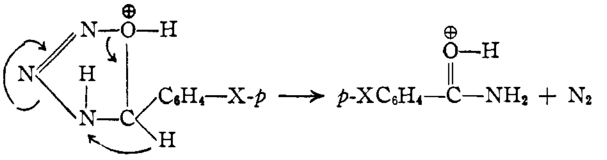
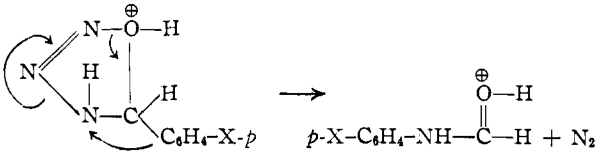


IX



X

From the theoretical standpoint, the point of attack of the azide ion on styrene oxide is of considerable interest. Attack at the secondary carbon of styrene oxide is clearly indicated. Considering the fact that as a linear structure the azide ion probably possesses only relatively small steric requirements, this fact is in line with the observations of other investigators[18] on the position of attack of less bulky anions on styrene oxide. Additional work on this interesting epoxide reaction is now in progress in these laboratories.

[18] See D. Swern, G. N. Billen and H. B. Knight, THIS JOURNAL, **71**, 1152 (1949); C. C. Guss, *ibid.*, **71**, 3460 (1949).

LAWRENCE, KANSAS RECEIVED AUGUST 8, 1951

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

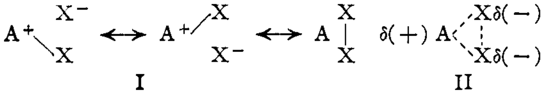
The Interaction of Bromine with Substituted Tetraphenylethylenes[1]

BY ROBERT E. BUCKLES AND NORMAN A. MEINHARDT

The electrical conductivities of methylene chloride solutions containing bromine and various substituted tetraphenylethylenes have been measured. A comparison has been made with the conductivity of tetrabutylammonium iodide in the same solvent. Tetraphenylethylenes with methoxyl or dimethylamino groups in at least two of the para positions gave highly colored solutions, which had molar conductances of the same order of magnitude as the ionic ammonium salt. Tetraphenylethylenes substituted with halogen or phenyl groups in the para positions had lower molar conductances on interaction with bromine, but the complexes formed still showed definite ionic character. Lowering the temperature in most cases increased the conductance of the solutions. This behavior roughly paralleled the qualitative observation of the amount of complex present based on changes in color.

Some sort of ionic complex formed by the interaction of an aromatic compound or an olefin with a halogen is generally considered as an intermediate in aromatic substitution or olefin addition reactions.[2] Several recent studies have yielded conclusive spectrophotometric evidence that certain simple aromatic compounds form 1:1 complexes with iodine,[3] bromine[4] and iodine chloride.[5] Possible structures for such complexes as well as those formed by halogens with oxygen-containing solvents known to give brown solutions with iodine have been extensively discussed recently.[6]

The general structure of the complex appears to involve the aromatic ring (or the oxygen or nitrogen of the "brown" solvents) as a source of electrons—a base according to the generalized concept—for bonding to the halogen which is somewhat electron deficient, *i.e.*, acidic. The two halogen atoms can be represented in equivalent positions with respect to the aromatic compound as in the resonance hybrid (I) or the partial bond structure (II) in which A is a complexing compound



I II

Analogous to I and II are III and IV in which the halogen atoms have assumed non-equivalent positions

$$\underset{\text{III}}{A^+\text{—}XX^- \longleftrightarrow A\ X\text{—}X} \qquad \underset{\text{IV}}{A\delta(+)\text{----}X\text{----}X\delta(-)}$$

A third possibility is that the complex formation involves a heteropolar dissociation of the halogen. In the relatively non-polar solvents usually used for the preparation of such complexes the ions formed would be expected to be associated as ion pairs, triple ions and higher ion aggregates.[7]

$$AX^+ + X^- \rightleftharpoons AX^+X^-,\ \text{etc.}$$

Such a complex in the case of the action of iodine on pyridine has been shown to be ionic by electrical conductance,[8] to involve the PyI^+ ion by comparison of its absorption spectrum with those of other PyI^+ salts,[9] and to be formed by a rapid equilibrium from iodine and pyridine by the rapid exchange of radioactive iodine with various PyI^+ salts in pyridine.[10]

