[CONTRIBUTION FROM THE CHEMICAL CORPS, CHEMICAL WARFARE LABORATORIES]

Organic Phosphorus Compounds. IV.[1] A Study of the Transesterification of Dialkyl Alkylphosphonites

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A study of the effect of the reactant ratio on the composition of the reaction mixture obtained by transesterification of diethyl methyl- and of diethyl ethylphosphonite with 1-octanol demonstrated that this reaction proceeds for all practical purposes by random distribution of the alkoxy groups. Good agreement between the calculated and experimentally observed values for the product composition was noticed with molar phosphonite:octanol ratios of 2:1 to 4:1.

The alcohol-exchange reaction between trialkyl phosphites, $(RO)_3P$, and aliphatic alcohols, R'OH, having boiling points higher than that of the replaced alcohol results in the formation of a reaction mixture containing all four possible alkyl phosphites, $(RO)_3P$, $(RO)_2POR'$, $ROP(OR')_2$ and $(R'O)_3P$, if the liberated alcohol ROH is removed from the reaction mixture.[3] The ratio of products in the residual mixture is dependent on the molar ratio of the reactants. Dialkyl methylphosphonites undergo a similar alcohol exchange reaction.[4]

As this exchange reaction of phosphites and phosphonites with alcohols involves the rupture of P–O bonds,[3] equal affinity of the OR and OR' radicals for the phosphorus-containing moiety will result in random distribution of the alkoxy groups. The equilibrium state resulting in a system of dialkyl methylphosphonite and a suitable alcohol in a molar ratio of 2:3 is illustrated by equation 1.

$$2CH_3P(OR)_2 + 3R'OH \rightleftharpoons CH_3P(OR)OR' + CH_3P(OR')_2 + 3ROH \quad (1)$$

Removal of the lower boiling alcohol from such a system will result in a complete consumption of the higher boiling alcohol R'OH and the formation of a three-component system containing the components in an equilibrium state according to equation 2.

$$CH_3P(OR)_2 + CH_3P(OR')_2 \rightleftharpoons 2CH_3P(OR)OR' \quad (2)$$

While the equilibrium reaction 1 is a classical alcohol exchange reaction, reaction 2 is a redistribution reaction, composed of the forward transesterification[5] and the reverse disproportionation. The composition of the final three-component product system of equation 2 will be dependent on the molar ratio of reactants and readily can be calculated.[6]

A study of the product composition by distillation appeared to be a simple technique to prove the statistical distribution of the alkoxy groups in the transesterification. Agreement between the yield values of the various components calculated for a random distribution and the actual yields would prove the character of the reaction as a redistribution reaction. The composition of the product mixture from the reaction of diethyl methyl- and ethylphosphonite with 1-octanol was studied, therefore, in some detail to determine the effect of the molar ratio of reactants and to possibly characterize the nature of the reaction.

Experimental

Diethyl methylphosphonite was prepared by the method described previously.[4] Only cuts having boiling points in the range from 48 to 50° (50 mm.) and indices of refraction of 1.4165 to 1.4172 at 25° were used in the transesterification study.

Anal. Calcd. for $C_5H_{13}O_2P$: C, 44.11; H, 9.63; P, 22.75. Found: C, 44.5; H, 9.7; P, 22.78.

Diethyl ethylphosphonite, b.p. 60° (35 mm.), $n^{25}D$ 1.4206, was prepared in yields better than 60% from ethylphosphonous dichloride,[7] b.p. 112–115°, by the same method as used for the preparation of the methylphosphonite.

Anal. Calcd. for $C_6H_{15}O_2P$: C, 47.99; H, 10.07; P, 20.63. Found: C, 48.0; H, 10.1; P, 20.4.

1-Octanol (Eastman practical grade) was purified by distillation under reduced pressure; a constant boiling cut, b. p. 79° (1.9 mm.), $n^{25}D$ 1.4272, was used for the transesterifications.

