

C4 or reversed), 132.6 (C2), 124.4 (C3), 34.1 (C5), 33.2 (C6), 139.3 (C7), 134.9 (ipso carbon of C1 phenyl), 132.7 (ipso carbon of C2 phenyl), 165.6 (COOH).

Precise mass calcd for  $C_{25}H_{20}N_2O_2$ : 380.152. Found: 380.151.

**Decarboxylation of 17. Preparation of the Authentic Sample of 3,4-Diphenyl-6-(2-phenylethyl)pyridazine (16).** In a 10-mL round-bottom flask fitted with a  $CaCl_2$  drying tube was placed 1.0 g (0.0026 mol) of 17. The flask was immersed in an oil bath held at 225 °C for 30 min. As the sample melted, gas was evolved. The crude residue was dissolved in ether and crystallized by standing at room temperature. The resulting light yellow solid was recrystallized from ether-petroleum ether to yield 17 (0.86 g, 98%) as an analytical sample: mp 114.5–115.5 °C;  $^1H$  NMR  $\delta$  3.19 (m, 2 H,  $CH_2CH_2Ph$ ), 3.37 (m, 2 H,  $CH_2CH_2Ph$ ), 7.09–7.44 (m, 16 H, aromatic);  $^{13}C$  NMR  $\delta$  158.0 (C1), 136.9 (C2), 126.2 (C3), 161.2 (C4), 37.7 (C5), 35.6 (C6), 140.9 (C7), 138.8 (ipso carbon of C1 phenyl), 137.0 (ipso carbon of C2 phenyl).

Precise mass calcd for  $C_{24}H_{20}N_2$ : 336.163. Found: 336.164.

**Preparation of (E)-2-(3-Methyl-5-phenyl-1H-pyrazol-1-yl)-1,2-diphenyl-1-(benzoyloxy)ethene (24).** In a 100-mL flask fitted with  $CaCl_2$  tube, 0.16 g (0.005 mol) of dry methanol was added to 0.42 g (57% assay, 0.010 mol) of NaH in 10 mL of ether. When hydrogen evolution ceased, the solution was cooled to -20 °C, and 1.76 g (0.005 mol) of pyrazole 23<sup>2a</sup> was added (reaction mixture changed to a deep-yellow color). When gas evolution had ceased, 1.48 g (0.0105 mol) of benzoyl chloride was added and stirred for 2 h at ambient temperature. The reaction mixture was filtered, and the filtrate was concentrate to dryness in vacuo to yield 1.5 g (65.7%) of 24 as a white solid: mp 148–149 °C; IR (KBr) 1745, 1600, 1495, 1450  $cm^{-1}$ ;  $^1H$  NMR  $\delta$  2.34 (s, 3 H,  $C_3$   $CH_3$ ), 6.11 (s, 1 H, C4 H), 6.66 (d,  $J = 7.7$  Hz, 2 H, aromatic), 6.95–7.60 (m, 16 H, aromatic), 8.00 (d,  $J = 7.7$  Hz, 2 H, aromatic ortho to  $C=O$ );  $^{13}C$  NMR  $\delta$  164.7 (C1  $OCOPh$ ), 150.2 (C1), 77.4 (C2), 146.6 (C3), 106.6 (C4), 145.9 (C5), 13.7 ( $C_3$   $CH_3$ ).

Precise mass calcd for  $C_{31}H_{24}N_2O_2$ : 456.184. Found: 456.186.

**Reduction of (Z)- and (E)-2-(3-Methyl-5-phenyl-1H-pyrazol-1-yl)-1,2-diphenyl-1-(benzoyloxy)ethene (22 and 24).** In each of two 100-mL flasks was dissolved 0.7 g (0.00153 mol) of O-benzoylated pyrazole 22 and 24 in 30 mL of ether. These solutions were cooled with an ice bath, and 0.04 g (0.00105 mol) of  $LiAlH_4$  was added with stirring. The reaction mixture stirred at room temperature for 1 h and worked up with standard procedure to yield quantitatively the same known pyrazole, 23 (by  $^1H$  NMR,  $^{13}C$  NMR, IR and mmp with authentic sample<sup>2a</sup>) in both cases: mp 105–106.5 °C; IR (KBr) 1700, 1595, 1580, 1555, 1500  $cm^{-1}$ ;  $^1H$  NMR  $\delta$  2.20 (s, 3 H,  $C_3$   $CH_3$ ), 6.15 (s, 1 H, C4 H), 6.64 (s, 1 H, C2 H), 7.22–7.42 (m, 13 H, aromatic), 7.57–7.61 (m, 2 H, aromatic ortho to  $C=O$ );  $^{13}C$  NMR  $\delta$  192.7 (C1), 66.9 (C2), 149.0 (C3), 106.8 (C4), 145.0 (C5), 13.6 ( $C_3$   $CH_3$ ).

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**Registry No.** 1, 63570-24-1; 11a, 81724-88-1; 11b, 81724-89-2; 11c, 81724-90-5; 12, 81724-91-6; 13a, 81724-92-7; 13b, 81724-93-8; 13c, 81724-94-9; 13d, 81724-95-0; 13e, 81724-96-1; 14, 81724-97-2; 15, 81724-98-3; 16, 81724-99-4; 17, 81725-00-0; 22, 81725-01-1; 23, 63570-09-2; 24, 81725-02-2; diethyl 3-phenylpropionyl malonate, 62984-12-7; ethyl 3-oxo-5-phenylpentanoate, 17071-29-3; benzil monohydrazone, 5344-88-7; methyl iodide, 74-88-4; allyl bromide, 106-95-6; benzyl chloride, 100-44-7; benzoyl chloride, 98-88-4; ethyl chloroformate, 541-41-3.

## Photodehalogenation of the Monochloro- and Monofluoroanisoles

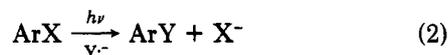
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Evidence is presented for a plurality of mechanisms in the photoreduction and photonucleophilic substitution of the monochloroanisoles in alcohol solvents. 4-Chloroanisole appears to react partly via a radical anion and partly by radicals, while the reactions of 3-chloroanisole are more consistent with aryl cations and aryl radicals. The intermediates in the reaction of 2-chloroanisole, which gives no photosubstitution, are as yet not identified but are probably not radical anions. In the case of 4-chloroanisole, substitution and reduction may proceed from different states. Preliminary results on the fluoroanisoles show the 2-F isomer giving both reduction and substitution and the 3- and 4-F isomers only substitution.

