chloroform, and methyl chloroacetate was unsuccessful, suggesting that carboalkoxy groups, unlike the ketone group, cannot be successfully correlated by the present scheme (although more data would be necessary for verification). Therefore, any attempt to extend Taft's list of σ^* values to include the carboethoxy group by use of the polarographic data of series 7 would likely lead to an erroneous assignment.

In general, attempts to extend the list of σ^* values by using polarographic data did not lead to consistent results, especially for the case of halomethyl substituents. For example, Taft[4c] lists σ^* values for $—CH_2Cl$ and $—CH_2Br$, but not for $—CH_2I$. A precise value for the substituent constant of the latter group is readily obtained by plotting the data for the three monohaloacetones. However, use of this value to correlate $E_{1/2}$ for the three haloforms does not give a straight line. As a second example, the success of the correlation for the three polarographic waves of ethyl trichloroacetate (series 5, which is equivalent to the series of the three ethyl esters of the chloroacetic acids), encouraged the belief that the data for ethyl bromoacetate might fall on the same line; it does not.

Actually, in series 5 the Taft substituent constants are being used somewhat improperly, since they are intended to measure the effect of substituents on a *nearby* reaction center. In the reduction of the haloacetates, the halogen is being attacked, leading to carbon-halogen bond fission, *i.e.*, the entity being used as a substituent is itself at the reaction center. Whether the success of the Taft-Hammett equation in the face of this misuse is only fortuitous or whether it indicates a greater generality for this equation than has been suspected, cannot now be decided.

It should be noted that in addition to predicting the effect of substituents on carbon-halogen bond fission, the Taft-Hammett equation is successful in predicting their effect upon the reduction of both carbonyl and carbon-carbon double bonds (series 3 and 4). Furthermore, the success of correlation is somewhat independent of solution environment, a good fit being achieved at each of two different pH values (series 3).

The Taft-Hammett equation was unsuccessful when applied to the nitroalkanes and hydroxynitroalkanes; values based on the Taft substituent values for the structure $R_1R_2R_3CNO_2$ were completely scattered, regardless of the bulk of the R groups.

Conclusions. Like the Hammett equation, the Taft-Hammett equation appears to be generally useful in discussing the ease of electrochemical reduction (and presumably of oxidation) of certain series of structurally related compounds. It is likely that those series or those members of a series which follow the equation are subject to polar effects only, as far as the structural effect on $E_{1/2}$ is concerned, or that the energetic magnitude of polar effects overshadows the energetic contributions of other effects such as adsorption. Thus, the Taft-Hammett relation may have possibilities for serving as a type of screen for pure polar effects in examining the electrode mechanisms of organic compounds, with deviations from the predicted behavior indicating the influence of factors in the electrochemical process other than polar effects due to structure.

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ANN ARBOR, MICH.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

Tetrabutylammonium Iodotetrachloride as a Chlorinating Agent

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Tetrabutylammonium iodotetrachloride has been used successfully as a source of chlorine for addition on a small scale to the double bonds of *cis-* and *trans*-stilbene, tetraphenylethylene, cyclohexene, and styrene, and to the triple bond of diphenylacetylene. A successful substitution was carried out on the α-carbon atom of acetophenone, and some chlorination of phenol to trichlorophenol was observed. Of particular interest was the fact that with *cis-* or *trans*-stilbene stereospecific *trans* addition was observed. When molecular chlorine reacted with *cis-* or *trans*-stilbene in the dark, the addition was not stereospecific even when antimony pentachloride or tetrabutylammonium chloride was present.

The observation[1] that tetrabutylammonium iodotetrachloride (tetrabutylammonium tetrachloroiodate [III]) chlorinated itself when illuminated to yield the (1-chlorobutyl)tributylammonium ion has led to the consideration of this salt as a source of chlorine for small scale chlorinations. In the present investigation tetrabutylammonium iodotetrachloride has been tried for

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[1] R. E. Buckles and J. F. Mills, *J. Am. Chem. Soc.*, **76**, 3716 (1954).