Anal. Calcd. for $C_8H_{18}O$: C, 73.78; H, 13.93. Found: C, 73.74; H, 13.95.

Transesterification of Phosphonites. General Procedure.—Predetermined amounts of an appropriate alcohol (or of phenol) and phosphonite were placed into a round-bottom flask previously flushed with dry nitrogen. The flask was then fitted with a 10-in. electrically heated column (packed with glass helices), a still-head and receiver, and the entire apparatus flushed with nitrogen. The mixture was heated to the reflux temperature and reflux was maintained until the lower boiling alcohol ceased to distil. The pot temperature increased gradually during the removal of the liberated ethanol. The yields of ethanol were usually above 90%; however, this fraction always was contaminated with small amounts of the lower boiling phosphonite. After removal of the alcohol, heating was discontinued and a slow stream of nitrogen was passed through the system until the reaction mixture had cooled to approximately 40°. Vacuum then was applied and the mixture fractionally distilled through the packed column.

The results of the transesterification of diethyl methylphosphonite (I) and of diethyl ethylphosphonite (II) with varying amounts of *n*-octyl alcohol (III) are listed in Tables I and II. The transesterification with other alcohols or those involving a modification of the general procedure are described in detail. The boiling points, $n^{25}D$ values and analytical data of the resulting transesterification products are given in Table III.

In many cases, the residue remaining after the removal of the mono*trans*-esterified product was taken as the *ditrans*-ester, since distillation of these residues had indicated that they were almost pure materials.

Transesterification of Diethyl Ethylphosphonite (II) and Phenol.—Compound II (83.0 g., 0.552 mole), 26.0 g. (0.276 mole) of phenol (Mallinckrodt Chemical Co.) and a cata-

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(1) Paper III of this series: F. W. Hoffmann, Donald H. Wadsworth and Herbert D. Weiss, THIS JOURNAL, **80**, 3945 (1958).

(2) To whom inquiries concerning this paper should be addressed.

(3) F. W. Hoffmann, R. J. Ess and R. P. Usinger, THIS JOURNAL, **78**, 5817 (1956).

(4) F. W. Hoffmann and T. R. Moore, *ibid.*, **80**, 1150 (1958).

(5) Although the term "transesterification" is strictly applicable only to the forward reaction of equation 2, it seems permissible to use it as a description for the combined reactions 1 and 2, since the final equilibrium product is theoretically identical with that obtained from the two symmetrical phosphonites by a true transesterification.

(6) G. Calingaert and H. Beatty, THIS JOURNAL, **61**, 2748 (1939).

(7) M. S. Kharasch, E. V. Jensen and S. Weinhouse, *J. Org. Chem.*, **14**, 429 (1949).

TABLE I

TRANSESTERIFICATION OF DIETHYL METHYLPHOSPHONITE (I) WITH 1-OCTANOL (III)

Run	Amts. used, g. I	Amts. used, g. III	Mole ratio I:III	Yields in mole C_2H_5OH	Yields in mole I	Yields in mole X[a]	Yields in mole IX[b]
1	54.5	52.1	1:1	0.36	...	0.148	....
2	54.5	52.1	1:1	0.35	0.088	.145	0.119[c]
3	75.0	38.0	2:1	.2	.214	.202	.044
4	68.0	35.5	2:1	.29	.228	.182	.041[c]
5	163.2	52.0	3:1	.38	.75	.325	.036[c]
6	207.7	49.5	4:1	..	...	.335	.025[c]
7	68.0	30.0	2:1[d]	.22	.243	.221	.53[c]
8	141.0	65.1	2:1[e]	.50	.544	.464	.115

[a] $CH_3P(OC_2H_5)OC_8H_{17}$. [b] $CH_3P(OC_8H_{17})_2$. [c] The crude distillation residue was regarded as IX. [d] IX (12.5 g., 0.05 mole) added. [e] IX (38.7 g., 0.12 mole) added.