In the case of the more complex aromatic–olefin systems of highly arylated ethylenes evidence for ionic complexes with halogens has been presented.[11] A number of such compounds both substituted tetraphenylethylenes[11a] and substituted *unsym*-diphenylethylenes,[11b,c] interacted with halogen to give highly colored, salt-like solids containing varying amounts of halogen depending on the nature of the ethylene and the identity of the halogen. The structures suggested[11] for the salt-like complexes were stable carbonium ions associ-

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[1] From the Ph.D. Thesis of Norman A. Meinhardt.

[2] C. C. Price, "Mechanisms of Reactions of Carbon–Carbon Double Bonds," Interscience Publishers, Inc., New York, N. Y., 1946, Chap. 2.

[3] J. H. Hildebrand and H. A. Benesi, THIS JOURNAL, **70**, 2382 (1948); **71**, 2703 (1949).

[4] R. M. Keefer and L. J. Andrews, *ibid.*, **72**, 4677 (1950).

[5] R. M. Keefer and L. J. Andrews, *ibid.*, **72**, 5170 (1950).

[6] R. S. Mulliken, *ibid.*, **72**, 600 (1950).

[7] R. M. Fuoss, *Chem. Revs.*, **17**, 27 (1935).

[8] L. F. Audrieth and E. J. Birr, THIS JOURNAL, **55**, 668 (1933).

[9] R. A. Zingaro, C. A. VanderWerf and J. Kleinberg, *ibid.*, **73**, 88 (1951).

[10] J. Kleinberg, *ibid.*, **73**, 1865 (1951).

[11] (a) R. Wizinger and J. Fontaine, *Ber.*, **60**, 1377 (1927); (b) P. Pfeiffer and R. Wizinger, *Ann.*, **461**, 132 (1928); (c) P. Pfeiffer and P. Schneider, *J. prakt. Chem.*, **129**, 129 (1931).

ated with chloride, triiodide or tribromide ions such as

$$(Ar_2C—CAr_2)^{++}2Br_3^- \text{ and } (Ar_2C—CH_2Br)^+Br_3^-$$

Compounds which gave stable complexes of these types had groups, such as the dimethylamino group, which are capable of assuming the positive charge or of complexing with halogens themselves, substituted in some of the para positions.

A different point of view was presented[12] concerning complexes formed in the reactions between bromine and tetraphenylethylenes substituted in the para positions with phenyl groups or halogens. In these cases, complex formation was observed only by color changes as the solution was cooled to Dry Ice-bath temperature. It was found that *cis* and *trans* isomers underwent no isomerization as a result of the reversible reaction of complex formation. On the basis of these results the ionic types of structures were discounted but no clearly defined alternatives were presented.

The present work is concerned with establishing the ionic character of the complexes formed when tetraphenylethylenes, substituted in the para position with methoxyl, dimethylamino, halogen and phenyl groups, interacted with bromine.

Discussion of Results

Preliminary experiments with 1,2-bis-(*p*-dimethylaminophenyl)-1,2-diphenylethylene (V) showed that interaction with excess bromine gave rise to complexes of varying composition. In carbon tetrachloride at room temperature a light red, granular solid, which appeared to contain three bromine atoms per molecule of ethylene, was obtained. At 10° an orange-red precipitate with five bromine atoms per ethylene was isolated. Both of these products gave blood red aqueous solutions which had molar conductance–concentration relationships characteristic of strong electrolytes.