Irradiation of aryl halides produces products of reductive dehalogenation (eq 1), nucleophilic substitution (eq 2), and



inter- and intramolecular arylations. There has been little consensus on the mechanism of these reactions. In the photoreduction, triplet excited states,<sup>1</sup> singlet eximers and charge-transfer complexes,<sup>2</sup> radical pairs,<sup>3</sup> radical anions,

and radical cations<sup>2a,4</sup> have all been suggested intermediates. The photonucleophilic substitution of aryl halides was first reported by Pinhey and Rigby,<sup>5</sup> who proposed a Meisenheimer type of intermediate but did not exclude an aryl cation. Subsequently, others have proposed reaction via aryl radical cations,<sup>2a,6</sup> radical anions,<sup>2b,7</sup> and

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Table I. Effect of Solvent on the Quantum Yields of Photoreduction and Photosubstitution of the Chloroanisoles

| solvent                        | $\epsilon^a$ | 4 isomer                |                     |                         |                     |                                       | 3 isomer                |                     |                         |                     |                                       | 2 isomer                |                     |
|--------------------------------|--------------|-------------------------|---------------------|-------------------------|---------------------|---------------------------------------|-------------------------|---------------------|-------------------------|---------------------|---------------------------------------|-------------------------|---------------------|
|                                |              | $10^2\phi_{\text{red}}$ | $\phi_{\text{red}}$ | $10^2\phi_{\text{sub}}$ | $\phi_{\text{sub}}$ | $\phi_{\text{red}}/\phi_{\text{sub}}$ | $10^2\phi_{\text{red}}$ | $\phi_{\text{red}}$ | $10^2\phi_{\text{sub}}$ | $\phi_{\text{sub}}$ | $\phi_{\text{red}}/\phi_{\text{sub}}$ | $10^2\phi_{\text{red}}$ | $\phi_{\text{red}}$ |
| MeOH                           | 32.70        | 7.67                    | 1                   | 1.94                    | 1                   | 3.95                                  | 18.4                    | 1                   | 4.70                    | 1                   | 3.93                                  | 13.5                    | 1                   |
| MeOH-EtOH<br>(1:1)             |              | 6.33                    | 0.83                | 0.625 <sup>b</sup>      | 0.32                | 10.1                                  |                         |                     |                         |                     |                                       |                         |                     |
| EtOH                           | 24.58        | 5.41                    | 0.70                | 0.258                   | 0.13                | 21.0                                  | 25.6                    | 1.36                | 3.88                    | 0.826               | 6.59                                  | 25.2                    | 1.86                |
| <i>i</i> -PrOH                 | 19.92        | 5.49                    | 0.72                | 0.06 <sup>c</sup>       | 0.03                | 87.                                   | 26.6                    | 1.41                | 4.82                    | 1.03                | 5.52                                  | 24.9                    | 1.84                |
| <i>t</i> -BuOH                 | 12.47        | 0.34                    | 0.044               | 0.0                     | 0.0                 |                                       | 8.70                    | 0.463               | 0.0                     | 0.0                 |                                       | 10.9                    | 0.803               |
| C <sub>6</sub> H <sub>12</sub> | 2.02         | 35.6                    | 17.0                | 0.0                     | 0.0                 |                                       | 63.5                    | 3.38                | 0.0                     | 0.0                 |                                       | 40.9                    | 3.02                |

<sup>a</sup> Dielectric constant. <sup>b</sup> Sum of 0.285 for 4-ethoxyanisole and 0.340 for 4-methoxyanisole. <sup>c</sup> Estimated from one data point.

concerted reactions.<sup>8</sup> Two papers in particular are most germane to the work reported here. As this paper was being prepared, a communication was published by Soumillion and De Wolf<sup>9</sup> on the photoreduction and photosubstitution of chlorobenzene and the chloroanisoles in methanol. While some of their results parallel ours, we are in disagreement on the interpretation of others (see Results and Discussion). Cornelisse and Havinga<sup>6b</sup> studied the photocyanation of chloro- and fluoroanisole in a 3:1 water-*tert*-butyl alcohol mixture at 280 nm. They proposed the intermediacy of a radical cation, ArX<sup>+</sup>, and a solvated electron, formed from the ionization of triplet ArX, on the evidence that the product composition is similar to that found in anodic oxidations of ArX and that attack occurs mainly at the position predicted by Pariser-Parr-Pople calculations to have the highest positive charge density in the radical cation. In these highly aqueous solutions photoreduction is almost completely suppressed while in alcoholic or hydrocarbon solvents reduction is the preferred or exclusive process. In this paper we will present evidence for the existence of several mechanisms, depending on solvent and on substituent placement, for the photoreactions of the monochloro- and monofluoroanisoles at 2537 Å in a variety of media.

### Results and Discussion

The three chloroanisoles exhibit several differences in their photochemistry (Table I). Most obviously, the 2-Cl isomer gives only photoreduction, while the other two show varying amounts of photosubstitution. On the other hand, the 3- and 4-Cl isomers respond differently to changes in solvent and to the presence of oxygen or amines during photolysis. Accordingly, the three isomers are discussed separately. Initially it had been assumed that the photoproducts were arising solely from the T<sub>1</sub> state of the chloroanisoles, both because the heavy-atom effect should promote intersystem crossing for these compounds<sup>10</sup> and because the triplet state had previously been implicated in the photoreactions of other aryl halides.<sup>1b,4c</sup> Our results to date, however, show that for the 3- and 4-chloroanisoles photoreduction and photosubstitution proceed at least partly from different intermediates, the nature of which is not yet certain.