TABLE II

TRANSESTERIFICATION OF DIETHYL ETHYLPHOSPHONITE (II) WITH 1-OCTANOL (III)

Run	Amts. used, g. II	Amts. used, g. III	Mole ratio II:III	Yields in mole C_2H_5OH	Yields in mole II	Yields in mole XII[a]	Yields in mole XI[b]
9	83.0	72.0	1:1	0.485	0.126	0.231	0.185[c]
10	83.0	36.0	2:1	.21	...	.213	.016[c]
11	124.3	36.0	3:1	.25	.52	.232	.023[c]
12	123.0	27.3	4:1	.22	.58	.188	.028[c]
13	83.0	38.0	1.89:1	.202	.298	.187	.048

[a] $C_2H_5P(OC_2H_5)OC_8H_{17}$. [b] $C_2H_5P(OC_8H_{17})_2$. [c] The crude distillation residue was regarded as XI.

TABLE III

BOILING POINTS, REFRACTIVE INDICES AND ANALYSES OF VARIOUS ALKYLPHOSPHONITES[a]

Compound	Boiling point °C.	Boiling point Mm.	$n^{25}\mathrm{D}$	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Phosphorus, % Calcd.	Phosphorus, % Found
$CH_3P(OC_2H_5)OC_8H_{17}$ (X)	65	0.1	1.4372	59.97	60.3	11.49	11.4	14.06	14.18
$CH_3P(OC_8H_{17})_2$ (IX)	125–130	.3	1.4460	67.06	66.4	12.25	12.1	10.17	10.67
$CH_3P(OC_2H_5)OC_{10}H_{21}$ (V)	85	.25	1.4414	62.87	62.7	11.77	11.7	12.47	12.59
$CH_3P(OC_{10}H_{21})_2$ (VI)	138	.075	1.4493	69.95	69.5	12.58	12.4	8.59	8.58
$C_2H_5P(OC_2H_5)OC_6H_5$ (IV)	51	.080	1.5055	60.59	60.4	7.63	7.6	15.63	15.7
$C_2H_5P(OC_2H_5)OC_8H_{17}$ (XII)	72	.3	1.4387	61.50	61.5	11.61	11.6	13.22	14.05
$C_2H_5P(OC_8H_{17})_2$ (XI)	123	.05	1.4475	67.88	67.4	12.34	12.2	9.73	9.78
$C_2H_5P(OC_2H_5)OC_{10}H_{21}$ (VII)	100	.06	1.4426	64.08	63.7	11.91	11.8	11.81	12.15
$C_2H_5P(OC_{10}H_{21})_2$ (VIII)	150	.05	1.4509	70.53	69.5	12.65	12.4	8.27	8.54

[a] C_8H_{17} and $C_{10}H_{21}$ represent the normal alkyl groups.

lytic amount (*ca.* 0.1 g.) of sodium yielded 8.6 g. (0.187 mole) of ethanol; 45.7 g. (0.302 mole) of unreacted II, b.p. 62° (38 mm.), $n^{25}\mathrm{D}$ 1.4207; and 39.5 g. (0.199 mole) (72.3%) of ethyl phenyl ethylphosphonite (IV). The attempted distillation of the remaining material led to its decomposition. The calculated yields of III and IV for this run are 0.311 and 0.206 mole, respectively.

Transesterification of Diethyl Methylphosphonite (I) **with 1-Decanol.**—From 75 g. (0.55 mole) of I and 43.6 g. (0.275 mole) of 1-decanol (Eastman, reagent grade) were obtained 14 g. (0.304 mole) of crude ethanol, $n^{25}\mathrm{D}$ 1.3688, 31.5 g. (0.232 mole) of unreacted I, b.p. 50° (51 mm.), $n^{25}\mathrm{D}$ 1.4165, 36.4 g. (0.147 mole) of ethyl *n*-decyl methylphosphonite (V) and 19.0 g. (0.033 mole) of di-*n*-decyl methylphosphonite (VI). The yields of the reactions products, calculated in moles for random distribution, are 0.310, 0.205 and 0.034 for I, V and VI, respectively.

