionyl chloride to provide a crude sample of the acid chloride. After removing the excess thionyl chloride, the residue was reduced with 6 g. of lithium aluminum hydride. A 10-g. yield of crude p-iodobenzyl alcohol, m.p. 50–63° (lit.[9] m.p. 72°), was obtained. The alcohol was converted to the corresponding bromide, m.p. 77–79° (lit.[9] m.p. 79°), by refluxing with 48% hydrobromic acid. Methyl p-iodobenzyl ether [b.p. 106–108° (4 mm.)] was obtained from 10.0 g. of the bromide in 5.8 g. (69%) yield by essentially the same procedure as was used in preparing its o-isomer.

Anal. Calcd. for C_8H_9OI: C, 38.71; H, 3.63; I, 51.21. Found: C, 38.81; H, 3.94; I, 51.16.

(e) **Phenyl o- and p-Iodobenzyl ethers** were prepared from the corresponding iodobenzyl bromides and phenol by essentially the same procedure as has been reported for the preparation of phenyl benzyl ether.

From 6.0 g. of o-iodobenzyl bromide 5.0 g. (74% yield) of the phenyl ether was obtained.

Anal. Calcd. for $C_{13}H_{11}OI$: C, 50.32; H, 3.55; I, 40.97. Found: C, 50.43; H, 3.35; I, 40.86.

From 50.0 g. of p-iodobenzyl bromide 20 g. of phenyl ether of m.p. 97–98° was obtained after recrystallization of the crude product from petroleum ether.

Anal. Calcd. for $C_{13}H_{11}OI$: C, 50.32; H, 3.55; I, 40.97. Found: C, 50.40; H, 3.67; I, 40.68.

(b) **The o- and p-iodobenzophenones** were prepared from the o- and p-iodobenzoyl chlorides and benzene by the method described by Vogel for the synthesis of benzophenone.[10] The o-substituted ketone was collected as a yellow-colored liquid, b.p. 175–177° (1 mm.) [lit.[11] b.p. 210–211° (13 mm.)]. The p-isomer, after recrystallization from methanol, melted at 100–101° (lit.[10] m.p. 101°).

(g) **The o- and p-iodoacetophenones** were prepared from the corresponding o- and p-aminoacetophenones (respectively from Aldrich Chemical Co. and Eastman Organic Chemicals) by a procedure already described for preparation of the p-isomer.[12] The o-isomer was obtained as a liquid of b.p. 125–127° (8 mm.) [lit.[13] b.p. 139–140° (12 mm.)]. The *para* melted at 84–85° (lit.[12] m.p. 85°).

The Dichlorides.—Most of these were precipitated as yellow solids by gassing solutions of the iodo compounds in acetic acid with chlorine by procedures which have been described in detail previously.[3] Attempts to isolate solid samples of the dichlorides of o-iodobenzophenone and o-iodoacetophenone were unsuccessful; other solvents including carbon tetrachloride, chloroform, nitromethane, and petroleum ether were substituted for acetic acid, but in no case were crystalline adducts of these iodo ketones precipitated. The solid dichlorides were washed with carbon tetrachloride, air-dried briefly, and used immediately. The melting points and iodometric equivalent weights of the various adducts, and also their molecular extinction coefficients in acetic acid solution at the wave length used in rate runs, are summarized in Table I. Melting generally was accompanied by decomposition.

The Kinetic Studies.—The kinetics of dissociation of the dichlorides in acetic acid were investigated by the spectrophotometric methods referred to in earlier publications.[2,3] Samples of freshly prepared solutions of the dichlorides in acetic acid, the concentrations of which were established by iodometric methods, were mixed in 1-cm. absorption cells with samples of stock solutions of durene in acetic acid. The durene was included in the reaction mixtures in sufficient quantity so that it removed free

(9) I. Heilbron, "Dictionary of Organic Compounds," Vol. III, Oxford University Press, New York, N. Y., 1953.

(10) Reference 8, p. 743.

(11) M. S. A. Koopal, *Rec. trav. chim.*, **34**, 156 (1915).

(12) R. W. Strassburg, R. A. Gregg, and C. Walling, *J. Am. Chem. Soc.*, **69**, 2141 (1947).

(13) K. v. Auwers, M. Lechner, and H. Bundesmann, *Ber.*, **58**, 50 (1925).