**4-Chloroanisole.** On irradiation in methanol 4-chloroanisole is both reduced to anisole and substituted

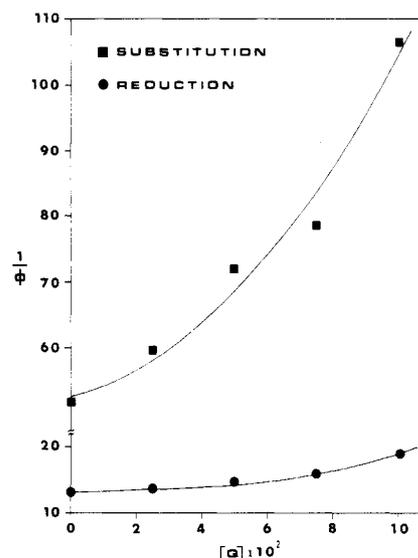


Figure 1. Stern-Volmer plots for quenching of 4-chloroanisole photoreactions by *cis*-1,2-dichloroethene.

by solvent to give 1,4-dimethoxybenzene. A Stern-Volmer plot was constructed for the 4-chloroanisole photolysis by using *cis*-1,2-dichloroethene as the quencher (Figure 1). From the obvious curvature of the plots we infer that the quencher is interacting with more than one species, probably two, though at present it is unclear whether these are excited species, "hot" ground-state intermediates, or both. What is apparent is that quenching by dichloroethene is chemical, not physical, because within experimental error, the quantum yield of disappearance of 4-dichloroanisole ( $\phi_{\text{dis}}$ ) is independent of quencher concentration (correlation coefficient -0.067; probability of no correlation 0.92). Furthermore, though the relative error is higher in measuring small differences in starting material concentration at short reaction times, the material balance of the reaction is significantly worse when the quencher concentration is greater than 0.03 M. While the sum of  $\phi_{\text{red}}$  and  $\phi_{\text{sub}}$  in the absence of quencher is typically 75–90% of  $\phi_{\text{dis}}$ , in the presence of quencher this sum is only 55–65% of  $\phi_{\text{dis}}$ . If the dichloroethene is quenching two species, a quadratic dependence of reciprocal quantum yield of quencher concentration is expected.<sup>11</sup> The solid curves in Figure 1 are the best-fit lines resulting when the data are fit to a second-degree polynomial.<sup>12</sup> It is significant

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(10) Cornelisse reports  $\phi_{\text{isc}} = 0.75$  for 4-fluoro- and 4-chloroanisole in *t*-BuOH-H<sub>2</sub>O.<sup>6b</sup>

(11) The mathematics should be the same as for the situation where the quencher deactivates two excited states. See: Barltrop, J. A.; Coyle, J. D. "Excited States in Organic Chemistry"; Wiley: New York, 1975; pp 151–2.

(12) The equations for these lines are as follows: for reduction,  $1/\phi = 608[Q]^2 - 6.19[Q] + 13.1$ ; for substitution,  $1/\phi = 3870[Q]^2 + 123[Q] + 52.7$ .

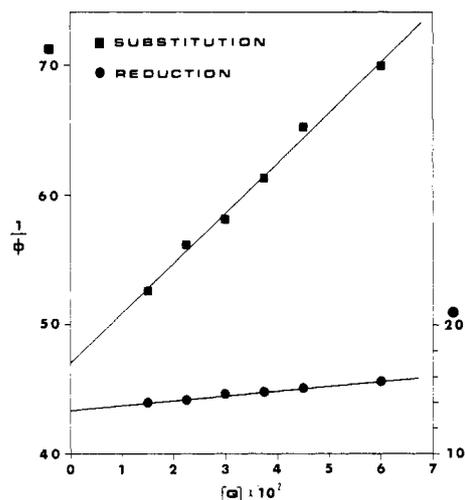


Figure 2. Stern-Volmer plots for quenching of 4-chloroanisole photoreactions by *cis*-2-butene.

that the curves for the quenching of reduction and substitution are not parallel, having a ratio of initial slopes of approximately 9:1 in favor of the substitution. The two reactions, then, cannot proceed from a common intermediate. The Stern-Volmer analysis was repeated with *cis*-2-butene (Figure 2). In this case the plots are linear, with correlation coefficients for the reduction and the substitution quenchings of 0.9905 and 0.9965, respectively, and with slopes of  $37.7 \pm 2.6$  and  $391 \pm 16$ , respectively. Owing to experimental difficulties, the effect here of quencher concentration on  $\phi_{\text{dia}}$  was not measured, so the possibility of chemical quenching by 2-butene can not be discounted. However, the linearity of the Stern-Volmer plots means that only one species is being quenched in each case, and, again, photosubstitution is about 10 times more sensitive to quencher concentration than is photoreduction. Thus 2-butene is quenching either two excited states, two ground-state intermediates, or one of each. It would seem impossible for 2-butene or 1,2-dichloroethene to quench by simple energy transfer an  $S_1$  state populated by irradiation at 2537 Å (113 kcal/mol) because the first excited singlets of these olefins lie about 138 kcal/mol above their ground states. Therefore, if two different excited states are involved in photoreduction and photosubstitution (and the quenching is physical), they must both be triplets. Several examples of participation of a higher triplet state, usually  $T_2$ , in the photoreactions of aromatic compounds appear in the literature.<sup>13</sup> Furthermore, if 2-butene is quenching two triplets, the greater influence of quencher concentration on  $\phi_{\text{sub}}$  than on  $\phi_{\text{red}}$  suggests that the triplet state of the quencher ( $T_{1q}$ , 78 kcal/mol) lies farther below that state of 4-chloroanisole leading to substitution than that leading to reduction. When 4-chloroanisole is photolyzed in the presence of triplet sensitizers (durene, benzamide, and benzoic acid) having  $E_T$ 's in the range 78–80 kcal/mol, the reduction/substitution ratio is increased from 4:1 to about 6:1, a fact also consistent with the placement of the state leading to substitution higher than that yielding reduction and probably significantly higher than 80 kcal/mol.

Irradiation of 4-chloroanisole in  $O_2$ -saturated methanol gives exclusively reduction. Photoreduction of a carbon-halogen bond almost certainly involves radicals which may be captured to some extent by  $O_2$ , and so the fact that

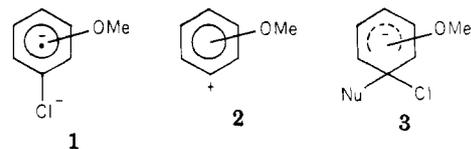
Table II. Total Energies of the Chloroanisoles and Various Proposed Intermediates by the INDO Method

| compd | config | $E_{\text{total}}$ kcal/mol |
|-------|--------|-----------------------------|
|       | ortho  | -54 165                     |
|       | meta   | -54 166                     |
|       | para   | -54 166                     |
|       | ortho  | -54 089                     |
|       | meta   | -54 086                     |
|       | para   | -54 088                     |
|       | ortho  | -44 362                     |
|       | meta   | -44 364                     |
|       | para   | -44 362                     |
|       | ortho  | -44 235                     |
|       | meta   | -44 238                     |
|       | para   | -44 220                     |
|       | ortho  | <i>a</i>                    |
|       | meta   | -54 142                     |
|       | para   | -54 142                     |
|       | ortho  | -65 670                     |
|       | meta   | -65 574                     |
|       | para   | -65 669                     |

