oxy)-2,3,5,6-tetrachlorophenyl)]-phosphate (X), m.p. 162–164° (benzene), band at 7.82 μ (strong).

Anal. Calcd. for $C_{10}H_{12}O_8Cl_4P$: C, 25.9; H, 2.6. Found: C, 26.5; H, 2.3.

(b) Tetrachlorohydroquinone was treated with one mole equivalent of sodium ethoxide in ethanol solution. A suspension of the dry salt in benzene was treated with one mole equivalent of diethyl phosphorochloridate or dimethyl phosphorochloridate. The phenolic phosphates XVIII and XIX were isolated in *ca.* 10%, together with *ca.* 20% of bis-phosphates IX and X and *ca.* 25% of recovered tetrachlorohydroquinone.

Diethyl (4-hydroxy-2,3,5,6-tetrachlorophenyl)-phosphate (XVIII), m.p. 179–180° (cyclohexane), bands (KBr) at 2.9–3.4 and 7.95 μ bonded P→O.

Anal. Calcd. for $C_{10}H_{11}O_5Cl_4P$: C, 31.3; H, 2.9. Found: C, 31.5; H, 3.1.

Dimethyl (4-(hydroxy-2,3,5,6-tetrachlorophenyl)-phosphate (XIX), m.p. 236–238° (methanol), bands (KBr) at 3.0–3.4 μ and 7.97 μ.

Anal. Calcd. for $C_8H_7Cl_4O_5P$: C, 27.0; H, 2.0. Found: C, 27.2; H, 2.2.

(c) From the phenolic phosphates XVIII and XIX, the corresponding ether phosphates VII and VIII were prepared in *ca.* 90% yield utilizing diethyl sulfate or dimethyl sulfate, sodium carbonate and water (3 hr. reflux).

Reaction of Chloranil (I) with Triphenyl Phosphite (V).—(a) A suspension of 10.0 g. of chloranil in 24.3 g. of freshly distilled triphenyl phosphite was heated to 100° for 16 hr. After some time, the chloranil went into solution and a red color was formed. The color faded and the mixture became viscous. Some benzene (25 ml.) was added to effect dilution of the mixture. An additional 13.0 g. portion of chloranil was added and heating was continued. After 24 hr., the mixture was dissolved in 100 ml. of benzene and the solution was extracted with cold 3% aqueous sodium hydroxide. Acidification afforded 21.6 g. of tetrachlorohydroquinone. The benzene layer was washed with water, dried and evaporated. The residue crystallized and was washed with cold hexane; it was shown to be triphenyl phosphate (17.8 g.). The products were identified by melting points and by comparison of the infrared spectra with authentic samples.

(b) When triphenyl phosphite was added to a solution of chloranil in benzene at room temperature, no reaction took place.

(c) A series of experiments were carried out to detect possible photoacceleration; these were negative. Suspensions of chloranil in excess of triphenyl phosphite were irradiated in a quartz flask with a Hanovia ultraviolet lamp; after 20 hr. at room temperature, all the chloranil was recovered. At 100°, in the dark or with irradiation, after 12 hr., 44% of tetrachlorohydroquinone (after hydrolysis) was obtained.

Reduction of Chloranil by Phosphorous Acid.—When chloranil (1.0 g.) and an excess of phosphorous acid (H_3PO_3, m.p. 74°) was kept 18 hr. on the steam-bath, no change was noticed. After 4 hr. at 125° and 4 hr. at 170°, the mixture was cooled, diluted with water and filtered. The yield of tetrachlorohydroquinones was 0.89 g.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TENNESSEE]

The Kinetics of the Esterification of the Cyclohexanedicarboxylic Acids with Diphenyldiazomethane

BY HILTON A. SMITH AND PAUL P. HUNT

RECEIVED AUGUST 4, 1958

The isomeric 1,2-, 1,3- and 1,4-cyclohexanedicarboxylic acids together with their monomethyl esters have been prepared, and their rates of reaction with diphenyldiazomethane studied in absolute ethanol solution. Rate constants at 15, 25, 35 and 45° have been calculated and tabulated, together with the heats of activation. The differences between rate constants for reaction of the dicarboxylic acids and the corresponding monomethyl esters are, in general, less than for the processes of acid- or base-catalyzed esterification. The *cis*-1,3- and *trans*-1,4-acids behave quite similarly. This is also true for the *trans*-1,4 and *cis*-1,3 forms. The results are discussed in the light of the conformations of the cyclohexanedicarboxylic acids and esters and of the mechanisms of the reactions involved.