TABLE I

PROPERTIES OF THE DICHLORIDES ($XC_6H_4ICl_2$)

X	M.p., °C.	Equiv. wt. Calcd.	Equiv. wt. Found	λ, mμ	$\epsilon_{XC_6H_4ICl_2}$
2-CH_2OCH_3	85–86.5	318	324	360	116
4-CH_2OCH_3	64–66	318	325	400	34.0
2-$CH_2OC_6H_5$	90–92	381	443[a]	360	195
4-$CH_2OC_6H_5$	110–113	381	384	370	118
2-$CH_2CO_2CH_3$	101–102	347	352	360	102
4-$CH_2CO_2CH_3$	84–85	347	354	390	82.1
4-$COCH_3$	103–105	379	378	380	141
4-COC_6H_5	102[b]	317	320	395	37.2

[a] The equivalent weights of the prepared samples of this dichloride generally were high. Solvents other than acetic acid were used in unsuccessful attempts to obtain this material in purer form. [b] The pure iodo compound melts at 100–101°. It is possible that in this case the solid dichloride loses chlorine completely before melting occurs.

chlorine (by reaction to form chlorodurene) as soon as it was liberated. The optical densities of the cell contents were measured as a function of time against acetic acid blanks at wave lengths at which absorptions of the undissociated dichlorides were appreciable (Table I). The cell housing of the Beckman spectrophotometer used in these measurements was temperature controlled to ±0.1° during the course of the runs. Under the reaction conditions which were employed, the dichloride dissociation rates were independent of the durene concentrations of the media. In most runs the absorption of the products was negligible. In a few cases the measured optical densities were corrected for small readings at infinite time before calculation of rate constants (see eq. 2 in which D_c represents the corrected optical densities).

$$-d[ArICl_2]/dt = k_1[ArICl_2]$$

or

$$-dD_c/dt = k_1D_c \qquad (2)$$

Values of k_1 which are later reported were calculated from the slopes of plots of log D_c *vs.* time ($k_1 = -2.303$ slope). All runs were followed to completion.

To investigate the dissociation of the dichlorides of o-iodoacetophenone and o-iodobenzophenone, rate samples were prepared by adding a considerable excess of durene (in acetic acid) to previously prepared mixtures of the iodo compound (also in large excess) and chlorine in acetic acid. That the dichloride was initially present in these solutions was established by the fact that their initial optical densities were substantially greater than could be accounted for on the basis of the absorption of the pure components. Wave lengths of 390 and 395 mμ were used in following the reaction of o-iodoacetophenone dichloride. The reaction of o-iodobenzophenone dichloride was followed using wave lengths of 380 and 385 mμ. Reported rate constants are based on D_c values recorded after destruction of free chlorine initially present in the rate samples.

Results

As has been explained in the Experimental section, the dissociation reactions which have been studied in the present investigation have been conducted under conditions such that they proceed to completion. Equilibration of the iodobenzene dichlorides with their components has been prevented by the inclusion of durene in the reaction mixtures. Rate constants, k_1, for the decomposition of the various dichlorides under consideration are summarized in Table II.

The Effects of o-CH_2OR and o-COR.—At 25° the k_1 values for the dichlorides substituted with p-CH_2OCH_3 and p-$CH_2OC_6H_5$ groups are about the same as that for $Cl_2IC_6H_4CH_2OH$-p. While the ratio of rate constants for the o- and p-isomers is 57:1 for the –CH_2OH substituted reactants, it drops to 18:1 for the analogous –CH_2OCH_3 derivatives and to 1:1 for the –$CH_2OC_6H_5$ substituted dichlorides. The o-CH_2-OC_6H_5 group can be classed as nonparticipating. Apparently the phenyl-bound ether oxygen is a poor nucleophile.