TABLE I

CHLORINATION REACTIONS OF TETRABUTYLAMMONIUM IODOTETRACHLORIDE IN ETHYLENE CHLORIDE

Compound Chlorinated		$(C_4H_9)_4$-$NICl_4$	Reaction	Light (L)[a] or	Products				
Name	Wt. G.	Wt. G.	time, days	Dark (D)	Identity	Crystn. Solvent	M.P.[b]	Wt. G.	Yield, %
trans-Stilbene	2.0	5.7	3	D	*meso*-Dichloride	C_2H_5OH	191–192	1.4	50
cis-Stilbene	2.0	5.7	3	D	DL-Dichloride	C_2H_5OH	91–92	1.4	50
cis-Stilbene	5.0	14.2	3–14	D	DL-Dichloride[c]	C_2H_5OH	91–92	3.0	43
					meso-Dichloride[c]	C_2H_5OH	191–193	0.5	7
Tetraphenylethylene	2.0	3.1	21	D	Dichloride	CCl_4[d]	183–184	0.8	33
Diphenylacetylene	2.0	5.7	5	D	*trans*-Dichloride	C_2H_5OH	138–139	1.3	47
Cyclohexene	5.0	31.2	3	D	Dichloride[e]	—	—	4.5	48
Styrene	10.0	49.1	4	D	Dichloride[f]	—	—	12.4	74
Tetraanisylethylene	4.0	4.6	7–35	D	Starting material	$(CH_3)_2C{=}O$	183–184	1.5	38
Cinnamic acid	2.0	6.9	3–5	D	Mixture	C_6H_{14}	130–160	0.6	—
Crotonic acid	2.0	11.9	5	D	Oily mixture	$(C_2H_5)_2O$	—	—	—
Acetophenone	2.0	8.5	5	L	Phenacyl chloride	CH_3OH	57–58	1.4	54
Triphenylmethane	2.0	4.2	5	L[g]	Starting material	C_6H_{14}	85–86	1.4	70
Bibenzyl	2.0	11.2[h]	5	L[g]	Starting material	C_2H_5OH	50–51	1.5	75
Toluene	5.0	27.8	3	L	Mixture[i]	—	—	—	—
Phenol	2.0	32.7[j]	5	D	2,4,6-Trichlorophenol	—	51–58	0.5	12
Acetic acid[k]	2.0	17.0	5	L	Liquid mixture	—	—	0.2	—

[a] Unless otherwise noted the light was diffuse daylight. [b] All melting points were corrected. [c] This type of result was obtained in several experiments. The most *meso*-isomer was obtained from reaction mixtures which were allowed to become too warm during the initial reaction. [d] This solvent was used to wash the finely ground product. [e] The boiling point was 180–185° (745 mm.). [f] The boiling point was 95–97° (7.0 mm.). The crude product was shown by gas chromatography to be mostly dichloride contaminated by a little styrene. [g] The illumination was carried out in a silica flask with a quartz mercury arc. [h] Two moles of $(C_4H_9)_4NICl_4$ were used for one of bibenzyl. [i] B.p. 120–130°. [j] Three moles of $(C_4H_9)_4NICl_4$ were used for one of phenol. [k] Two drops of phosphorus trichloride were added.

both addition reactions and substitution reactions. The results are summarized in Table I.

In general the salt did not appear to be as reactive as molecular chlorine, but the reactions that were successful were more easily controlled. This controlled addition was especially important in the addition of chlorine to *cis*- and *trans*-stilbenes. When tetrabutylammonium iodotetrachloride was used in the dark, *cis*-stilbene consistently yielded mostly *dl*-α,α'-dichlorobibenzyl while *trans*-stilbene gave the *meso* isomer. Such stereospecific *trans* additions of molecular chlorine to double bonds would be expected[2] for simple alkenes—especially in the presence of antimony pentachloride,[2a] but such results have not been observed for the *cis* and *trans*-stilbenes. In fact the chlorination of *trans*-stilbene by molecular chlorine under ultraviolet radiation[3] and by sulfuryl chloride in the presence of a peroxide[4] has been reported to give mixtures of *meso*- and *dl*-α,α'-dichlorobibenzyl often with the low melting point (91–92°) *dl*-isomer[5] as the predominant product.[3a] With molecular chlorine in the present investigation both *cis*- and *trans*-stilbene yielded mixtures of *dl*- and *meso*-dichloride which were difficult to separate in the small scale experiments carried out. The *meso* form which is the less soluble diastereomer was isolated

