

compared to that for the dimethyl ether of hydroquinone and also the size of the moments for *p*-bromophenyl and *p*-nitrophenyl trifluoromethyl ethers (compared to the values for vector sum and to those of the corresponding anisoles) can be explained in one of two ways: (1) The angle for the OCF₃ group with the axis in the plane of the ring is closer to 180° than to 90°; or (2) the angle is still near 90° but the OCF₃ group rotates almost freely so that it is restricted to only a small extent to a coplanar position with the aromatic ring. This latter explanation is considered most reasonable since the resonance contribution by the quinoidal forms is grossly reduced by the electron-withdrawing

effect of the CF₃ group (note that for OCF₃ σ_R ranges from -0.13 to -0.23 while for OCH₃, σ_R is -0.47). With the precision of the data in mind, a tenuous conclusion can be drawn that the *p*-nitro group behaves as expected and helps to stabilize the quinoidal form compared to the *p*-bromo group. A more quantitative analysis of the dipole moment results is not appropriate in view of the problems discussed in ref. 24b.

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

Photodecomposition of *p*-Benzoquinone Diazides: Copolymerization with Tetrahydrofuran^{1,2}

BY J. K. STILLE, P. CASSIDY AND L. PLUMMER

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p-Benzoquinone diazide and 2,6-dimethyl-*p*-benzoquinone diazide decompose in various solvents in the presence of heat or light with the loss of nitrogen to give different products. Whereas the light-catalyzed decomposition in many solvents affords substituted phenols, in tetrahydrofuran nearly a 1:1 copolymer with solvent is obtained. The polymer, which contains the polyether structure, is probably an alternating copolymer and is formed through a cationic ring opening of tetrahydrofuran.

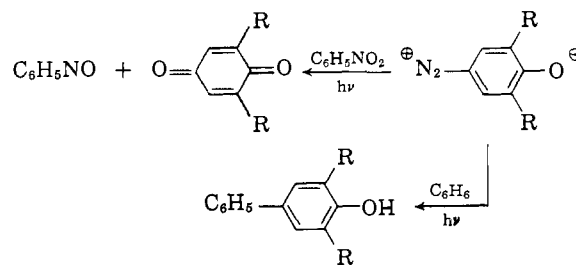
Introduction

The potential thermal stability of polymers containing the poly-(phenylene oxide) chain have made them the object of recent investigation with respect to the methods of formation of such a polymer.³⁻¹⁰ Compounds containing the *p*-benzoquinone diazide structure decompose readily in the presence of light or heat and should lend themselves readily to the preparation of poly-(phenylene oxides). However, decomposition in the solvents benzene, anisole, and *N,N*-dimethylaniline provides the substituted hydroxybiphenyl derivatives,^{3,11,12} while the photodecomposition of solid *p*-benzoquinone gives insoluble polymer.¹¹ The thermal decomposition of 2,6-dibromo-*p*-benzoquinone diazide in chlorobenzene affords a polymer containing the expected recurring unit as well as incorporated solvent.³ In this decomposition, a mildly electrophilic diradical has been proposed as the reactive intermediate.^{3,13}

Results

The monomers *p*-benzoquinone diazide (I) and 2,6-dimethyl-*p*-benzoquinone diazide (II) were prepared in anhydrous (red) and tetrahydrated (yellow) forms which could not be distinguished spectrally except for the fact that the anhydrous forms have lower molar extinction coefficients (Table I). The anhydrous form of *p*-benzoquinone diazide and the tetrahydrate form of

2,6-dimethyl-*p*-benzoquinone diazide have not been previously described. The preparation and polymerization of 2,6-dibromo-*p*-benzoquinone diazide (III) was undertaken for comparison purposes. All the monomers are very difficultly soluble in non-polar solvents, but are very soluble in such solvents as ethanol or water. Decomposition of the monomers by either heat or light in benzene produced the expected hydroxybiphenyl. The photodecomposition of *p*-benzoquinone diazide in nitrobenzene afforded nitrosobenzene and *p*-benzoquinone. Photolysis of 2,6-dimethyl- and 2,6-dibromo-*p*-benzoquinone diazides in nitrobenzene gave nitrosobenzene and presumably the corresponding quinones.