The fact that the o-$OCOCH_3$ group also does not participate has been explained on similar grounds.[3] Presumably the aryl oxygen of the acetoxy group is

TABLE II

RATE CONSTANTS FOR DISSOCIATION OF $XC_6H_4ICl_2$ IN ACETIC ACID[a]

| X	Temp., °C.	Number of determinations	10^4k_1, sec.$^{-1}$
o-CH₂OCH₃	25.2	4	32.1 ± 0.9
o-CH₂OCH₃	35.3	2	83.7 ± 3.8
p-CH₂OCH₃	24.1	2	1.53 ± 0.06
p-CH₂OCH₃	45.2	4	14.8 ± .9
o-CH₂OC₆H₅	25.4	2	1.83 ± .04
o-CH₂OC₆H₅	44.4	2	9.9 ± .2
p-CH₂CC₆H₅	25.4	2	1.81 ± .11
p-CH₂OC₆H₅	44.4	2	8.48 ± .13
o-CH₂OH	25.0	b	130
p-CH₂OH	25.0	b	2.34 ± 0.10
o-CH₂COOCH₃	25.0	4	9.3 ± 1.1
o-CH₂COOCH₃	45.2	4	110 ± 2
p-CH₂COOCH₃	25.0	4	1.39 ± 0.05
p-CH₂COOCH₃	45.2	2	16.3 ± 0.2
o-COOCH₃	25.0	c	Very large
p-COOCH₃	25.0	c	1.50 ± 0.04
o-COCH₃	24.6	3	117 ± 1
o-COCH₃	18.0	3	88.2 ± 0.7
p-COCH₃	24.6	3	0.94
p-COCH₃	46.2	2	7.7 ± 0.3
o-COC₆H₅	24.6	3	147 ± 2
o-COC₆H₅	18.0	3	84.3 ± 3.1
p-COC₆H₅	24.6	4	0.87 ± 0.14
p-COC₆H₅	46.2	2	7.50 ± 0.30

[a] The rate constants which are reported are, in most cases, the averages of values obtained for a series of runs. The k_1 values were found generally to be insensitive to changes in initial concentrations of dichloride and durene. These initial concentrations ranged, respectively, from 2×10^{-1} to 2×10^{-2} M and from 0.03 to 0.15 M in the various runs which are summarized in the table. [b] From ref. 3. [c] From ref. 2.

sufficiently positively polarized by the aromatic ring so that the carbonyl oxygen cannot release electrons to iodine in the activation process. The fact that the o-CH₂OCH₃ group is a less effective participant than o-CH₂OH is surprising, at first glance, since the ether methyl should be electron releasing relative to the hydroxyl hydrogen of the hydroxymethyl group. Three explanations deserve consideration. Possibly the larger –CH₂OCH₃ group has an unfavorable bulk effect relative to that produced by –CH₂OH. This seems unlikely, however, since large o-substituents in general do not have a steric influence on the dichloride dissociation rate, supposedly because in the transition state the Cl–I–Cl linkage is perpendicular to the ring to which it is attached.[14] The second possibility—that the hydroxyl hydrogen of o-CH₂OH may assist, through hydrogen bonding to departing chlorine, in the polarization of the I–Cl bond—cannot be ruled out on the basis of a consideration of molecular models. A third explanation, which is preferred by the authors, is based on the likelihood that the oxygen of the o-substituent must be desolvated before group participation can occur. The ether oxygen should be more basic than the carbinol oxygen and therefore less readily disengaged from associated acetic acid molecules. Further studies of the ethers and the hydroxymethyl derivatives with solvents other than acetic acid may help to clarify this matter.

The k_1 values for the p-COCH₃ and p-COC₆H₅ substituted dichlorides are approximately the same, and the corresponding o-isomers also are of about the same reactivity. In the cases of both the acetophenone and benzophenone derivatives the o-isomers are substantially more reactive than the p-. At 25°, the o/p re-

(14) R. M. Keefer and L. J. Andrews, *J. Am. Chem. Soc.*, **81**, 2374 (1959).

activity ratios for the –COCH₃ and –COC₆H₅ substituted dichlorides are, respectively, 124 and 170. No accurate value of the o/p reactivity ratio has been determined for the carbomethoxyiodobenzene dichlorides because of the extremely high reactivity of the o-isomer. Through reconsideration of data recorded earlier[2] for the reactions in acetic acid at 25° it has been estimated that the k_1 ratios for those two dichlorides are of the order of 1000:1.