Transesterification of Diethyl Ethylphosphonite (II) **with 1-Decanol.**—A mixture of 83 g. (0.552 mole) of II and 43.6 g. (0.276 mole) of 1-decanol gave in the general transesterification procedure 6.6 g. (0.142 mole) of ethanol, 39.1 g. (0.261 mole) of unreacted II, 51.3 g. (0.196 mole) of ethyl *n*-decyl ethylphosphonite (VII) and 10.5 g. (0.028 mole) of di-*n*-decyl ethylphosphonite (VIII). The calculated yields are 0.310, 0.205 and 0.034 mole for II, VII and VIII, respectively.

Redistribution Reaction of Diethyl Methylphosphonite (I) **with Di-*n*-octyl Methylphosphonite** (IX).—Compound I (122.4 g., 0.9 mole) and 91.4 g. (0.3 mole) of IX were mixed and allowed to stand at room temperature for a period of two weeks. The flask then was attached to the fractionation column and the mixture was heated to reflux at a pressure of 52 mm. (reflux temperature, 70°) for a period of approximately 1 hr. Fractionation of the mixture under reduced pressure yielded 93.5 g. (0.687 mole) of recovered I and 90.1 g. (0.409 mole) of ethyl *n*-octyl methylphosphonite (X). In the distillation flask remained 28.3 g. (0.093 mole) of crude IX, $n^{25}\mathrm{D}$ 1.4475. The yields of I, X and IX, calculated for random distribution, are 0.676, 0.448 and 0.076 mole, respectively.

Redistilled I (53.9 g., 0.396 mole), $n^{25}\mathrm{D}$ 1.4170, and 40.2 g. (0.132 mole of redistilled IX, $n^{25}\mathrm{D}$ 1.4460, were mixed and slowly heated to 139°, where refluxing began, and maintained for approximately 2 hr. at gentle reflux. Fractional distillation of the cooled mixture under reduced pressure yielded 32.1 g. (0.236 mole) of I and 37.4 g. (0.169 mole) of X. In the distillation flask remained 13.3 g. (0.044 mole) of crude IX, $n^{25}\mathrm{D}$ 1.4450. An additional 8.6 g. of crude I (total yield 0.299 mole), $n^{25}\mathrm{D}$ 1.4168, was collected in an attached Dry Ice–acetone cold trap. The yields of I, X and IX calculated for this run were 0.297, 0.197 and 0.033 mole, respectively.

The distillation residues from three redistribution runs were combined and a portion of 49.4 g. of the mixture, $n^{25}\mathrm{D}$ 1.4463, was distilled to yield 45.8 g. of purified VIII, b.p. 125–130° (0.3 mm.), $n^{25}\mathrm{D}$ 1.4460, 92.8% recovery.

Disproportionation of Ethyl *n*-Octyl Methylphosphonite (X).—Redistillation under reduced pressure of a six-month old sample of X (145 g., 0.658 mole), $n^{25}\mathrm{D}$ 1.4378, gave 7.1 g. (0.052 mole) of I and 103.4 g. (0.465 mole) of X. The distillation residue (25.2 g., 0.083 mole), $n^{25}\mathrm{D}$ 1.4470, was regarded as IX. An attached Dry Ice–acetone trap contained 2.5 g. (0.019 mole) of impure I, $n^{25}\mathrm{D}$ 1.4112, bringing the total yield of this product to 0.071 mole. Complete disproportionation would have yielded 0.158 mole each of I and IX. The experimental results indicate approximately 48% disproportionation.