I, R = H; II, R = CH₃; III, R = Br

Decomposition of the *p*-benzoquinone diazides in tetrahydrofuran gave good yields of polymer. However, decomposition in 2,2,5,5-tetramethyltetrahydrofuran afforded little or no polymeric product. As shown in Table II the greatest percentage conversion and highest viscosities were obtained using light catalysis and the anhydrous forms of the monomers.

Polymerizations were also attempted using catalysts such as boron trifluoride etherate,^{14,15} copper salts,^{16,17} auric chloride¹⁸ and trimethyl borate¹⁵ which have been

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(2) (a) Presented in part at a symposium in honor of C. S. Marvel at the University of Arizona, December 27-28, 1961; (b) This research was supported in part by a grant from the Petroleum Research Fund, administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

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known to effect the polymerization of diazoalkanes; however, no polymeric products were obtained.

The analytical data for the polymeric products (Table III) show that the polymer is nearly a 1:1 copolymer with tetrahydrofuran rather than a homopolymer. The difference in the calculated and found values for the 1:1 copolymer may be due to solvent occluded on the polymer lattice, a small amount of nitrogen (1.0%), or a larger incorporation of tetrahydrofuran. Further proof of the structure of this copolymer is presented by Price by nuclear magnetic resonance investigation of a product obtained by decomposition of 2,6-dimethyl-*p*-benzoquinone diazide in tetrahydrofuran.¹⁹

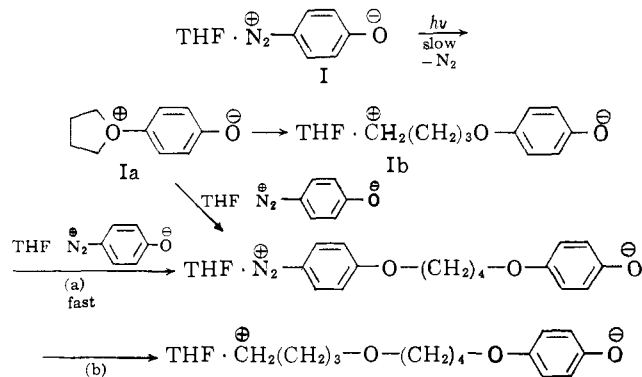
The infrared spectra of the polymers show the ether C-O-C stretching maxima as well as characteristic bands for the phenyl group. In certain polymer samples, particularly those prepared from tetrahydrate monomers, weak conjugated carbonyl maxima are observed, but in most samples, no carbonyl maximum was present. A comparison of the ultraviolet spectra of the polymers with the spectra of selected model compounds demonstrates the presence of the phenylene oxide moiety in the polymers (Table IV).

Determinations of thermal stabilities made on copolymers formed from *p*-benzoquinone diazide-THF and of 2,6-dimethyl-*p*-benzoquinone diazide-THF in atmospheres of air and nitrogen showed that the polymers are stable to about 350°. It should be noted that introduction of aliphatic portions into an otherwise aromatic polymer decreases considerably the thermal stability.²⁰

The photopolymerization of 2,6-dimethyl-*p*-benzoquinone diazide in tetrahydrofuran at 0° was found to display zero-order kinetics between diazide concentrations of 3×10^{-3} and 7×10^{-4} M (Fig. 1); while at concentrations between 7×10^{-4} and 1×10^{-4} M the decomposition showed reasonable first-order kinetics ($K = 1.06 \times 10^{-3}$) within the limits of experimental error (Table V). A low quantum yield, 4.4×10^{-2} , was obtained for the photolysis. These results may be explained by the fact that the number of excited diazide molecules which succeed in decomposing by loss of nitrogen rather than losing energy by some other process is at any instant extremely low compared to the total diazide concentration. This condition would necessitate 100% absorption, but a very low quantum yield.

Discussion

The following mechanism is proposed for the formation of the 1:1 copolymer.