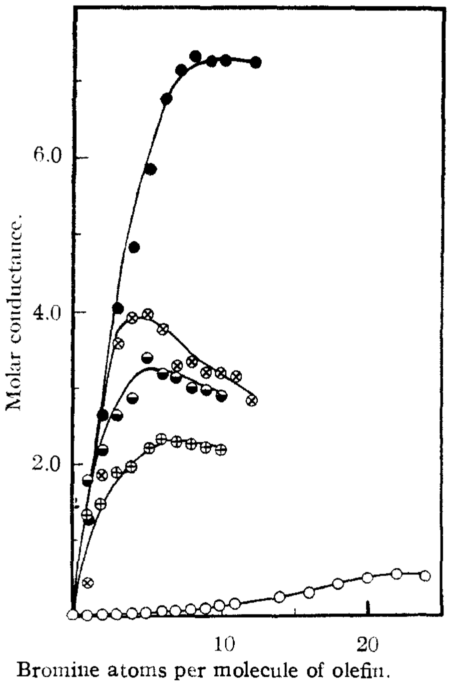

Fig. 1.—The dependence of the molar conductance of the tetraphenylethylenes in methylene chloride on the relative amount of bromine present at −78°: ○, 0.01 *M trans*-1,2-bis-(4-biphenylyl)-1,2-diphenylethylene (VIII); ◒, 0.0025 *M* and ⊕, 0.01 *M* 1,2-bis-(*p*-dimethylaminophenyl)-1,2-diphenylethylene (V); ⊗, 0.0025 *M* 1,2-bis-(*p*-dimethylaminophenyl)-1,2-bis-(*p*-methoxyphenyl)-ethylene (VI); ●, 0.0025 *M* 1,2-bis-(*p*-methoxyphenyl)-1,2-diphenylethylene (VII).

Treatment of solid V with bromine vapor gave a black liquid which on standing lost bromine to give a brittle, black solid containing from ten to eleven bromine atoms per olefin molecule. This solid was water insoluble but gave moderately stable, red solutions in aqueous acetone which had electrical conductivity behavior characteristic of a strong electrolyte.

Pursuant to the results of Bockemüller and Janssen[12] conductance measurements were carried out on eight tetraphenylethylenes in methylene chloride containing bromine. Methylene chloride though not very polar in character was a suitable solvent for the complexes. The dielectric constant of the solvent is sufficiently high (8.3 at 17–19°),[13] to give appreciable conductance values with electrolytes. The relatively low m.p. (−96.7°) of methylene chloride also made it particularly suitable for measurements down to Dry Ice-bath temperatures.

The presence of either bromine or one of the tetraphenylethylenes in solution did not appreciably increase the specific conductance of the pure solvent (less than 2.98×10^{-8} ohm^{-1}). Measurable conductances were observed when both bromine and one of the ethylenes were present in solution.

The effect on the molar conductance of the number of bromine atoms per ethylene molecule is shown in Fig. 1. Up to a point increasing the relative amount of bromine increased the concentration of the conducting species. In each case a bromine–ethylene ratio was reached beyond which the molar conductance remained relatively constant or was actually decreased. From the results shown in Fig. 1 convenient bromine–ethylene ratios were chosen for measurements of conductances at various temperatures and at various concentrations.

The relative amount of bromine which leads to a maximum conductance value in any given case is that amount which gives the most favorable formation of conducting species by way of the several equilibria of complex formation and of ion aggregate dissociation.[7] Any attempt to interpret the data in terms of composition of the complex or complexes is not warranted without more data, *e.g.*, a spectroscopic study of the complex formation.

The dependence of molar conductance on temperature is shown in Fig. 2 for those ethylenes which formed complexes with conductivities of the same order of magnitude as that of tetrabutylammonium iodide, a strong electrolyte in polar solvents. Those complexes with conductivities of somewhat lower values are given in Fig. 3. In all cases, the

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(12) W. Bockemüller and R. Janssen, *Ann.*, **542**, 166 (1939).

(13) P. Walden, This Journal, **35**, 1649 (1913).