TABLE II

CHLORINATION OF *cis*- AND *trans*-STILBENE BY CHLORINE IN ETHYLENE CHLORIDE IN THE DARK TO GIVE α,α'-DICHLOROBIBENZYL

		Product		
Isomer	Added Reagent	Yield, %	*meso* %	DL %
cis	None	47	92	8
cis	$(C_4H_9)_4NCl$	40	91	9
cis	$SbCl_5$	48	97	3
cis[a]	None	43	99	1
trans	None	86	35[b]	65[b]
trans	$(C_4H_9)_4NCl$	68	32[b]	68[b]
trans	$SbCl_5$	93	96	4

[a] In this experiment the reaction mixture was left in diffuse daylight for three days. [b] These percentages were estimated from the infrared spectra of the mixtures in carbon disulfide.

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(2) (a) M. C. Hoff, K. W. Greenlee, and C. E. Boord, *J. Am. Chem. Soc.*, **73**, 3329 (1951); (b) H. J. Lucas and C. W. Gould, Jr., *J. Am. Chem. Soc.*, **63**, 2546 (1941).

(3) (a) R. E. Buckles, W. E. Steinmetz, and N. G. Wheeler, *J. Am. Chem. Soc.*, **72**, 2496 (1950); (b) P. Pfeiffer, *Ber.*, **45**, 1810 (1912); (c) T. Zincke, *Ber.*, **10**, 999 (1877); *Ann.*, **198**, 115 (1879).

(4) M. S. Kharasch and H. C. Brown, *J. Am. Chem. Soc.*, **61**, 3432 (1939).

(5) A. Weissberger and H. Bach, *Ber.*, **64**, 1095 (1931).

in much larger amounts than the more soluble *dl* form. These nonstereospecific additions are summarized in Table II. The addition in the presence of antimony pentachloride was expected to be stereospecific and *trans* on the basis of the results reported[2a] with various alkenes, but it was not when applied to the stilbenes.

In the case of tetrabutylammonium iodotetrachloride reacting with stilbene, conditions must be satisfactory for a controlled, polar *trans*-addition of chlorine to the double bond possibly with the aid of the iodotetrachloride ion or the iododichloride ion which is present. Under other conditions with chlorine and stilbene addition by way of an intermediate allowing relatively free rotation about the central carbon-carbon bond must modify the stereochemical results expected from a polar addition by way of a chloronium ion[2] or its molecular equivalent.

With *trans*-cinnamic acid and with *trans*-crotonic acid tetrabutylammonium iodotetrachloride appeared to react incompletely so that the products were mixtures from which no dichloride could be isolated. From *trans*-cinnamic acid with chlorine both stereoisomeric dichlorides have been reported[6]—the one with low melting point (84–86°) in the dark or in subdued light and the one of high melting point (167–168°) under strong illumination. In the present investigation chlorine yielded the high melting isomer in very subdued light. With either *cis*- or *trans*-crotonic acid, on the other hand, chlorine has been reported to yield only the isomer of low melting point (63°) whether the reaction mixture was illuminated or not.[7] The problems of stereochemistry in these cases of chlorine addition were not resolved by the use of tetrabutylammonium iodotetrachloride.

Further evidence of the control possible in the use of tetrabutylammonium iodotetrachloride for the addition of chlorine is given in the reaction with diphenylacetylene. In this case a 47% yield of *trans*-α,α'-dichlorostilbene was obtained. The reaction of diphenylacetylene with chlorine in the cold has been reported[8] to yield $\alpha,\alpha,\alpha',\alpha'$-tetrachlorobibenzyl rather than the dichlorostilbene, but in one instance the isolation of an unspecified yield of α,α'-dichlorostilbene (m.p. 143, presumably *trans*) was reported.[9]

The reaction of tetrabutylammonium iodotetrachloride with tetraphenylethylene yielded only one 1,2-dichloro-1,1,2,2-tetraphenylethylene, m.p. 183–184°. No second isomer melting at 175° as reported[10] for the chlorination of tetraphenylethylene by chlorine was obtained. In the course of the isolation of the product by fractional crystallization samples of melting point lower than 184° were obtained, but in each case x-ray powder diagrams showed the presence of two crystalline phases and carbon-hydrogen analysis showed that the sample was not pure dichloride. In some of the lower melting fractions, the dichloride appeared to be contaminated by tetraphenylethylene as shown by powder diagrams and analyses.