In this mechanism, loss of nitrogen followed by the cationic ring opening of tetrahydrofuran affords Ib, which may then react with more monomer in a typical

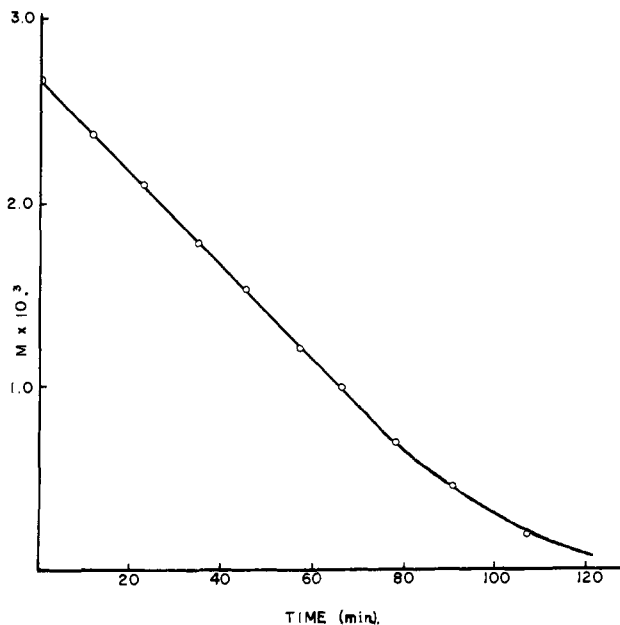
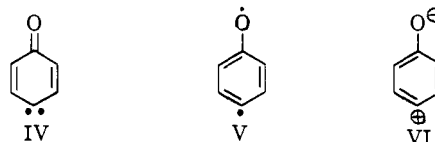


Fig. 1.—Rate of photodecomposition of 2,6-dimethylbenzoquinone 4-diazide.

propagation or with growing polymer (path a). Alternately, attack by phenoxide on the oxonium ion avoids the primary carbonium ion and requires the formation of a 1:1 copolymer. A successive ring opening reaction with tetrahydrofuran could also occur (path b) and an occasional reaction by this path could account for a slightly higher incorporation of tetrahydrofuran in the copolymer. Although tetrahydrofuran is present in large excess, path a would be expected to be followed instead of path b since the phenoxide ion is a better nucleophile.

Dewar^{3,13} has suggested that although the carbene IV, the diradical V and the zwitterion VI may be formulated as the reactive intermediate species in the decomposition of benzoquinone diazides, the zwitterion VI is an unlikely candidate both on the basis of electron binding energies and on the basis of experimental evidence for a diradical (V). Certainly the substitution reactions observed in non-polar solvents seem to proceed by a radical mechanism.^{3,13,19} A polar Lewis base such as tetrahydrofuran, however, would stabilize the zwitterion species (VI, Ia) formed from the decomposition.



This mechanism is consistent with the structure of the product in that it allows only ether linkages, and the composition of the copolymer since it necessarily must produce a 1:1 alternating copolymer. In addition, cyclic ethers,²¹ including tetrahydrofuran,²² have been found to suffer ring opening only by use of cationic catalysts to yield polyethers. This mechanism also accounts for the lower conversion to polymer when the monomers are employed since monomer would be surrounded by water rather than tetrahydrofuran. Finally, this mechanism explains the fact that little or no polymer is obtained in the solvent 2,2,5,5-tetramethyltetrahydrofuran as this Lewis base presents steric inhibition to attack by the diazide or to the formation of ion Ia.

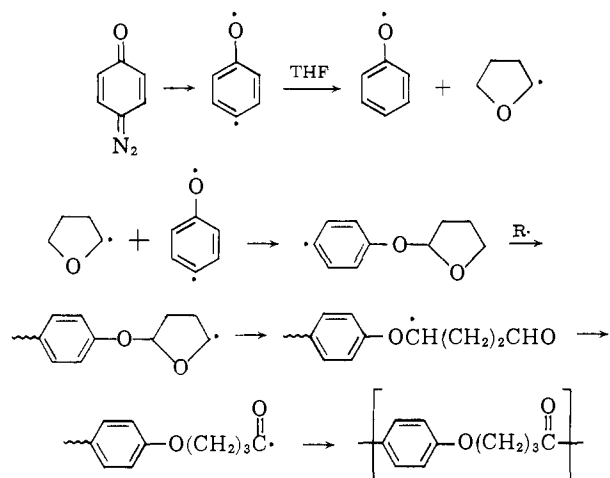
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The trace of conjugated carbonyl detected in the infrared spectra of certain polymer samples may be due to some radical polymerization since tetrahydrofuran is known to undergo homolytic ring opening in the presence of free radicals to give aliphatic ketones.^{23,24}



This study indicates that *p*-benzoquinone diazides would copolymerize with monomers (Lewis bases) which would undergo a ring-opening polymerization reaction by cationic catalysts. The copolymerization of *p*-benzoquinone diazides with other cyclic ethers is currently being investigated.