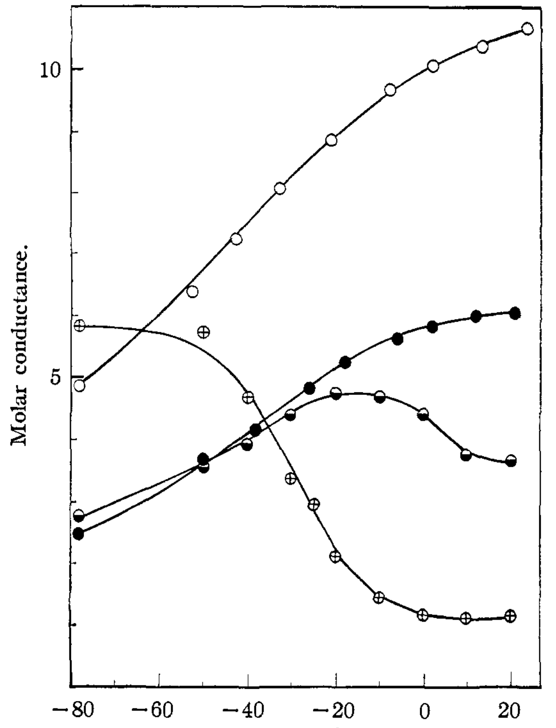


Fig. 2.—The dependence on temperature of the molar conductance (based on the olefin) of methylene chloride solutions of the bromine-olefin complexes (0.01 *M* olefin + 0.025 *M* bromine): ⊕, 1,2-bis-(*p*-methoxyphenyl)-1,2-diphenylethylene (VII); ◒, 1,2-bis-(*p*-dimethylaminophenyl)-1,2-bis-(*p*-methoxyphenyl)-ethylene (VI); ●, 1,2-bis-(*p*-dimethylaminophenyl)-1,2-diphenylethylene (V). The results are compared with ○, 0.01 *M* tetrabutylammonium iodide.

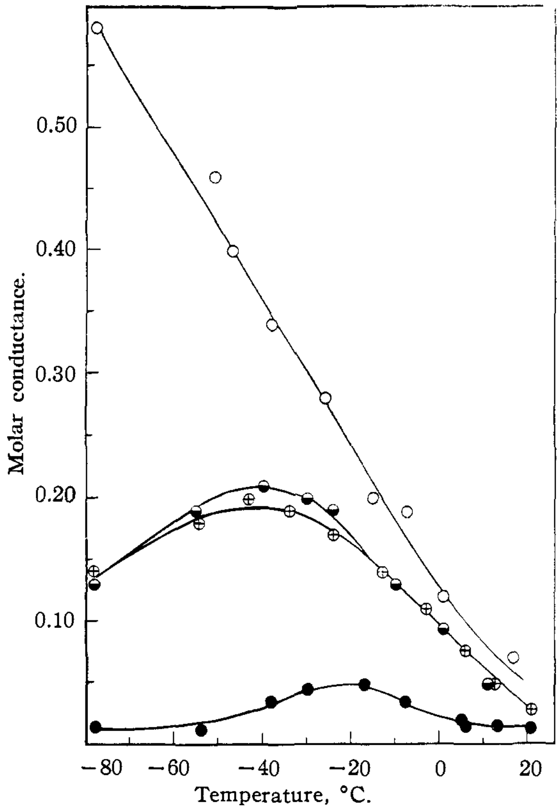


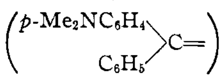
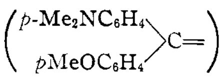
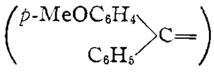
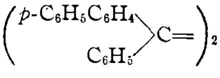
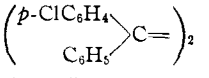
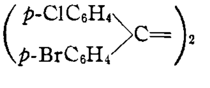
Fig. 3.—The dependence on temperature of the molar conductance (based on the olefin) of methylene chloride solutions of bromine-olefin complexes (0.01 *M* olefin + 0.11 *M* bromine): ○, *trans*-1,2-bis-(4-biphenylyl)-1,2-diphenylethylene (VIII); ◒, *trans*-1,2-bis-(*p*-chlorophenyl)-1,2-diphenylethylene (IX); ⊕, *cis*-1,2-bis-(*p*-chlorophenyl)-1,2-diphenylethylene (IX); ●, 1,2-bis-(*p*-chlorophenyl)-1,2-bis-(*p*-bromophenyl)-ethylene (X).