Redistillation at 0.1 mm. pressure of 192.4 g. (0.873 mole) of a sample of X, $n^{25}\mathrm{D}$ 1.4380, which had been stored at room temperature for a period of 10 days, yielded 33 g. (0.242 mole) of I, collected in an attached Dry Ice–acetone cold trap, 90.2 g. (0.41 mole) of X and 67 g. (0.22 mole) of distillation residue, $n^{25}\mathrm{D}$ 1.4470, taken as IX. Complete disproportionation to the equilibrium mixture of the three phosphonites should have yielded in this run 0.218 mole each of I and IX and 0.437 mole of X.

Discussion of Results

The product mixtures resulting from the transesterifications of diethyl methylphosphonite (I) and of diethyl ethylphosphonite (II) with 1-octanol (III) consisted in all runs of a three-component mixture containing the corresponding phosphonites (diethyl, ethyl *n*-octyl and di-*n*-octyl alkylphosphonite) in ratios varying in dependence on the ratio of starting components. Analogous results were obtained in similar transesterifications of I and II with 1-decanol as well as with phenol.

Because of the relatively large experimental error involved in the determination of the product com-

TABLE IV

OBSERVED AND CALCULATED YIELDS IN THE TRANSESTERIFICATIONS OF I AND II WITH III

		Yields, %					
		$RP(OC_2H_5)_2$		$RP(OC_2H_5)OC_8H_{17}$		$RP(OC_8H_{17})_2$	
Run	Molar ratio I or II:III	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.
2[a]	1:1	22	25.0	36.2	50.0	29.8	25.0
3[a]	2:1	38.8	56.4	36.4	37.3	8.2	6.3
4[a]	2:1	45.6	56.4	36.4	37.3	8.2	6.3
5[a]	3:1	62.5	69.4	27.1	27.8	3.0	2.8
6[a]	4:1	..	..	22.0	21.8	1.6	1.6
7[a]	2:1[c]	44.2	49.1	40.2	42.0	9.6	9.1
8[a]	2:1[d]	46.9	46.3	40.0	43.4	9.9	10.2
9[b]	1:1	22.8	25.0	43.1	50.0	35.5	25.0
10[b]	2:1	..	..	38.6	37.3	11.1	6.3
11[b]	3:1	62.8	69.4	28.0	27.8	2.8	2.8
12[b]	4:1	70.7	76.5	22.9	21.8	3.4	1.6
13[b]	1.89:1	54.0	54.2	33.9	38.6	8.7	7.1

[a] R = CH_3. [b] R = C_2H_5. [c] IX added; see footnote *d*, Table I. [d] IX added; see footnote *e*, Table I.

position by distillation, the observed values can only approximate the calculated percentage yields of the resulting products but they are, nevertheless, sufficiently close to allow the characterization of the transesterification of dialkyl alkylphosphonites as a random distribution reaction. Table IV lists the experimentally observed and the calculated yields of I, X and IX for runs 2 through 13. The largest discrepancy between observed and calculated yields was noted in the runs using 1:1 molar ratios of phosphonite to III (runs 2 and 7), however, molar reactant ratios of 2:1 and higher resulted, in general, in good agreements between calculated and observed values demonstrating that under these conditions the exchange reaction proceeds by random distribution. No explanation can be given at the present time for the large deviations observed with equimolar reactant mixtures. In all runs, the experimental yields of recovered I and II were lower than calculated, while the observed yields of the di-transesterification products IX and XI were higher. The entrainment of I (or II) in the liberated ethanol is to a large extent responsible for the general low recovery of the starting phosphonite. On the other hand, the apparently higher yields of IX and XI, respectively, are mainly the result of the column hold-up. The best agreement between calculated and observed values for the mono-transesterification products was obtained in the runs which employed phosphonite to alcohol ratios of 2:1 to 4:1.