The capacity of oxygen-bearing o-substituents to participate varies in the order

$$-CH_2OCH_3 < -\overset{O}{\underset{\|}{C}}-CH_3 << -\overset{O}{\underset{\|}{C}}-OCH_3$$
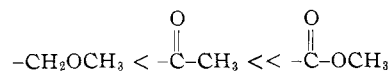
The fact that ether oxygen is considerably less readily disposed to release electrons to iodine in the activation process than is carbonyl oxygen suggests that the carbonyl group has been correctly identified as the center of nucleophilicity of the o-COOCH₃ substituent. The fact that this last substituent enhances dichloride reactivity so much more than does an acetyl or benzoyl group is regarded as an indication that the right-hand structure makes an important contribution to the resonance hybrid II which has been written to describe the transition state for dissociation of $Cl_2IC_6H_4COOCH_3$-o.

The Effect of o-CH₂COOCH₃.—The rate constant ratio for the methyl o- and p-iodophenylacetates is approximately 7:1 at 25°. The o-CH₂COOCH₃ group, unlike o-COOCH₃, contributes little to stabilization of the transition state for dichloride dissociation. This is in keeping with current ideas of the authors concerning the geometry of the transition state when o-participation takes place. In the solid state the iodine of an iodobenzene dichloride molecule is at the center of a trigonal bipyramid with two chlorine atoms at apical positions and two electron pairs and the aromatic ring at equatorial positions (I^V); the ring plane is perpendicular to the linear trihalide link and, as mentioned above, this perpendicular arrangement is apparently at least approximately maintained in the transition state.[15] It is suggested that in the activation process the o-substituent X displaces chloride from an apical position by attack at an equatorial position. This should result in a transition state structurally similar to V. In earlier publications the two chlorine atoms have been shown as more closely oriented as a result of activation. The present picture is, however, more in keeping with dsp[3] hybridization of iodine orbitals. An inspection of molecular models indicates that considerably less strain should be induced in bonds within the o-COOCH₃ groups than in those of o-CH₂COOCH₃ in forming a cycle of type V.


IV   V
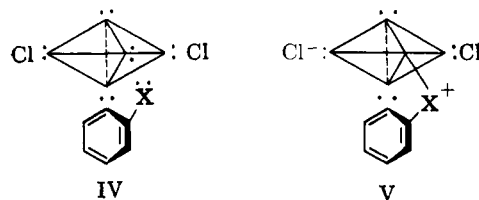
In an incidental way it is interesting to consider structure V as a geometric prototype for the compound VI which is isolated as the product of reaction of o-iodobenzoic acid with chlorine.[2]

The I–Cl bond may in fact lie perpendicular, rather than parallel, to the plane which more or less encompasses the aromatic and heterocyclic rings. If this is the correct description of VI, this compound should be subject to optical resolution.

(15) (a) E. M. Archer and T. G. D. Van Schalkwyk, *Acta Cryst.*, **6**, 88 (1953); (b) J. D. McCullough, *ibid.*, **6**, 746 (1953).

VI
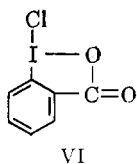
Thermodynamic Constants.—The energies and entropies of activation for a number of the dichloride dissociation reactions (Table III) have been calculated in

TABLE III

THERMODYNAMIC CONSTANTS FOR DISSOCIATION OF $XC_6H_4ICl_2$ IN ACETIC ACID

X	E_1, kcal./mole	$\Delta S_1^{\ddagger}$, e.u.	E_1, kcal./mole	$\Delta S_1^{\ddagger}$, e.u.
	o-Derivative		p-Derivative	
$CH_2OC_6H_5$	17.4 ± 1.0	-14 ± 3	20.2 ± 0.6	-10 ± 2
$CH_2OC_6H_5$	15.9 ± 0.3	-24 ± 1	$14.6 \pm .5$	-29 ± 2
CH_2COOCH_3	23.0 ± 1.1	$+ 3 \pm 4$	$23.0 \pm .2$	$- 1 \pm 1$

cases in which appropriate data (Table II) are available. As can be expected when the *ortho* located substituent participates in the reactions, the E_1 and $\Delta S^{\ddagger}$ values for o-CH_2OCH_3 substituted iodobenzene dichloride are less (less positive or more negative) then those for the

p-isomer. In the case of the corresponding phenyl ethers this situation is reversed. For reasons which are not obvious at this point, the entropies and energies of activation for o- and p-$CH_3OOCCH_2C_6H_4ICl_2$ are larger than those for any of the other substituted dichlorides which have been investigated currently or previously.