From the reaction of tetraanisylethylene (tetrakis-(*p*-methoxyphenyl)-ethylene) with tetrabutylammonium iodotetrachloride only starting ethylene was obtained. With chlorine, however, 1,2-dichloro-1,1,2,2-tetrakis(3,5-dichloro-4-methoxyphenyl)-ethane was isolated. This decachloride was dehalogenated with zinc to tetrakis(3,5-dichloro-4-methoxyphenyl)ethylene.

The only substitution reaction of tetrabutylammonium iodotetrachloride which gave a satisfactory yield of pure product on a small scale was that with acetophenone to give phenacyl chloride. Phenol gave a low yield of impure 2,4,6-trichlorophenol. Bibenzyl, triphenylmethane, toluene, and acetic acid (in the presence of a catalytic amount of phosphorus trichloride) gave only impure starting material from the reaction with tetrabutylammonium iodotetrachloride under illumination in each case. Bibenzyl with chlorine has never been reported to give chlorination of the side chain but stilbene has been reported[11] as a product, so that dihalides or higher substitution products would be expected[3a] with excess chlorine under illumination. With chromyl chloride, bibenzyl has been reported[12] to give a low yield of α,α'-dichlorobibenzyl. Triphenylmethane has also not been reported as chlorinated directly, but with sulfuryl chloride in the presence of lauryl peroxide[13] or of α,α'-azodiisobutyronitrile[14] good yields of triphenylmethyl chloride have been reported.

EXPERIMENTAL

Tetrabutylammonium iodide. A solution of 156 g. (0.84 mol.) of tributylamine and 159 g. (0.87 mol.) of butyl iodide in 400 ml. of anhydrous ethyl acetate was boiled under reflux for 4 days. This solution yielded crystalline product which was dissolved in 200 ml. of 95% ethanol. This solution was extracted with 20% aqueous sodium hydroxide. The alcohol layer was separated and evaporated nearly to dryness on a steam bath. The crystalline product was dried to constant weight (263 g.). This crude product was crystallized twice from anhydrous benzene–ethyl acetate (300 ml. of each) to give 256 g. (82%), m.p. 144–145°. This

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[6] A. Michael and H. D. Smith, *Am. Chem. J.*, **39**, 16 (1908).

[7] A. Michael and O. D. E. Bunge, *Ber.*, **41**, 2907 (1908).

[8] W. Redsko, *Zhur. Russ. Fiz.-Khim. Obshchestva* **21**, 421 (1889); *Chem. Zentr.*, **1880 I**, 533.

[9] C. Liebermann and J. Homeyer, *Ber.*, **12**, 1971 (1879).

[10] H. Bassett, N. Thorne, and C. L. Young, *J. Chem. Soc.*, 85 (1949).

[11] R. Kade, *J. prakt. Chem.*, [2] **19**, 461 (1879).

[12] M. Weiler, *Ber.*, **32**, 1050 (1899).

[13] M. S. Kharasch and H. C. Brown, *J. Am. Chem. Soc.*, **61**, 2142 (1939).

[14] M. C. Ford and W. A. Waters, *J. Chem. Soc.*, 1851 (1951).

method is a modification of one in which no solvent was used for the reaction mixture.[15] Another such method,[16] which was run at considerably higher temperatures over longer periods of time, gave a solid product which yielded no quaternary ammonium salt when crystallization from benzene–ethyl acetate was attempted.

Tetrabutylammonium iodotetrachloride (*tetrabutylammonium tetrachloroiodate* (III)). This salt of m.p. 137–139° (dec.) was prepared in 99% yield as described.[17] It was found that the point at which the solution became orange and product began to precipitate, was also the point at which the temperature of the reaction mixture reached a maximum (about 37°).