Perfect random distribution in the transesterification of the diethyl alkylphosphonites with octanol could only be expected if ethanol and octanol exhibited exactly identical reactivities in the alcoholysis of a given phosphonite. Although no comparative reactivity values are available for the alcoholysis of phosphonites, the values for the "replacement power" of alcohols in the equilibrium reaction $CH_3CO_2CH_3 + ROH \rightleftarrows CH_3CO_2R + CH_3OH$ determined by Adkins and co-workers[8] indicate an increase in reactivity of less than 5% for 1-octanol as compared to ethanol.

If the composition of the reaction mixture is determined solely by random distribution, an equilibrium mixture of all three possible products will be attained either by a redistribution reaction from the dialkyl alkylphosphonite and the ditransesterification product or by a disproportionation of the mono*trans*ester according to the equation $RP(OR')_2 + RP(OR'')_2 \rightleftarrows 2RP(OR')OR''$. In both the disproportionation and the redistribution reaction, as in the transesterification proper, the ratio of products in the resulting three-component mixture will be determined by the ratio of reactants. Two redistribution runs performed with I and IX in a molar ratio of 3:1 gave very good agreement between calculated and experimentally observed values for the composition of the mixture of reaction products formed by redistribution.

Additional proof for random distribution in the transesterification of I with III was obtained from two runs, carried out in the presence of an added amount of di*trans* ester IX (runs 7 and 8), in which good agreement was obtained between the experimental and calculated yields.

The calculated molar ratio of the components of an equilibrium mixture formed by disproportionation of mono*trans* ester is the same as that obtained by transesterification of dialkyl alkylphosphonite with an equivalent amount of an alcohol. Complete disproportionation, therefore, will lead to a mixture of 25% each of dialkyl alkylphosphonite and di*trans*ester and 50% of the mono*trans*ester. It is noteworthy that different samples of X exhibited upon storage at room temperature different degrees of disproportionation. While one sample had undergone after 6 months at room temperature disproportionation only to the extent of 48%, another sample was disproportionated completely after 10 days. The different behavior of the two seemingly identical samples appears to be due to the presence of an unidentified catalyst, at least in the sample exhibiting the higher rate of disproportionation. Although no added catalyst was necessary for rapidly attaining equilibrium by redistribution from I and IX, or from I and III, the relative stability of one of the ethyl *n*-octyl methylphosphonite samples suggests that the transesterification, redistribution and disproportionation reactions require the presence of a catalyst. Preliminary experiments for the disproportionation of mono*trans*ester demonstrated that traces of added ethanol increase the rate of the reaction considerably. Contamination of the reactants in the redistribution and disproportionation reactions by traces of an alcohol might be sufficient for rapid equilibration. However, the transesterification of I with phenol required the addition of catalytic amounts of sodium without which no reaction occurred. It might very well be that the transesterification with 1-octanol also requires a catalyst and that the catalysis of the reaction has to be attributed here to a contamination of the starting diethyl alkylphosphonites. To elucidate the nature of the catalysis of the disproportionation in some of the mono*trans*ester samples will require a study of the effect of various possible catalysts on the rate of the disproportionation as well as on the rate of the alcoholysis of the diethyl alkylphosphonites.

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(8) P. R. Fehlandt and H. Adkins, THIS JOURNAL, **57**, 193 (1955); G. B. Hatch and H. Adkins, *ibid.*, **59**, 1694 (1937).

It should be noted that no differences in the infrared and nuclear magnetic resonance spectra were found for the samples of mono*trans*ester which showed complete disproportionation within a short period of time as compared to those which exhibited a much greater stability.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PRATT INSTITUTE AND BROOKLYN COLLEGE]

Applications of the Hammett Equation to Non-aromatic Unsaturated Systems. I. *trans*-3-Substituted Acrylic Acids[1]

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Dissociation constants for *trans*-3-substituted acrylic acids, *trans*-3-methyl-3-substituted acrylic acids and *trans*-3-carboxy-3-substituted acrylic acids are correlated with the Hammett equation. The ρ-values and correlation coefficients are 2.230, 0.975; 2.977, 0.991; and 1.918, and 0.925, respectively. New substituent constants are calculated for a number of substituents. The non-applicability of the Hammett equation to the dissociation constants of the corresponding *cis*-acids is discussed.