effect of temperature on the conductances of the complexes was reversible. These results can be compared with the qualitative observation of color changes of solution with temperature shown in Table I. It would appear that only V and 1,2-bis-(*p*-dimethylaminophenyl)-1,2-bis-(*p*-methoxyphenyl)-ethylene (VI) yield ionic complexes with bromine at room temperature to such an extent that the characteristic bromine color is masked and at the same time the conductance temperature behavior approaches that of the quaternary ammonium salt. In the rest of the cases: 1,2-bis-(*p*-methoxyphenyl)-1,2-diphenylethylene (VII), 1,2-bis-(4-biphenylyl)-1,2-diphenylethylene (VIII), *cis*- and *trans*-1,2-bis-(*p*-chlorophenyl)-1,2-diphenylethylene (IX) and 1,2-bis-(*p*-chlorophenyl)-1,2-bis-(*p*-bromophenyl)-ethylene (X), the bromine color in methylene chloride solutions containing bromine gave way to the characteristic colors of the complexes when cooled, and the conductances correspondingly increased. In each of these cases, then, the tendency of the conductance of electrolytes to decrease with temperature (as shown by the quaternary ammonium salt) is counteracted by the increase in the amount of ionic complex at the lower temperatures.

TABLE I

TEMPERATURE DEPENDENCE OF THE COLOR OF SOLUTIONS OF TETRAPHENYLETHYLENES IN METHYLENE CHLORIDE CONTAINING BROMINE

Concentrations were the same as those of Figs. 2 and 3

Ethylene		Color 20°	Color −78°
 $\left(\begin{matrix}p\text{-Me}_2\text{NC}_6\text{H}_4\\ \text{C}_6\text{H}_5\end{matrix}\!>\!\text{C=}\right)_2$	(V)	Blood red	Blood red
 $\left(\begin{matrix}p\text{-Me}_2\text{NC}_6\text{H}_4\\ p\text{MeOC}_6\text{H}_4\end{matrix}\!>\!\text{C=}\right)_2$	(VI)	Greenish-violet	Almost black
 $\left(\begin{matrix}p\text{-MeOC}_6\text{H}_4\\ \text{C}_6\text{H}_5\end{matrix}\!>\!\text{C=}\right)_2$	(VII)	Bromine red	Deep blue
 $\left(\begin{matrix}p\text{-C}_6\text{H}_5\text{C}_6\text{H}_4\\ \text{C}_6\text{H}_5\end{matrix}\!>\!\text{C=}\right)_2$	(VIII)	Bromine red	Olive green
 $\left(\begin{matrix}p\text{-ClC}_6\text{H}_4\\ \text{C}_6\text{H}_5\end{matrix}\!>\!\text{C=}\right)_2$	(IX)	Bromine red	Red violet
 $\left(\begin{matrix}p\text{-ClC}_6\text{H}_4\\ p\text{-BrC}_6\text{H}_4\end{matrix}\!>\!\text{C=}\right)_2$	(X)	Bromine red	Red violet

The variation of molar conductance with the square root of the concentration is shown in Figs. 4 and 5 and in Table II. In Fig. 4 and Table II the complexes with higher conductances are compared with tetrabutylammonium iodide while in Fig. 5 those with lower conductances are

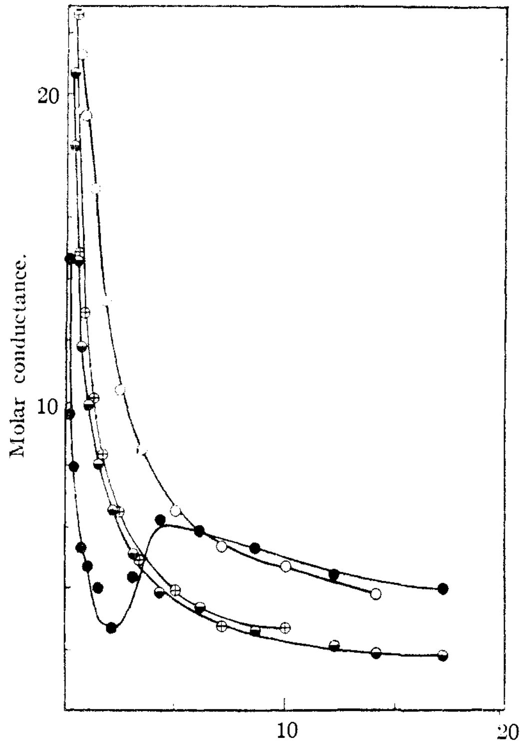


Fig. 4.—The dependence of molar conductance (based on the olefin) on the concentration of bromine–olefin complexes in methylene chloride at −78° (mole ratio of bromine to olefin = 2.5): ◒, 1,2-bis-(*p*-dimethylaminophenyl)-1,2-diphenylethylene (V); ⊕, 1,2-bis-(*p*-dimethylaminophenyl)-1,2-bis-(*p*-methoxyphenyl)-ethylene (VI); ●, 1,2-bis-(*p*-methoxyphenyl)-1,2-diphenylethylene (VII). The results are compared with O, tetrabutylammonium iodide.