Comparative values of E_1 and $\Delta S_1^{\ddagger}$ are not reported for the o- and p-$COCH_3$ and o- and p-COC_6H_5 derivatives. Because of the rapidity of the reactions at temperatures much above 25°, k_1 values for the o-isomers cannot be determined at sufficiently widely varying temperatures so that thermodynamic constants can be reported with reasonable confidence. While check rate runs on the o-isomers were in exceptionally good agreement, it was not possible for technological reasons to vary starting concentrations of reactants sufficiently so that the limits of error reported for the k_1 values (Table II) can be accepted with certainty. The two o-isomers and also the two p-isomers show very similar rate responses to temperature changes.

# Condensation of B-Aminoborazines with Dimethylformamide and Amine Hydrochlorides

BY R. H. TOENISKOETTER* AND K. A. KILLIP

B-Aminoborazines condense with dimethylformamide and amine hydrochlorides to yield borazyl oxides. Amidine hydrochlorides and amines are by-products in the reaction. The stoichiometry of the reaction has been established and a reaction mechanism proposed. Some observations relating to the effect of changing amino groups of the reactants on the composition of the amines and amidine salts formed are recorded and discussed in terms of the proposed mechanism.

Introduction

Mono- and dichloroborazines do not form stable complexes with dimethylformamide (DMF).[1] Nevertheless, when solutions of these borazines in DMF are treated with primary or secondary amines, borazyl oxides, rather than aminoborazines, are produced. For example, the reaction of dimethylamine with B-chloro-B-dimethyl-N-trimethylborazine (I) in DMF produces bis-(pentamethylborazyl) oxide (II), rather than B-dimethylamino-B-dimethyl-N-trimethylborazine (III); poly-(tetramethylborazylene) oxide (IV) is obtained similarly from B-dichloro-B-methyl-N-trimethylborazine.

I   II

III   IV
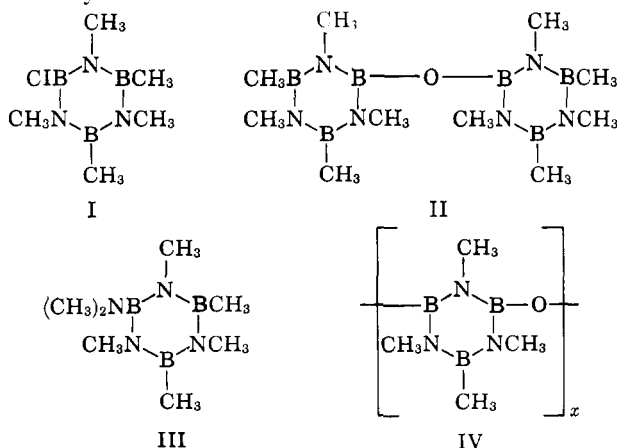
Superficially, these reactions appeared to be analogous to those between amines and phosphorus oxychloride–DMF[2] or cyanuric chloride–2DMF.[3] However, further investigation showed that aminoborazines condense with DMF in the presence of amine hydrochloride, thereby producing borazyl oxides. Since the reaction of a chloroborazine with an amine in inert medium produces an aminoborazine and amine hydrochloride,[1,4] it appeared likely that the same reaction took place in DMF medium, and that borazyl oxide formation resulted from the subsequent condensation of aminoborazine with DMF and amine hydrochloride. We wish to report here the initial observations with the chloroborazines, and the more definitive experiments with aminoborazines which have led to a workable hypothesis regarding the reaction mechanism.

Results and Discussion

I. Reaction of Amines with Chloroborazines in Dimethylformamide.—The reaction of a chloroborazine with dimethylamine and DMF is essentially quantitative according to the equation

$$2>BCl + (CH_3)_2NC(H)O + 2(CH_3)_2NH \longrightarrow$$
$$>BOB< + (CH_3)_2NH_2Cl + [(CH_3)_2NC(H)N(CH_3)_2]Cl \quad (1)$$
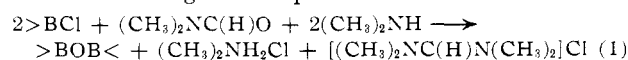
Observed ratios were: $(CH_3)_2NH/>BCl = 0.96$ and $DMF/>BCl = 0.50$. Yields of borazyl oxides were usually above 90%. Dimethylamine or monomethylamine were employed in this reaction for conversion of

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