When tetrabutylammonium iodotetrachloride was used as a chlorinating agent it was possible to isolate the crude tetrabutylammonium iododichloride,[1] the unchanged iodotetrachloride, or a mixture of the two as a by-product. This crude salt was accumulated and chlorinated in a relatively large batch. A solution of 67.5 g. of the crude salt, which was accumulated from reactions using a total of 74.5 g. of tetrabutylammonium iodotetrachloride, in 500 ml. of chloroform was clarified by filtration and then treated with dry chlorine until solid product no longer precipitated. The reaction mixture was heated on a steam bath in a hood for 10 min. Cooling yielded 64.0 g. of tetrabutylammonium iodotetrachloride of m.p. 138–139° (dec.). This yield represents a recovery of 86% from the tetrachloroiodide originally used in the chlorination reactions.

All samples of tetrabutylammonium iodotetrachloride were kept in the dark because of tendency of the compound to photochlorinate itself even in the solid state.[1]

Other reagents. Most of the other reagents and materials used were available commercially or were synthesized by methods given in the *Organic Syntheses* series. Tetraanisylethylene was kindly supplied by Mr. Ronald E. Erickson of this laboratory.

Chlorination reactions of tetrabutylammonium iodotetrachloride. In each case, 0.005 mol. to 0.06 mol. of the compound to be chlorinated was mixed with an equimolar amount of tetrabutylammonium iodotetrachloride in 25 ml. of ethylene chloride. The mixture was allowed to stand either in the dark or under illumination for the desired length of time. The reaction mixture was then evaporated to dryness and the residue was extracted with ether. The ether-insoluble solid was the tetrabutylammonium salt mixture which was saved for rechlorination. The ether solution was evaporated and the residue was crystallized or distilled. The results are summarized in Table I.

When tetraphenylethylene was used in this reaction a 33% yield of dichloride, m.p. 183–184°, was obtained. This product checks reasonably well with the isomer melting at 188.5°.[10] This pure product was found by means of x-ray powder diagrams to have the same crystalline phase present as other samples which were crystallized from chloroform, methylene chloride, or ethylene chloride.

Anal. Calcd. for $C_{26}H_{20}Cl_2$: C, 77.4; H, 4.96. Found: C, 77.4; H, 4.75.

In some experiments of this type a fraction melting around 172–175° was isolated as well as the fraction of higher melting point already described. This lower melting compound checks for the isomer reported[10] to have m.p. 175°. By analyses and x-ray powder diagrams, however, these samples appeared to be mixtures of the dichloride of m.p. 184° with tetraphenylethylene or an unidentified substance. Particular trouble with some of the samples was encountered when ethyl alcohol was used as a solvent for crystallization. There appeared to be a solvolysis reaction and badly contaminated products were obtained.

Chlorination of tetrakis(p-methoxyphenyl)ethylene. A solution of 2.0 g. (0.0044 mol.) of tetrakis(*p*-methoxyphenyl)ethylene in 25 ml. of ethylene chloride was mixed with a saturated solution of chlorine in ethylene chloride. The reaction mixture turned purple and became warm. It was allowed to stand in the dark for 10 days. At the end of this time the solution was orange and 1.7 g. of a solid, m.p. 220–221° (dec.), was obtained by filtration. Evaporation of the mother liquor yielded 0.4 g. more of product of m.p. 205–210° (dec.). Crystallization of the total crude product from hexane–carbon tetrachloride yielded 1.7 g. (74%) of 1,2-dichloro-1,1,2,2-tetrakis(3,5-dichloro-4-methoxyphenyl)ethane of variable melting point depending on how fast the sample in the capillary was heated. Even with a bath preheated to 215° the melting point varied from 217–218° to 220–221° (dec.). This decomposition of the solid during the melting point determination may explain the low melting point (195–196°) reported[10] for this compound.

Anal. Calcd. for $C_{30}H_{20}Cl_{10}O_4$: C, 45.1; H, 2.52. Found: C, 44.8; H, 2.69.