The acid-catalyzed esterification of the cyclohexanedicarboxylic acids and the base-catalyzed hydrolysis of their methyl esters have been previously investigated.[1,2] It was shown that for both processes, the *cis*-1,3 and *trans*-1,4 configurations gave similar rate constants, which differed from those for the *trans*-1,3 and *cis*-1,4 forms, the latter two also resembling each other. The results were explained on the basis of the conformations of the isomers.

For the 1,3- and 1,4-configurations, the ratio of the rate constants for the diacid or diester to the corresponding monomethyl ester was always equal to or greater than the statistical value of 2. This was explained on the basis of steric considerations plus electrical repulsion of the negatively charged half-ester ion and the attacking hydroxyl ion in the case of the base-catalyzed hydrolysis.

Esterification with diphenyldiazomethane would be greatly influenced by steric considerations if the mechanism involved attack on the carbonyl carbon of the acid in a manner similar to that for acid-catalyzed esterification. However, Roberts, Watanabe and McMahon[3] propose a one-step reaction between the diazo compound and the acid which should not be greatly influenced by steric considerations. Also there is no net charge on the half-ester or the attacking diphenyldiazomethane, so that gross electrical effects similar to those found in base-catalyzed ester hydrolysis should not be encountered.

Experimental

The isomeric cyclohexanedicarboxylic acids and their monomethyl esters were prepared in the same manner as that previously described.[1,2] The melting points of the purified acids were: *cis*-1,2, 194°; *trans*-1,2, 227.5–229.4°; *cis*-1,3, 167–168°; *trans*-1,3, 150–151°; *cis*-1,4, 170–172°; *trans*-1,4, 312–313°. The melting points of the purified monomethyl esters were: *cis*-1,2, 67.8–68.6°; *trans*-1,2, 95.2–96.2°; *cis*-1,3, 66.0–66.6°; *trans*-1,3, liquid, $n^{20}\mathrm{D}$ 1.4671; *cis*-1,4, 106.8–107.4°; *trans*-1,4, 125.5–126.5°.

Diphenyldiazomethane was prepared from benzophenone hydrazone by treatment with yellow mercuric oxide.[4] After recrystallization from methanol and from petroleum ether,

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(1) H. A. Smith and F. P. Byrne, THIS JOURNAL, **72**, 4406 (1950).

(2) H. A. Smith and T. Fort, Jr., *ibid.*, **78**, 4000 (1956).

(3) J. D. Roberts, W. Watanabe and R. E. McMahon, *ibid.*, **73**, 760 (1951).

(4) L. I. Smith and K. L. Howard, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 351.

the product melted at 30–31°.[5] Since diphenyldiazomethane decomposes on standing at room temperature, solutions in ethanol were prepared immediately and stored in a refrigerator.

Kinetic runs were made in baths held at temperatures of 15 ± 0.03, 25 ± 0.02, 35 ± 0.01 and 45 ± 0.01°. Stock solutions in absolute ethanol of diphenyldiazomethane (0.006 to 0.008 M) and the desired cyclohexenedicarboxylic acid (0.06 M) were allowed to come to temperature equilibrium after which equal volumes were pipetted into a small erlenmeyer flask equipped with a two-hole rubber stopper through which ran two capillary tubes. One of these was connected to a small rubber bulb. At desired times, small samples of the reaction mixture could be squirted into a standard Corex cuvette. As soon as the sample was obtained, the cuvette was placed immediately in a Beckman DU spectrophotometer and optical density readings procured. The entire time interval between the sampling and optical density reading was less than 30 seconds. The spectrophotometer readings were all obtained with light of wave length 525 mμ, which represents a maximum in the absorption curve.

Under the experimental conditions of this research, diphenyldiazomethane reacts with the solvent, ethanol, as well as with the acids present. In order to determine the per cent. diphenyldiazomethane which reacted with the cyclohexanedicarboxylic acids or their monomethyl esters, an equimolar solution of the two was made and allowed to react until all of the diphenyldiazomethane was consumed as indicated by the disappearance of color. The unreacted acid then was determined by titration with standard base.

Experimental Calculations and Results

The rate of the reaction of diphenyldiazomethane with acids is first order with respect to each reactant. In the present experimental technique, the concentration of organic acid was much greater than that of diphenyldiazomethane and hence remained essentially constant throughout the reaction. In addition the large excess of the dicarboxylic acid allowed virtually no contribution to the rate by reaction with the second carboxyl group after esterification of the first. Thus pseudo first-order rate constants could be calculated from the slopes of the straight lines obtained by plotting the logarithm of the optical density against time. Second-order rate constants were then found by dividing the first-order rate constants by the initial acid concentration, 0.03 mole per liter. These are given in Table I. Table I also includes the heats of activation calculated from the slopes of the straight lines obtained by plotting logarithms of the rate constants *versus* the reciprocal of the absolute temperature.