given. The results show the characteristic behavior of electrolytes in solvents of low dielectric constant.[14] Association into ion pairs would be important even at the lowest concentrations represented. The Ostwald dilution function (equations (1) and (2)) would apply only approximately to these lowest concentrations. In fact, most of the points on the curves were obtained at concentrations above the critical concentration (about 10^{-4} M in methylene chloride at 25°) where the conductance equation corrected for long range interionic interactions (equation (3)) would not hold.[7] At higher concentrations ion aggregates such as triple ions and quadrupoles would become increasingly important and be responsible for the presence of minima and maxima in some of the curves.

$$K = \frac{\Lambda^2 c}{\Lambda^0(\Lambda^0 - \Lambda)} \qquad (1)^{15}$$

$$\frac{1}{\Lambda} = \frac{1}{\Lambda^0} + \frac{c\Lambda}{K(\Lambda^0)^2} \qquad (2)^{15}$$

$$\Lambda = \alpha(\Lambda^0 - A\sqrt{\alpha c}) \qquad (3)^{15}$$

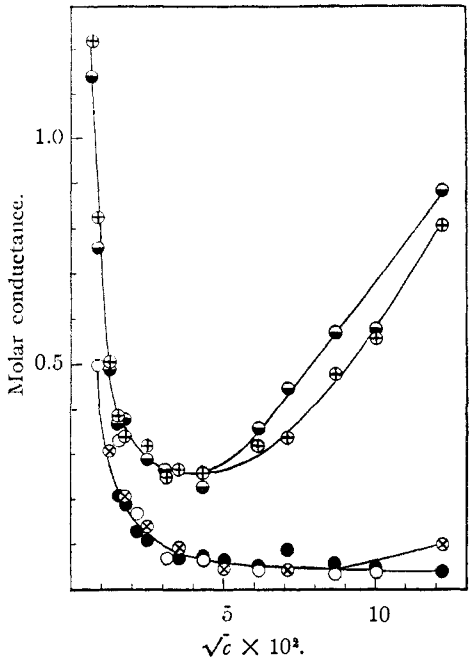


Fig. 5.—The dependence of molar conductance (based on the olefin) on the concentration of bromine–olefin complex in methylene chloride at −78° (mole ratio of bromine to olefin = 11): O, *cis*-1,2-bis-(*p*-chlorophenyl)-1,2-diphenylethylene (IX); ⊗, *trans*-1,2-bis-(*p*-chlorophenyl)-1,2-diphenylethylene (IX); ●, 1,2-bis-(*p*-chlorophenyl)-1,2-bis-(*p*-bromophenyl)-ethylene (X); ⊕, *cis*-1,2-bis-(4-biphenylyl)-1,diphenylethylene (VIII); ◒, *trans*-1,2-bis-(4-biphenylyl)-1,2-diphenylethylene (VIII).

TABLE II

DILUTION DATA FOR FIG. 4

	Molar conductance			
$\sqrt{c} \times 10^2$	$(n\text{-Bu})_4$NI	V	VI	VII
17.1	...	1.88	...	4.05
14.1	3.84	1.93	...	...
12.2	...	21.5	...	4.45
10.0	4.71	...	2.73	...
8.66	...	2.66	...	5.30
7.10	5.39	...	2.79	...
6.13	...	3.40	...	5.85
5.00	6.52	...	3.99	....
4.33	...	3.90	...	6.22
3.54	8.52	...	4.90	..
3.12	...	5.12	...	4.38
2.50	10.4	...	6.50	...
2.16	...	6.52	...	2.72
1.77	13.3	...	8.35	...
1.54	...	8.01	...	4.06
1.25	16.9	...	10.1	...
1.08	...	9.95	...	4.73
0.88	19.3	...	12.9	...
.77	...	11.8	...	5.32
.63	21.3	...	14.8	...
.54	...	14.6	...	..
.44	...	...	22.6	7.97
.38	...	18.3	...	...
.31	...	20.7	...	...
.27	...	...	...	9.60
.19	...	...	...	14.6

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(14) It has been pointed out by the referee that the fact that compound VII behaves differently from Compounds V and VI both when concentration is varied (Fig. 4) and when temperature is varied (Fig. 2) might conceivably be related to the fact that the bromine-olefin ratio in the case of VII is significantly lower than that shown to give maximum conductance in Fig. 1.