<sup>a</sup> Would not converge.

reduction proceeds in the presence of  $O_2$  while substitution is completely quenched implies for the latter an intermediate more sensitive to  $O_2$  than are radicals. Radical anions are reasonable candidates, as these are known to be quenched very efficiently by  $O_2$ <sup>14</sup> and have been implicated by Bunnett<sup>7</sup> in other photoneophilic substitutions. The effect of solvent polarity on  $\phi_{\text{sub}}$  for 4-chloroanisole (Table I) is consistent with the appearance of a polar or charged intermediate in the rate-determining step but says nothing about the nature of such a species. That the rapid falloff of  $\phi_{\text{sub}}$  is not due simply to decreasing nucleophilicity in the alcoholic solvents is shown by the fact that the quantum yield of formation of 4-ethoxyanisole increased from 0.00258 in pure ethanol to 0.00285 in the more polar mixed solvent, while that of 4-methoxyanisole dropped from 0.0194 in pure methanol to 0.00340 in the less polar mixed solvent. Some solvent nucleophilicity is apparently required for substitution to occur, however, when 4-chloroanisole is photolyzed in the polar, but only slightly nucleophilic, 2,2,2-trifluoroethanol, the only isolable products are anisole, 4-fluoroanisole, and 1-(4-anisyl)-2,2,2-trifluoroethanol. This last compound, identified by its <sup>1</sup>H and <sup>13</sup>C NMR and IR spectra, is presumed to be a radical coupling product.

At this point let us note that there are two other possible charged species that could be intermediates in nonaqueous solvents, in addition to the radical anion 1. These are the aryl cation 2 and the Meisenheimer intermediate 3. To



gauge the relative importance of these and other intermediates, we performed INDO calculations with geometry optimization on the species listed in Table II to yield total energies. As the program was limited to 20 atoms, 3 had to be approximated by the hydroxy derivative as shown. While the absolute magnitudes of such energies are

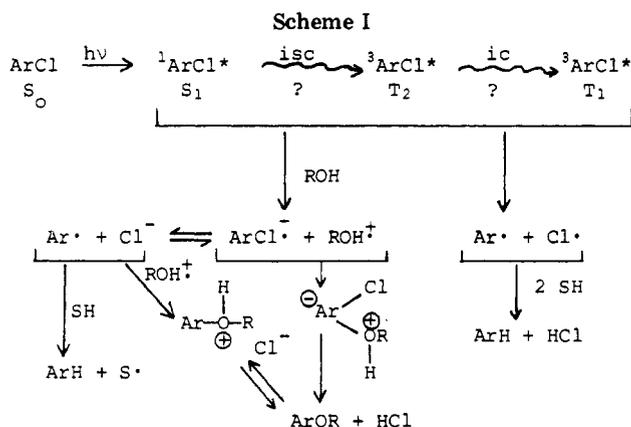
(13) (a) Ladwig, C. S.; Liu, R. S. H. *J. Am. Chem. Soc.* 1976, 98, 8093. (b) El'tsov, A. V.; Kul'bitskaya, O. V.; Frolov, A. N. *Zh. Org. Khim.* 1972, 8 (1), 86.

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Table III. Concentration of Reduction and Substitution Products Present After Irradiation of 4-Chloroanisole in Methanol-Water Mixtures for 30 min

| mol %<br>of water | yields, mM |                |                |       |
|-------------------|------------|----------------|----------------|-------|
|                   | PhOMe      | 4 <sup>a</sup> | 5 <sup>b</sup> | total |
| 0                 | 9.59       | 2.18           | 0.0            | 11.77 |
| 10                | 8.86       | 2.02           | 0.0            | 10.88 |
| 20                | 9.14       | 2.22           | 0.0            | 11.66 |
| 50                | 8.26       | 1.63           | 0.48           | 11.37 |

<sup>a</sup> 1,4-Dimethoxybenzene. <sup>b</sup> 4-Methoxyphenol.



probably not meaningful, the relative values are considered to have some validity. For example, the stabilities of the Meisenheimer complexes are predicted to be in the order ortho  $\approx$  para  $\gg$  meta, with the meta isomer at least 95 kcal/mol higher than the other two. Since the actual order of the  $\phi_{\text{sub}}$ 's is meta  $>$  para, with ortho failing to react, the Meisenheimer complex is an unlikely intermediate in these cases. On the other hand, the stability order for the anisyl cations is meta  $\approx$  ortho  $>$  para. This parallels the meta and para reactivities but not the ortho reactivity. It must be considered, however, that the nonreactivity of the ortho isomer may be due to factors other than the stability of the intermediate. To investigate the possibility of the intermediacy of an aryl cation, we conducted the photolysis of 4-chloroanisole in methanol water mixtures, the two expected substitution products being 1,4-dimethoxybenzene (4) and 4-methoxyphenol (5). The highly reactive aryl cation would be expected to show little selectivity in reacting with water or methanol. However, as seen in Table III, reaction with methanol is by far the favored process, which argues for a more selective species than an aryl cation. Furthermore, this result is in accord with the mechanism in Scheme I which posits electron transfer from solvent to the triplet state of 4-chloroanisole, since the ionization potentials of water and methanol are 12.6 and 10.84 eV, respectively. If radical anions produced by electron transfer from solvent precede photosubstitution, then addition of more efficient one-electron donors to the solvent should increase  $\phi_{\text{sub}}$ . Surprisingly, it is found that both substitution and reduction yields are increased. Addition of 0.01 M Et<sub>2</sub>NH, 0.099 M Et<sub>3</sub>N, and 0.099 M FeCl<sub>2</sub> to the methanolic 4-chloroanisole increases the yield of anisole by 22%, 51%, and 64%, respectively, and the yield of 4 by 15%, 23%, and -45%, respectively. The apparent decrease in the yield of 4 in the presence of FeCl<sub>2</sub> is presumably due to its destruction by the Fe<sup>3+</sup> formed, a reaction that was confirmed in a separate dark experiment. As these data were derived from "one-tube" experiments, a detailed study of the effect of added Et<sub>2</sub>NH on the rates of reduction and substitution in methanol was made.<sup>15</sup> The results, given in Table IV, show that the  $\phi_{\text{red}}$