It should be noted that these constants actually represent a combination of two rate constants, one for the reaction of the diphenyldiazomethane with the acids, and the other for its reaction with the solvent. This has been thoroughly discussed by Roberts and co-workers.[3] The average percentages of reaction of the diphenyldiazomethane at 25, 35 and 45° for all of the compounds studied and for various individual temperatures and compound types together with their standard deviations are given in Table II. In view of the constancy of these values plus the fact that there is relatively little variation in either rates or heats of activation, rate comparisons may be made directly on the basis of Table I. Rate constants for the reaction of acid and diphenyldiazomethane only would be approximately 60% of the tabulated values.

Discussion

An examination of Table I shows some very interesting facts. First, the rate constants for the reaction of diphenyldiazomethane with the cyclohexanedicarboxylic acids shows a total variation by a factor of less than 2. For both acid-catalyzed esterification of these acids and base-catalyzed hydrolysis of their esters, the total variation was a factor of about 20. This indicates the relatively minor importance of steric considerations in the reaction with diphenyldiazomethane as compared to the other processes.

TABLE I

RATE CONSTANTS AND ACTIVATION ENERGIES FOR THE ESTERIFICATION OF THE CYCLOHEXANEDICARBOXYLIC ACIDS AND THEIR MONOMETHYL ESTERS WITH DIPHENYLDIAZOMETHANE IN ETHANOL

	Rate constants, liters mole^{-1} min.$^{-1}$				E_A × 10^{-4}, cal. mole^{-1}
Acid	15°	25°	35°	45°	
Cyclohexanedicarboxylic acids					
cis-1,2	0.264	0.695	1.70	3.73	
	.263	.697	1.73	3.83	
				3.80	1.63
trans-1,2	.361	.891	2.14	4.69	
	.362	.886	2.11	4.73	1.56
			2.16		
cis-1,3	.275	.728	1.77	3.88	
	.280	.732	1.79	4.04	1.62
trans-1,3	.205	.524	1.27	2.91	
	.208	.525	1.29	2.88	1.62
cis-1,4	.209	.535	1.34	2.90	
	.211	.546	1.31	2.90	1.59
trans-1,4	.265	.679	1.61	3.54	
	.255	.678	1.62	3.58	1.58
Monomethyl esters					
cis-1,2	0.157	0.404	0.985	2.18	
	.159	.405	0.982	2.26	1.61
				2.20	
trans-1,2	.224	.568	1.36	3.00	
	.231	.565	1.37	2.98	1.58
			1.38		
			1.39		
cis-1,3	.150	.376	0.929	2.09	
	.149	.375	.922	2.12	1.61
trans 1,3	.117	.296	.717	1.61	
	.112	.297	.706	1.64	1.60
cis-1,4	.117	.296	.711	1.60	
	.116	.291	.723	1.62	1.61
trans-1,4	.135	.338	.835	1.87	
	.138	.336	.823	1.87	1.59

TABLE II

PERCENTAGE REACTION OF DIPHENYLDIAZOMETHANE REACTING WITH CYCLOHEXANEDICARBOXYLIC ACIDS AND THEIR MONOMETHYL ESTERS IN ETHANOL SOLUTION

Compound type and conditions	Reaction, %	Standard deviation
All compounds, all temp.	60.0	2.3
All diacids, all temp.	60.5	1.4
All half-esters, all temp.	59.5	3.5
All compounds, 25°	60.5	2.4
All compounds, 35°	59.5	2.5
All compounds, 45°	59.5	1.8

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[5] A. B. Hoefelmeyer and C. K. Hancock, THIS JOURNAL, **77**, 4746 (1955).

Second, the rate constants for the reaction of the monomethyl esters of these acids with diphenyldiazomethane also differs by less than a factor of 2, while the total variation for the other processes is much larger. Apparently the substitution of a methyl group for one of the carboxyl hydrogens does not materially increase steric hindrance to the reaction with diphenyldiazomethane.