(15) K is the dissociation constant of ion pairs going into ions, Λ is the equivalent conductance, Λ^0 is the equivalent conductance at infinite dilution, c is the concentration, α is the degree of dissociation and A is the Onsager coefficient.

Even at the lowest concentrations the application[7,16] of such equations to the calculation of dissociation constants cannot be applied in the present case. The equilibria of complex formation must first be studied separately, and the relationship of molar conductance to equivalent conductance of the complex must be determined.

Experimental

1,2-Bis-(*p*-dimethylaminophenyl)-1,2-diphenylethylene (IV).—The bimolecular reduction of *p*-dimethylaminobenzophenone[17a] with tin and hydrochloric acid in the cold[17b] gave rise to a product very difficult to purify. Adsorption on activated alumina was used as the method of removing impurities from the chloroform solution of the ethylene. The crystallization of the product was brought about by the addition of absolute alcohol to the chloroform solution. After several such adsorption–crystallization treatments a sample of the ethylene V of m.p. 225°[18] was obtained. The only contaminating compound isolated was the glycol, 1,2-bis-(*p*-dimethylaminophenyl)-1,2-diphenyl-1,2-ethanediol, m.p. 253°. No geometric isomer of V could be found.

1,2-Bis-(*p*-dimethylaminophenyl)-1,2-bis-(*p*-methoxyphenyl)-ethylene (VI).—In a method entirely analogous to the synthesis of V above, 21 g. of *p*-methoxy-*p'*-dimethylaminobenzophenone[19] was reduced to give 1.0 g. (5%) of the hitherto unreported ethylene VI of m.p. 217–218°. Only one isomer was obtained.

Anal. Calcd. for $C_{32}H_{34}N_2O_2$: C, 80.1; H, 7.16; N, 5.85. Found: C, 79.6; H, 7.07; N, 5.67.

1,2-Bis-(*p*-methoxyphenyl)-1,2-diphenylethylene (VII).—A solution of 76 g. (0.36 mole) of *p*-methoxybenzophenone[20] and 75 g. of phosphorus pentachloride in 200 ml. of benzene was boiled under reflux for eight hours. All of the volatile solvent and by-products were removed by distillation under reduced pressure. The residue was dissolved in 200 ml. of benzene and 200 g. of copper powder was added. The mixture was boiled under reflux for 12 hours. The reaction mixture was filtered and the filter cake washed with hot benzene. After evaporation of the benzene solution to dryness the residue was crystallized from 95% alcohol to give 22 g. (31%) of impure product, m.p. 153–173°. Crystallization from chloroform–alcohol followed by crystallization from glacial acetic acid yielded VII of m.p. 185–187°. Only one isomer was isolated.

Anal. Calcd. for $C_{28}H_{24}O_2$: C, 85.6; H, 6.16. Found: C, 85.0; H, 5.97.

The only synthesis reported[21] for this compound was the acid-catalyzed rearrangement of 2,2-bis-(*p*-methoxyphenyl)-1,2-diphenylethanol. No proof of structure was given. The m.p. was 191–192°.

cis- **and** *trans*-**1,2-Bis-(*p*-chlorophenyl)-1,2-diphenylethylene (IX).**—Dichloro-(*p*-chlorophenyl)-phenylmethane was treated with copper to give a mixture of the two isomers of IX.[12] Separation by crystallization alone was not satisfactory. A combination of adsorption on active alumina and crystallization from chloroform–alcohol yielded the high m.p. isomer, presumably *trans*, of m.p. 205°. The low m.p. isomer was obtained with m.p. 157–158° which does not agree with the reported m.p. of 179°.[12]

Anal. Calcd. for $C_{26}H_{18}Cl_2$: C, 78.0; H, 4.52. Found: C, 77.9; H, 4.48.

cis- **and** *trans*-**1,2-Bis-(4-biphenyl)-1,2-diphenylethylene (VIII).**—The isomers were prepared by the reaction of 4-biphenylyl-(dichloro)-phenylmethane with copper.[22] The separation of isomers was effected by crystallization. The isomer, presumed to be *trans*, had m.p. 252°, that presumed to be *cis*, 219°.