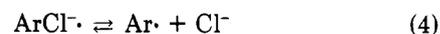
Table IV. Relative Quantum Yields of Reaction of 4-Chloroanisole Irradiated in Methanol in the Presence of Added Et<sub>2</sub>NH

| [Et <sub>2</sub> NH], mM | $\phi/\phi_0$ |      |
|--------------------------|---------------|------|
|                          | red           | sub  |
| 4.27                     | 1.01          | 1.23 |
| 10.2                     | 1.05          | 1.26 |
| 20.9                     | 1.07          | 1.08 |
| 39.5                     | 1.12          | 1.12 |
| 51.1                     | 1.11          | 1.13 |
| 99.9                     | 1.08          | 1.05 |
| 160.6                    | 1.10          | 0.97 |

rises until the amine concentration reaches 0.04 M and then levels off, while  $\phi_{\text{sub}}$  rises even more sharply, leveling off at between 0.01 and 0.02 M amine and actually declining somewhat at higher concentrations, indicative<sup>6b</sup> of a second-order reaction between the amine and some intermediate species. At the higher amine concentrations the solutions develop a yellow color, presumably due to the formation and decomposition of a reaction product of the chloroanisole with the amine, though the simple substitution product, 4-methoxy-*N,N*-diethylaniline (6) could not be detected by GC. Irradiation of 4-chloroanisole in neat diethylamine results in the development of a yellow color and production of a tarry substance, but again no detectable 6. In methanolic sodium methoxide, the quantum yields of both reduction and substitution rise, with the  $\phi_{\text{sub}}$  showing the greater effect. At a methoxide concentration of 0.05 M,  $\phi_{\text{red}}$  is increased 76% and  $\phi_{\text{sub}}$  302%. Doubling the methoxide concentration causes a further 15.3% increase in  $\phi_{\text{red}}$  and a 30.8% increase in  $\phi_{\text{sub}}$ . These enhancements are consistent with methoxide's acting as a one-electron donor, a reaction which has some precedent. For example, Ayscough and Wilson<sup>16</sup> have shown by ESR studies that ketyl radicals are produced from the action of alkoxide ions on aryl ketones (eq 3).



The rate enhancements by added methoxide are not due simply to the increase in ionic strength of the medium. Irradiation of 4-chloroanisole in the presence of NaNO<sub>3</sub> (0.11 M) produces no change in either  $\phi_{\text{sub}}$  or  $\phi_{\text{red}}$  within experimental error. On the other hand, the addition of LiCl (0.162 M) causes a decrease of 30% in  $\phi_{\text{red}}$  and 46% in  $\phi_{\text{sub}}$ . This we interpret as a common-ion effect. That is, we assume that the initially formed radical anion can decompose reversibly to an aryl radical and a chloride ion (eq 4). If the photosubstitution of 4-chloroanisole proceeds

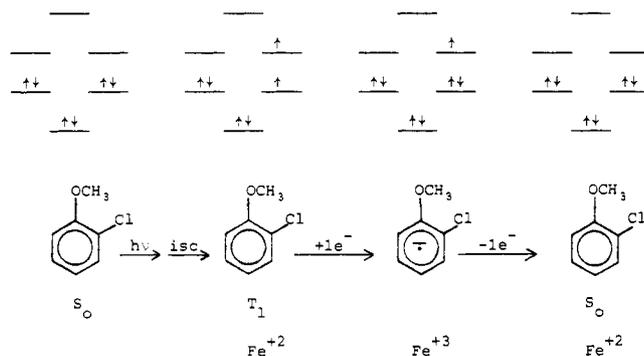


exclusively from the radical anion and if the rate changes caused by NaOMe and LiCl may be attributed entirely to their effect on the steady-state concentration of this intermediate, then the effect of these additives on the rate of photoreduction suggests that this process occurs anywhere from 50% to 65% via the radical anion also. The acceleration of the photoreduction in the presence of the one-electron donors further supports this conclusion.

(15) A comparison of the "one-tube" data with those in Table IV shows the problem which can arise when product yields after long reaction times are used, rather than initial rates (or quantum yields), to account for small differences in reactivity. According to the former, photoreduction is more sensitive than photosubstitution to the presence of one-electron donors, whereas the latter suggest the opposite. The asymptotic behavior of the rate with increasing amine concentration has much precedent<sup>6b</sup> and is taken as proof of chemical quenching of an excited state or intermediate by the amine.

(16) Ayscough, P. B.; Wilson, R. *J. Chem. Soc.* 1963, 5412, 5418.

Scheme II



Scheme I provides an interpretation of the above observations while acknowledging the uncertainty in the number and multiplicities of the initial excited states.

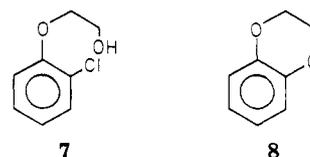
It is appropriate at this point to consider the mechanism advanced by Soumillion and De Wolf<sup>9</sup> (Scheme II). Two criticisms may be leveled against this mechanism. First, as one precedent for the triplet excimer the authors site a report of triplet excimer emission from chlorobenzene. It has been shown that while chlorobenzene does indeed form a triplet excimer, this does not lead to product since the quantum yield of benzene formation *decreases* with an increasing concentration of chlorobenzene.<sup>4b</sup> Second, the quenching of substitution by O<sub>2</sub>, the preference for reaction with methanol over water, and the acceleration of the substitution by one-electron donors all argue against a radical cation as the precursor of the substitution product.