The decachloride reacted only very slowly with a hot solution of sodium iodide in acetone to give a cloudy brown solution characteristic of vicinal dihalides. With hot alcoholic silver nitrate a very slow precipitation of silver chloride was observed.

Tetrakis(3,5-dichloro-4-methoxyphenyl)ethylene. A mixture of 0.32 g. (4.0×10^{-4} mol.) of the decachloride described above and excess (0.30 g.) zinc dust in 20 ml. of glacial acetic acid was boiled for 15 min. The solution was filtered and poured into 100 ml. of water. The crystalline product was washed thoroughly with water and then with acetone. The crude product was crystallized from hexane–carbon tetrachloride to give 0.16 g. (55%) of tetrakis(3,5-dichloro-4-methoxyphenyl)ethylene, m.p. 242–244°.

Anal. Calcd. for $C_{30}H_{20}Cl_8O_4$: C, 49.5; H, 2.77. Found: C, 48.8; H, 2.71.

The ultraviolet absorption spectrum of the octachloride in carbon tetrachloride ($9.2 \times 10^{-5}M$) show a peak at 325 mμ ($\epsilon = 12.1 \times 10^4$) which is characteristic of the stilbene chromophore of the tetraarylethylenes.[18] The decachloride on the other hand showed no absorption peak down to 260 mμ.

Reactions of the stilbenes with chlorine. A two-gram (0.011 mol.) sample of *cis*- or *trans*-stilbene in 25 ml. of ethylene chloride was mixed with 25 ml. of ethylene chloride saturated with chlorine. The mixture was then allowed to stand in the dark for 3 days. In some experiments 0.011 mol. of either antimony pentachloride or tetrabutylammonium chloride[19] were added. The reaction mixtures were filtered if necessary and evaporated to dryness. The residues were crystallized from 95% ethanol to give *meso*-α,α'-dichlorobibenzyl, m.p. around 190°. From the mother liquors small amounts of DL-α,α'-dichlorobenzyl m.p. around 90° were obtained. The results are summarized in Table II.

The reaction of cinnamic acid with chlorine. A solution of 2.0 g. (0.014 mol.) of *trans*-cinnamic acid in 25 ml. of ethylene chloride was treated with dry chlorine for 1 hr. in subdued light. Evaporation gave a residue which was crystallized from heptane to give 1.5 g. (51%) of 2,3-dichloro-3-phenylpropionic acid, m.p. 165–167°. This checks well for the isomer of high m.p. (167–168°) reported[6] for the reaction under strong illumination.

Gas chromatography. Some of the volatile compounds involved in this investigation were analyzed by gas chromatography. Measurements were carried out on a Perkin-Elmer Vapor Fractometer, Model 154B, with a 2-meter column (4 mm. ID) filled with silicone oil on Celite. Helium

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[15] H. A. Laitinen and S. Wawzonek, *J. Am. Chem. Soc.*, **64**, 1765 (1942).

[16] G. I. Mikhailov, *Zhur. priklad. khim.*, **27**, 217 (1954); *Chem. Abstr.*, **49**, 3785 (1955).

[17] A. I. Popov and R. E. Buckles, *Inorg. Syntheses*, **5**, 176 (1957).

[18] R. E. Buckles and W. D. Womer, *J. Am. Chem. Soc.*, **80**, 5055 (1958).

[19] R. E. Buckles and J. F. Mills, *J. Am. Chem. Soc.*, **76**, 4845 (1954).

was used as a carrier gas at 25 p.s.i. The flow rate was 1.30 ml. per sec. at 225° and 0.86 ml. per sec. at 150°. The elution times are summarized in Table III. The samples of *cis*-stilbene were often contaminated with quinoline and isoquinoline. A commercial mixture of these compounds was used as a solvent in the synthesis[20] of *cis*-stilbene. A maximum of 5% of the *trans*-isomer was detected as an impurity in the *cis*-stilbene. It was often considerably less, but there was always some present.