1,2-Bis-(*p*-chlorophenyl)-1,2-bis-(*p*-bromophenyl)-ethylene (X).—The compound was prepared by the reaction of *p*-bromophenyl-(*p*-chlorophenyl)-dichloromethane with copper.[12] The m.p. was 231.5°. As previously found only one isomer was isolated.

Methylene Chloride.—Commercial methylene chloride was washed with aqueous sodium thiosulfate followed by aqueous sodium carbonate and then dried over phosphorus pentoxide. The liquid was distilled from fresh phosphorus pentoxide through an efficient fractionating column. The product used had b.p. 39.5° (730 mm.).

Solid Complexes of Bromine with 1,2-Bis-(*p*-dimethylaminophenyl)-1,2-diphenylethylene (V).—A solution of 2.0 g. of V in 1100 ml. of carbon tetrachloride containing 2.0 g. of bromine gave a black precipitate which was washed free of excess bromine by carbon tetrachloride. The result was 3.27 g. of light red, granular product. It gave stable, blood-red aqueous solutions. In acetone, chloroform or acetonitrile the blood-red solutions obtained quickly decolorized to light yellow.

Anal. Calcd. for $C_{30}H_{30}N_2Br_3$: Br, 36.5. Found: Br, 36.9.

In a similar preparation carried out at 10°C. 3.61 g. of an orange-red product was obtained. Its solubility behavior was similar to that of the first preparation.

Anal. Calcd. for $C_{30}H_{30}NBr_5$: Br, 48.9. Found: Br, 48.9.

When 1.0 g. of V was kept in the presence of excess bromine vapor for five hours, a black liquid was obtained. This liquid was subjected to evaporation under reduced pressure to remove excess bromine. A brittle, black solid resulted. The powdered solid was kept over solid potassium hydroxide and it gradually lightened to a red-brown color. Except that it was insoluble in water this product behaved as the others in solution.

Anal. Calcd. for $C_{80}H_{30}N_2Br_{10}$: Br, 65.6. Calcd. for $C_{30}H_{30}N_2Br_{11}$: Br, 67.7. Found: Br, 66.9.

The first two preparations in water and the third in 50% aqueous acetone gave solutions for which the plots of molar conductance *vs.* the square root of the concentration were essentially linear with negative slopes.

Conductance Measurements.—Measurements were made in a glass cell with square platinum electrodes separated by glass rods fused to the platinum. The electrodes were carefully platinized. The cell constant was determined to be 0.268 with 0.1 *N* aqueous potassium chloride at 20°. A Leeds and Northrup Wheatstone bridge was used with a General Radio, type 13, 1000 cycle audio oscillator. The cell was cooled in Dry Ice–acetone-bath in a dewar flask.

The ethylene dissolved in methylene chloride was introduced into a volumetric flask. The flask was cooled to −78° and the desired amount of standard bromine in methylene chloride was added. The solution was made up to volume with additional methylene chloride. The cold solution was transferred to the cell and conductance measurements were carried out at −78° in the Dry Ice-bath. Determinations at other temperatures were carried out in baths of intermediate temperatures. Above −55° the temperature was measured with an alcohol thermometer. The concentrations were corrected for the expansion accompanying the increase in temperature of the solution. The reversibility of the temperature effect was demonstrated by the fact that the same curves were obtained on cooling down to −78° as on warming up from −78°. Conductance–concentration measurements were run in duplicate to insure the reproducibility of the curves.

The specific conductance of pure methylene chloride was determined to be less than 2.95×10^{-8} ohm^{-1}. No appreciable change was noted when either one of the ethylenes or bromine was dissolved in the solvent.

IOWA CITY, IOWA RECEIVED AUGUST 24, 1951

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