**3-Chloroanisole.** That 3-chloroanisole undergoes photoreaction by a different mechanism from that shown in Scheme I is clear from the different response of this compound to the various changes in reaction conditions described above. For example, a change in solvent from degassed to O<sub>2</sub>-saturated methanol causes the reduction/substitution ratio to change from 4:1 to 1:1, while for 4-chloroanisole in the latter solvent, the substitution is quenched completely. The effect of changing the alcohol solvent on  $\phi_{\text{sub}}$  is seen (Table I) to be small except for *tert*-butyl alcohol. In a 1:1 (molar ratio) water-methanol solution, while 4-chloroanisole exhibits a 3.4-fold preference for reaction with methanol (Table III), 3-chloroanisole shows a 1.2-fold preference for reaction with water. Moreover, the  $\phi_{\text{red}}:\phi_{\text{sub}}$  ratio in methanol is 4:1 for both 4- and 3-chloroanisole. Changing the solvent to 1:1 methanol-water produces no change in the ratio for the 4-Cl isomer but causes a drop to 0.65:1 for the 3-Cl isomer. Perhaps most significantly, irradiation of 3-chloroanisole in the presence of Fe<sup>2+</sup> ion or Et<sub>2</sub>NH causes a *decrease* in the amount of both reduction and substitution products, arguing against the intermediacy of a radical anion in these reactions. As may be seen in Table II, however, the *m*-methoxyphenyl cation is predicted to be 18 kcal/mol more stable than the para isomer, and reaction via the cation may be a lower energy pathway than reaction via the radical anion for 3-chloroanisole. Jaffé and Koser<sup>17</sup> have suggested that the geometry, and hence the energy, of a phenyl cation is highly dependent on its substitution pattern, and we are currently undertaking MNDO calculations on these systems in order to clarify this point. Finally, addition of a methyl group to the 4-position of 3-chloroanisole increases the rate of photosubstitution.<sup>18</sup>

(17) Jaffé, H. H.; Koser, G. F. *J. Org. Chem.* **1975**, *40*, 3082.

This too is more consistent with an electron-deficient intermediate. An aryl cation could arise from fragmentation of an excited singlet or by electron transfer from a 3-methoxyphenyl radical to a chlorine atom. This aryl radical, the probable precursor of anisole, could derive from either the excited singlet or triplet states of 3-chloroanisole. It is not yet clear what species is being quenched by O<sub>2</sub>, and in the absence of quencher studies on 3-chloroanisole, we will refrain from further speculation on the mechanism.

**2-Chloroanisole.** The most striking feature of the photochemistry of 2-chloroanisole is the previously reported<sup>6b,9</sup> total lack of photosubstitution. Photoreduction quantum yields in various solvents (Table I) are similar to those of the 3-Cl isomer, 3–4 times those of the 4-Cl isomer. The reason for the lack of photosubstitution remains unclear. It may be that in the relevant excited state (or intermediate) the oxygen-bound methyl group hinders the approach of the solvent alcohol. The resulting negative entropy effect could conceivably be overcome by incorporating a nucleophilic group at such a position in the alkoxy side chain that a cyclic transition state is possible. Photolysis of compound **7** in methanol, however, gave only reduction and no **8**.



As was the case with 3-chloroanisole, a radical anion intermediate does not seem to be involved in the photoreduction. Irradiation of 2-chloroanisole (0.05 M) in the presence of FeCl<sub>2</sub> (0.099 M) showed a decrease in  $\phi_{\text{red}}$  of 38%. Simultaneously, the  $\phi_{\text{dis}}$  decreased by 32%, showing that there was no diversion of starting material to other products. We attribute this decrease in  $\phi_{\text{red}}$  to electron-transfer quenching of the excited state (Scheme II). This type of quenching has been observed for ketones irradiated in the presence of amines.<sup>6b</sup> It is assumed that the electron acquired from the Fe<sup>2+</sup> ion would enter the orbital depleted by excitation.

**Photoreduction.** The photoreduction of 2-, 3-, and (in part) 4-chloroanisole is probably best accounted for by invoking methoxyphenyl radicals which abstract hydrogen atoms from the solvent. If one assumes that the number of equivalent hydrogens available for abstraction ( $N_{\text{H}}$ ) is 3 for MeOH, 2 for EtOH, 1 for *i*-PrOH, 9 for *t*-BuOH, and 12 for cyclohexane, one may divide the observed reduction quantum yields by a correction factor,  $[H]_s$ , the number of moles of abstractable H per liter, given by eq 5, where

$$[H]_s = 1000N_{\text{H}}\rho/\text{molecular weight} \quad (5)$$

$\rho$  is the density of the solvent. The reduction quantum yields thus corrected appear in Table V and parallel, for the most part, the strengths of the appropriate CH bonds. The  $D_{\text{CH}}$  for *t*-BuOH could not be found, but it is likely to be higher than that for cyclohexane, since in the former case a primary radical would be formed and in the latter a secondary.

**Fluoroanisoles.** Some preliminary experiments were carried out on the fluoroanisoles, and the quantum yields

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(19) Allan, J.; Robinson, R. *J. Chem. Soc.* **1926**, 378.

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(23) Goldsworthy, L. J. *J. Chem. Soc.* **1936**, 1148.

Table V. Quantum Yields of Photoreduction of the Chloroanisoles Corrected for Concentration of Abstractable Hydrogen in the Solvent

| solvent                        | $D_{CH}^a$ | $[H]_s$ | $10^3\phi_{red}/[H]_s$ |          |          |
|--------------------------------|------------|---------|------------------------|----------|----------|
|                                |            |         | 2 isomer               | 3 isomer | 4 isomer |
| <i>t</i> -BuOH                 |            | 95.1    | 1.15                   | 0.915    | 0.0358   |
| C <sub>6</sub> H <sub>12</sub> | 95.5       | 111.0   | 3.68                   | 5.72     | 3.21     |
| MeOH                           | 94         | 74.1    | 1.82                   | 2.48     | 1.04     |
| EtOH                           | 93         | 34.3    | 7.35                   | 7.46     | 1.58     |
| <i>i</i> -PrOH                 | 91         | 13.1    | 19.0                   | 20.3     | 4.19     |

<sup>a</sup> Appropriate CH bond dissociation energies in kcal/mol ("CRC Handbook of Chemistry and Physics", 59th ed.; CRC Press: Cleveland, OH, 1978-1979).

Table VI. Quantum Yields of Photoreduction and Photosubstitution of the Fluoroanisoles in Methanol

| isomer | $10^2\phi_{red}$ | $10^2\phi_{sub}$ |
|--------|------------------|------------------|
| 2      | 0.868            | 0.466            |
| 3      |                  | 0.014            |
| 4      |                  | 0.0029           |

for photoreduction and photosubstitution are included here (Table VI) for comparison with the chloroanisoles. With 2-fluoroanisole, not only do we have the first-reported example of the photoreduction of an aryl fluoride but this isomer also is by far the most reactive of the three, the 3- and 4-F isomers being less reactive by 2 orders of magnitude than the corresponding chloro compounds. Mechanistic speculation on the fluoroanisole reactions will be deferred pending further study.