The Hammett equation has been very useful in the correlation of equilibrium and rate data, and of various physical constants.[4,5] It has been applied to meta and para substituted benzene derivatives and, recently, to heterocyclic compounds.[6] In modified form, it also has been applied to aliphatic compounds, and ortho substituted benzene derivatives.[7a–e] Neither the Hammett equation nor any other linear free energy relationship has been applied to rate or equilibrium data for non-aromatic carbon-carbon unsaturated compounds, although many publications have appeared on the application of linear free energy relationships to non-aromatic carbonyl compounds.

TABLE I

DISSOCIATION CONSTANTS OF 3-SUBSTITUTED ACRYLIC ACIDS

Substituent	Configuration	10^5K	Method of evaluation	Acid	Ref.
H	..	5.56	Conductimetric	Acrylic	9
Me	*trans*	2.03	Conductimetric	Crotonic	9, 10
Me	*cis*	3.6^a	Conductimetric	Isocrotonic	12
Et	*trans*	2.02	Conductimetric	2-Pentenoic	11
Pr	*trans*	1.98	Conductimetric	2-Hexenoic	11
i-Pr	*trans*	1.99	Conductimetric	4-Methyl-2-pentenoic	11
Ph	*trans*	3.65	Conductimetric	Cinnamic	12
Ph	*cis*	13.2	Conductimetric	Cinnamic	12
CO_2H	*trans*	95.7^c	Conductimetric	Fumaric	10
CO_2H	*cis*	1200^d	Conductimetric	Maleic	10
CO_2^-	*trans*	4.13^e	Conductimetric	Fumaric	10
CO_2^-	*cis*	0.0505^f	Conductimetric	Maleic	10
CF_3	*trans*	70	Conductimetric	4,4,4-Trifluoro-2-butenoic	13
CF_3	*cis*	33	From *p*H	4,4,4-Trifluoro-2-butenoic	14
CO_2Et	*trans*	47.3^a	Conductimetric	Monoethyl fumarate	15
Cl	*trans*	$22.2^{a,b}$	From *p*H	Chloroacrylic	16
Cl	*cis*	$47.7^{a,b}$	From *p*H	Chloroacrylic	16
$4'$-ClC_6H_4	*trans*	3.86	Conductimetric	4-Chlorocinnamic	17
$4'$-$MeOC_6H_4$	*trans*	2.89	Conductimetric	4-Methoxycinnamic	18
$4'$-MeC_6H_4	*trans*	2.73	Conductimetric	4-Methylcinnamic	18
$3'$-$O_2NC_6H_4$	*trans*	7.58	Conductimetric	3-Nitrocinnamic	18
$4'$-$O_2NC_6H_4$	*trans*	8.99	Conductimetric	4-Nitrocinnamic	18
PhCH=CH	..	3.75	Conductimetric	5-Phenyl-2,4-pentadienoic	12
CH_2Cl	*trans*	7.25^a	Conductimetric	4-Chloro-2-butenoic	19

All data in water at 25°, reported as thermodynamic dissociation constants unless otherwise stated. [a] Non-thermodynamic dissociation constant. [b] Data at 18°. [c] K_1 of fumaric acid. [d] K_1 of maleic acid. [e] K_2 of fumaric acid. [f] K_2 of maleic acid.

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(1) This work is taken in part from the thesis submitted by M. Charton to the Graduate Faculty of Brooklyn College in partial fulfillment of the requirements for the degree of M.A., June, 1956.

(2) This work was presented in part at the 130th Meeting of the American Chemical Society, Atlantic City, N. J., Sept., 1956.

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