Third, the rate constants for reaction of the *trans*-1,2 forms with diphenyldiazomethane are the greatest, while for the other reactions studied they have been the smallest. Rate constants for reaction of the *cis*-1,2 compounds with diphenyldiazomethane are relatively large. Apparently the electron sink properties of a carboxyl or ester group on another carboxyl group are more important in governing the rate of the reaction than are steric influences. It is also interesting to note that the substituent groups in the *trans*-1,2-acid or ester are presumably in axial positions while for all other forms they are either both equatorial or one equatorial and one axial.[1]

These first three observations are consistent with the mechanism of this reaction as proposed by Roberts and co-workers.[3]

Fourth, if the methyl group of the monomethyl esters exerted no steric or electrical influence, then the reaction rate constants for the diacids should be greater than for the monomethyl esters by a statistical factor of 2. However, these ratios are always less than 2, varying from 1.6 for the *trans*-1,2 forms to 1.9 for the *trans*-1,4 forms. It would thus appear that the acid group in the monoester is more reactive than in the diacid. This apparently indicates that the ester group is a slightly stronger electron sink than the carboxyl group.

Fifth, one notes that for the 1,3- and 1,4-cyclohexanedicarboxylic acids, the *cis*-1,3 and *trans*-1,4 forms behave quite similarly to each other, while the *trans*-1,3 and *cis*-1,4 forms also resemble each other in reaction characteristics. This same result was found for other reactions of the cyclohexanedicarboxylic acids and their esters, and is readily explained on the basis of the conformations of these compounds.[1,2]

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Kinetics of the Reaction of Sodium *p*-Toluenethiolate (Alcohol) with Phenylacetylene[1,2]

BY WILLIAM E. TRUCE AND RICHARD F. HEINE

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The kinetics of the reaction of sodium *p*-toluenethiolate with phenylacetylene to produce *cis*-1-phenyl-2-*p*-tolylmercaptoethene have been investigated in absolute ethanol, deuterioethanol and N,N-dimethylformamide–ethanol solvent systems. The results can be interpreted in favor of a concerted mechanism for this addition.

There have been several recent articles concerning the mechanism of vinylation reactions, in particular, concerning the addition of alcoholic alkoxide to an acetylene.[3] The general finding is that the reaction is "pseudo"-first order, that is, first order in acetylene only (since the concentration of alkoxide remains essentially constant during a given run). The fact that no rate dependence on the solvent was observed was interpreted as indicating a mechanism involving initial attack of the alkoxide on acetylene in the slow, rate-determining step, and then a rapid abstraction of a proton from the solvent.

Since we had some reservation about this interpretation and its general applicability, we developed the present rate data concerning the vinylation mechanism, particularly the mechanism of the addition of sodium *p*-toluenethiolate reagent to phenylacetylene, which had previously been shown to be a high-yield stereospecific reaction.[4] This acetylenic compound is a desirable one to use in rate studies involving a thiolate reagent; alkyl acetylenes[4] react too slowly and acetylenes carrying strongly electron-accepting groups react too rapidly at moderate temperatures.

A comparison in deuterioethanol and ethanol solvents was undertaken with the expectation that in a concerted process, with the alcoholic proton (deuteron) involved in the rate-determining step, a rate difference would be observed between the two solvents.

A small rate difference or isotope effect ($k_D/k_H = 1.15$) is indicated by the data (Table I). The significance of this factor will be discussed in following paragraphs.

Rate studies also were made in an "inert," non-proton-donor solvent, containing various amounts of proton donor (ethanol). Of the inert solvents considered, dioxane, diglyme and N,N-dimethylformamide (DMF), the latter was chosen because of its greater solvent power toward the thiolate reagent. The results of these runs (Table II) show the reaction to be much faster in DMF, containing very small amounts of ethanol, than in absolute ethanol. This is contrary to what would normally be predicted on the basis that the rate of a reaction between an ion and a neutral molecule should be faster in the medium which has the lower dielectric constant.[5] Since the dielectric constant

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[1] No. IX in the series, "Stereospecific Reactions of Nucleophilic Agents with Acetylenes and Vinyl-type Halides"; for preceding paper see THIS JOURNAL, **80**, 6450 (1958).

[2] Abstracted from the Ph.D. Thesis of Richard F. Heine, Purdue University, 1957.

[3] (a) R. Rigamonti and L. Bernardi, *Chim. Ind.* (*Milan*), **34**, 561 (1952); *C. A.*, **47**, 2583 (1953); (b) S. I. Miller and G. Shkapenko, THIS JOURNAL, **77**, 5038 (1955); (c) T. Tsurato, *et al.*, *Bull. Chem. Soc. Japan*, **28**, 552 (1955).

[4] W. E. Truce and J. A. Simms, THIS JOURNAL, **78**, 2756 (1956).

[5] (a) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 135 ff.; (b) K. Laidler, "Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1950, p. 130.