### Experimental Section

Photolysis samples (15 mL, 0.05 M; except 3-chloroanisole, 0.10 M) were sealed in Vycor tubes after four freeze-pump-thaw degassing cycles and were irradiated in a prewarmed Rayonet equipped with 2537-Å lamps. Equal exposure of all samples was ensured by the use of a merry-go-round apparatus placed in the reactor and rotating at 4 rpm. The temperature in the reactor was customarily  $30 \pm 2$  °C. Samples were withdrawn periodically and analyzed. Conversions were limited to less than 20% to minimize the light-filtering effects of the photoproducts and because at least one of the photosubstitution products, 1,4-dimethoxybenzene, is photolabile. For elimination of the effects of lamp aging, in all cases where rates were measured, 4-chloroanisole was irradiated in parallel with the compound in question, and the rate constants for reduction and substitution of the former were used to correct those of the latter. These standard rate constants were 3.67 (average of 19 runs,  $\sigma = 0.28$ ) and  $0.926 \mu\text{M/s}$  (average of 16 runs,  $\sigma = 0.030$ ) for the reduction and substitution, respectively. The corresponding quantum yields were determined by using as an actinometer the photoreduction of chlorobenzene in cyclohexane ( $\Phi = 0.33$ )<sup>4b</sup> and were found to be  $0.075 \pm 0.001$  and  $0.020 \pm 0.001$ , respectively.

Analysis of the photoproducts was by gas chromatography with a Hewlett-Packard 5750 chromatograph equipped with a flame-ionization detector. A Hewlett-Packard 3380 digital integrator was used to measure peak areas. A 1.5 m  $\times$  4 mm glass column packed with 10% SP2100 on 80/100-mesh Supelcoport was used for the analysis of the monochloroanisole photoproducts; a 1.8 m  $\times$  4 mm glass column packed with 5% SP1200/1.75% bentone-34 on 100/120-mesh Supelcoport was used for the analysis of the fluoroanisole photoproducts. Typical instrumental conditions were as follows: injection port, 250 °C; detector, 380 °C; column oven, 120 °C; N<sub>2</sub> carrier gas flow rate, 60 mL/min. The internal standards were phenetole for the chloroanisoles and 4-chloroanisole for the fluoroanisoles. Five milliliters of the internal standard solution was mixed with 5 mL of the photolysate, and 2  $\mu\text{L}$  of this mixture was injected into the chromatograph. A linear least-squares computer analysis of the peak area vs. time data yielded the zero-order rate constants.

The chloro- and fluoroanisoles and the dimethoxybenzenes were purchased from commercial suppliers and were redistilled or

Table VII. Yields, Boiling Points, and <sup>1</sup>H NMR Spectral Data of Ethoxy- and Isopropoxyanisoles

| isomer                    | mp or bp (mmHg), °C                       | % yield | <sup>1</sup> H NMR <sup>a</sup>                                |
|---------------------------|---|---------|--|
| 2-ethoxy                  | 155 (100) [lit. <sup>19</sup> 213 (760)]  | 28.5    | 1.3 (t, 3), 3.65 (s, 3), 3.9 (q, 2), 6.72 (s, 4)               |
| 3-ethoxy                  | 67-68 (1) [lit. <sup>20</sup> 216 (760)]  | 46.9    | 1.30 (t, 3), 3.68 (s, 3), 3.80 (q, 2), 6.35 (m, 3), 7.0 (m, 1) |
| 4-ethoxy                  | 35 (lit. <sup>21</sup> 36-37)             | 32.9    | 1.3 (t, 3), 3.75 (s, 3), 3.82 (q, 2), 6.75 (s, 4)              |
| 2-isopropoxy              | 90 (4) [lit. <sup>22</sup> 210-215 (760)] | 25.3    | 1.35 (d, 6), 3.77 (s, 3), 6.8 (s, 4)                           |
| 3-isopropoxy <sup>b</sup> | 120-121 (18)                              | 35.2    | 1.25 (d, 6), 3.7 (s, 3), 4.35 (m, 1), 6.3 (m, 3), 7.0 (m, 1)   |
| 4-isopropoxy              | 160 (105) [lit. <sup>23</sup> 103 (12)]   | 32.0    | 1.75 (d, 6), 3.75 (s, 3), 4.3 (m, 1), 6.8 (s, 4)               |

<sup>a</sup> Peaks reported as  $\delta$  (multiplicity, relative area). <sup>b</sup> Not previously reported. C, H analysis not obtained because of agreement of the NMR spectrum with the predicted spectrum and because of the simplicity of the synthesis.

recrystallized before use. Solvents were reagent grade or spectrograde and were used without further purification. Syntheses of other starting materials and products were as follows.

**Ethoxy- and Isopropoxyanisoles.** The appropriate hydroxyanisole (0.05 mol) was dissolved in 10 mL of 20% NaOH in a 50-mL N<sub>2</sub>-purged flask. The alkyl halide (0.05 mol) was added, and the mixture was heated overnight on a steam bath, diluted with water, and extracted three times with ether. The combined ether extracts were washed once with 5% NaOH and twice with water and dried over Na<sub>2</sub>SO<sub>4</sub>. After removal of solvent, the product was distilled. Table VII gives the boiling points, yields, and <sup>1</sup>H NMR spectral data of the six compounds.

**3-*tert*-Butoxyanisole.** 3-Hydroxyanisole (0.10 mol) and *tert*-butyl chloride (0.22 mol) were stirred in a 100-mL flask at room temperature for 8 days. Water (100 mL) was added and the mixture extracted three times with ether. The combined ether extracts were washed with 5% NaOH and water, and the solvent was evaporated. Distillation gave a fraction boiling at 126 °C (1 mm) [lit.<sup>24</sup> 106 °C (9-10 mm)] which crystallized on standing overnight. GC analysis showed the product to be a 3:1 mixture of the desired material and an unidentified impurity. Recrystallization from hexane gave a 46% yield of pure product: <sup>1</sup>H NMR  $\delta$  1.35 (s, 9), 3.7 (s, 3), 6.25 (m, 3), 6.95 (m, 1) [lit.<sup>24</sup>  $\delta$  1.3 (s, 9), 3.71 (s, 3), 6.4-7.2 (m, 4)].