TABLE III

ANALYSIS BY GAS CHROMATOGRAPHY WITH A COLUMN CONTAINING SILICONE OIL ON CELITE

Compound	Temp., °C.	Elution Time, Min.
cis-Stilbene	225	6.6
trans-Stilbene	225	11.5
Quinoline	225	3.0
Isoquinoline	225	3.5
Diphenylacetylene	226	9.9
Styrene	150	2.6
Styrene dichloride	150	14.3

X-ray powder diagrams. These measurements were carried out by Dr. Norman C. Baenziger of this laboratory. A Straumanis-type camera of 114 mm. diameter was used. The powdered sample was placed in a 0.5-mm. capillary and irradiated with either the copper K_α or the iron K_α radiation.

Spectra. Infrared spectra were measured in the sodium chloride region with a Perkin-Elmer, Model 21, Spectrophotometer.[21] This type of data was used in the identification and analysis of samples of α,α'-dichlorobibenzyl dissolved in carbon disulfide. The DL-isomer had two characteristic bands at 645 and 675 cm.$^{-1}$ which were sufficiently different from the absorption of the *meso*-isomer at those frequencies that an estimate of the composition of mixtures could be made.

Ultraviolet absorption spectra were carried out on a Cary Recording Spectrophotometer, Model 11.

Acknowledgment. We would like to thank Dr. Norman C. Baenziger of this Laboratory for making the x-ray powder diagrams and interpreting them for us.

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[20] R. E. Buckles and N. G. Wheeler, *Org. Syntheses*, **33**, 88 (1953).

[21] The determination of the infrared data was aided by a grant from the National Science Foundation.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

Addition Reactions of Mixtures of Bromine and Chlorine

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Mixtures of bromine and chlorine have been used as sources of bromine chloride for the synthesis of bromochlorides from cyclohexene, styrene, ethylene, *trans*-cinnamic acid, *cis*- and *trans*-stilbene, and diphenylacetylene. With styrene and cinnamic acid the products isolated were those expected from the addition of positive bromine and negative chlorine to the unsymmetrically substituted double bonds. With *cis*- and *trans*-stilbene stereospecific *trans* addition was observed.

In an earlier report[1] the addition to a double bond of the elements of bromine chloride arising from *N*-bromoacetamide and hydrochloric acid was found to give the products expected of polar, stereospecific *trans* additions. In the present investigation mixtures of bromine and chlorine—presumably in equilibrium with bromine chloride—were used as reagents for addition reactions. The results are given in Table I. Bromochlorides predominated as products in most of the experiments although often in disappointing yields. The bromochloride products obtained are those expected of polar, *trans* addition of bromine chloride to the double bonds just as was found in the investigation[1] involving mixtures of *N*-bromoacetamide and hydrochloric acid.

The predominance of bromochlorides as products is consistent with results reported for the addition reactions of mixtures of bromine and chlorine with compounds containing double bonds[2] and triple bonds.[3] Of the compounds listed in Table I only ethylene[4] and cinnamic acid[5] have been previously reported as reacting with mixtures of bromine and chlorine to give the bromochloride products.

The results with styrene and cinnamic acid show the expected polar addition of bromine chloride to unsymmetrically substituted double bonds in that cinnamic acid yielded 2-bromo-3-chloro-3-phenylpropionic acid and styrene yielded 2-bromo-1-chloro-1-phenylethane. Such a mode of addition has been reported in the case of mixtures of bromine

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[1] R. E. Buckles and J. W. Long, *J. Am. Chem. Soc.*, **73**, 998 (1951).

[2] (a) P. B. D. de la Mare and S. Gandauer, *J. Chem. Soc.*, **36**, (1958); (b) A. Michael, *J. prakt. Chem.*, [2] **60**, 448 (1899); (c) P. Walden, *Ber.*, **30**, 2883 (1897).

[3] N. W. Hansen and T. C. James, *J. Chem. Soc.*, 2979 (1928).

[4] M. Simpson, *Bull. soc. chim. France*, [2] **31**, 409 (1879); J. W. James, *J. Chem. Soc.*, **43**, 37 (1883); M. Delepine and L. Ville, *Bull. soc. chim. France*, [4] **27**, 673 (1920).

[5] (a) N. W. Hanson and T. C. James, *J. Chem. Soc.*, 1955 (1928); (b) E. Erlenmeyer, *Ann.*, **289**, 259 (1896).