**1,2-Benzodioxane.** To catechol (0.25 mol) in a N<sub>2</sub>-purged flask was added with stirring 100 mL of a 5 M aqueous NaOH solution. Stirring was continued until a clear solution was obtained. 1,2-Dibromoethane (0.25 mol) was then added and the mixture refluxed overnight. The aqueous layer was drained from the cooled mixture, and the organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and distilled. The fraction boiling at 135 °C (10 mm) [lit.<sup>25</sup> 102-103 °C (19 mm)] was collected, and its IR spectrum was found to be identical with the published (Aldrich) spectrum.

**2-(2-Chlorophenoxy)ethanol.** To 2-chlorophenol (0.20 mol) and 2-chloroethanol (0.40 mol) in a N<sub>2</sub>-purged flask was added slowly with stirring 50 mL of a 4.5 M aqueous NaOH solution. The mixture was refluxed overnight, cooled, diluted with water, and extracted three times with ether. The combined ether extracts were washed with 5% NaOH and then twice with water and dried over Na<sub>2</sub>SO<sub>4</sub>. The ether was evaporated and the product distilled. The fraction boiling at 250 °C (50 mm) [lit.<sup>26</sup> 106 °C (0.1 mm)]

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(25) Heertjes, P. M.; Dahmen, E. A. M. F.; Wierda, T. G. *Recl. Trav. Chim. Pays-Bas* 1941, 60, 569.

was collected: 43% yield;  $^1\text{H NMR } \delta$  3.2 (t, 2), 3.95 (t, 2), 7.0 (m, 4).

**Registry No.** 1(3-OMe), 81740-38-7; 1(4-OMe), 81740-39-8; 2(2-OMe), 81740-40-1; 2(3-OMe), 81740-41-2; 2(4-OMe), 42766-42-7; 3-(Nu = OMe, 2-OH), 81740-87-6; 3(Nu = OMe, 3-OH), 81740-88-7;

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3(Nu = OMe, 4-OH), 81740-89-8; 3-*tert*-butoxyanisole, 15359-99-6; 1,2-benzodioxane, 493-09-4; 2-(2-chlorophenoxy)ethanol, 15480-00-9; 4-chloroanisole, 623-12-1; 3-chloroanisole, 2845-89-8; 2-chloroanisole, 766-51-8; 2-methoxyphenyl, 13799-56-9; 3-methoxyphenyl, 18815-11-7; 4-methoxyphenyl, 2396-03-4; 2-fluoroanisole, 321-28-8; 3-fluoroanisole, 456-49-5; 4-fluoroanisole, 459-60-9; 2-ethoxyanisole, 17600-72-5; 3-ethoxyanisole, 25783-45-3; 4-ethoxyanisole, 5076-72-2; 2-isopropoxyanisole, 2539-21-1; 3-isopropoxyanisole, 51241-41-9; 4-isopropoxyanisole, 20744-02-9.

## Specific and Selective Site Reactions of Alkanoate Derivatives. 2. Isomerization and Lactonization of Chloroalkanoic Acids in Strong Acid Media<sup>1</sup>

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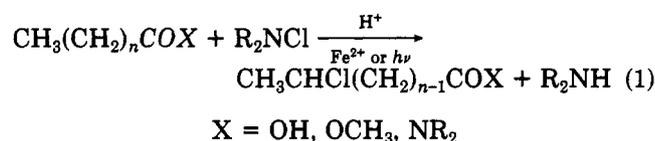
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( $\omega - 1$ )-Monochloro aliphatic acids (and positional isomers) react in a strong acid solvent to give a mixture of  $\gamma$ - and  $\delta$ -lactones, methyl-branched aliphatic acids, and dimeric acid products. The initial reaction involves rapid and extensive halogen migration along the aliphatic chain with formation of a mixture of isomeric chloro acids. The final products depend on the chain length of the monochloro acids; i.e., lactones are predominantly formed from the 6-chloroheptanoic and 7-chlorooctanoic acids and their positional chloro isomers, whereas methyl-branched aliphatic acids and dimeric acids are the predominant end products from the larger chain chloro acids. These formerly unobserved products from chloro acids in strong acid media explain the poor ( $\omega - 1$ ) positional selectivity of long-chain fatty acids to haloamine halogenation in the intermolecular variation of the Hoffman-Loeffler-Freytag reaction.

### Introduction

The intermolecular variation of the Hoffman-Loeffler-Freytag reaction (eq 1)—hereinafter conveniently referred to as IHLF—permits selective ( $\omega - 1$ ) positional halogenation of alkananoate derivatives.<sup>3-8</sup> The reaction was limited



scope since ( $\omega - 1$ ) substitution is selective in carboxylate derivatives of intermediate chain length [C<sub>6</sub> (82%)–C<sub>10</sub> (55%)], whereas selectivity is diminished in longer chain homologues [C<sub>12</sub> (43%)–C<sub>18</sub> (14%)].<sup>9</sup>

In our recent study of the parameter of the IHLF reaction<sup>9</sup> we found that the substrate concentration influenced the chloro isomer distribution and we noted that  $\gamma$ -

and  $\delta$ -lactones were formed as coproducts.<sup>9</sup> Other investigators have not previously observed the formation of lactones arising as products of fatty acid halogenation in the IHLF reaction. Although Deno and Pohl<sup>10</sup> observed the disappearance of isomeric chlorooctanoic acids by solvolysis in sulfuric acid, they did not determine the resultant products nor did they provide an understanding of the reaction course. We have therefore examined and report in this paper the details of the acid-catalyzed isomerization and lactonization of chloroalkanoic acids and esters that represent a new reaction of halogeno acids.

### Results and Discussion

The series of heptanoic, octanoic, nonanoic, and decanoic acids and esters were chlorinated by the IHLF reaction as previously described.<sup>9</sup> The resultant chloro products were isolated by distillation. In each chlorinated fatty acid mixture, the positional monochloro isomers contained the range of C<sub>5</sub> to terminally substituted products, among which the ( $\omega - 1$ )-chloro isomer predominated. The chloro isomers were subjected to 96% sulfuric acid (25–30 °C) at 0.5 and 1.0 M substrate concentrations, and the change in product distribution was periodically analyzed by capillary GLC.

Tables I and II record the results of the acid-catalyzed isomerization and lactonization of the chloroheptanoic and chlorooctanoic acids and methyl esters and methyl chloroundecanoate. Lactonization of chloroheptanoic and chlorooctanoic acids and esters in sulfuric acid proceeded more rapidly at 0.5 M than at 1.0 M. All of the chloro

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