Experimental

Preparation of Monomers.—*p*-Benzoquinone diazide^{25,26} and 2,6-dimethyl-*p*-benzoquinone diazide²⁷ were prepared by dehydrohalogenation of the corresponding diazotized phenols with freshly prepared moist silver oxide; and 2,6-dibromo-*p*-benzoquinone diazide²⁸ by the addition of bromine to the diazotized *p*-aminophenol.

The monomers are very unstable and sensitive to heat, light and shock. Therefore, nearly all work with the monomers was done at 0°, and the pure compounds were stored in a vacuum desiccator at 0° over phosphorus pentoxide and protected from light. The properties of the monomers are given in Table I.

TABLE I

<i>p</i> -BENZOQUINONE DIAZIDE MONOMERS					
Monomer	Color	M.p., °C.	λ_{max}^a	log ϵ	Infrared ^b
I	Orange	Explodes 92	348	4.48	2080
I 4H ₂ O	Yellow	38.5–39.5 ^c	348	4.56	2080
II	Red	109–111 ^d	357	4.27	2070
II 4H ₂ O	Yellow	64–66	357	4.75	2070
III	Yellow	Explodes 148	363	3.55	..

^a In anhydrous ethanol. ^b In chloroform. ^c Reported²⁶ 38–39°. ^d Reported²⁷ 121°.

A. *p*-Benzoquinone diazide (I) was prepared as the tetrahydrate as described²⁶ except that the final reaction mixture was diluted to 2 l. with anhydrous ether and stored at –80° for 2 days to crystallize the product in a 63% yield.

The tetrahydrate was recrystallized three times by dissolving it in 50 ml. of absolute ethanol, pouring into 2 l. of anhydrous ether and storing at –80° to obtain the anhydrous compound in a 57% yield. *Anal.* Calcd. for C₆H₄N₂O: C, 59.99. Found: C, 60.08.

B. 2,6-Dimethyl-*p*-benzoquinone Diazide (II).—A solution of 20 g. (0.12 mole) of 2,6-dimethyl-*p*-aminophenol hydrochloride, 20 ml. of concentrated hydrochloric acid and 350 ml. of absolute ethanol was cooled to –5° and 18 ml. (15.6 g., 0.13 mole) of freshly distilled isoamyl nitrite was added dropwise over a 20-minute interval. After stirring for 2 hours, the mixture was poured into 2 l. of anhydrous ether at 0°. The diazonium salt was collected by filtration, partially dried on the funnel, suspended in 110 ml. of absolute ethanol and cooled to –5°. To

this suspension was added 55 g. of freshly prepared moist silver oxide and the mixture was stirred for 3 hours at –5°. The suspension was then filtered, poured into 1 l. of anhydrous ether and stored at –80° for 1 day to precipitate out the diazide tetrahydrate in a 35% yield. *Anal.* Calcd. for C₈H₁₆N₂O₅: C, 43.60; H, 7.27. Found: C, 43.48; H, 7.53.

Two further recrystallizations were carried out by dissolving the solid in 50 ml. of cold absolute ethanol and pouring it into 1 l. of anhydrous ether and storing at –80° for 1 day to obtain the anhydrous compound in a 30% yield. *Anal.* Calcd. for C₈H₈N₂O: C, 64.84. Found: C, 65.29.

C. 2,6-Dibromo-*p*-benzoquinone diazide (III) was prepared as previously described²⁸ in a 74% yield.

Decomposition of Quinone Diazides.—Solutions of diazides were prepared at 0° and deoxygenated with nitrogen. Light-catalyzed reactions were carried out at 0° in Vycor flasks using a G.E. AH-4 mercury vapor lamp; thermal decompositions were run by placing the cold solution in a preheated oil-bath. At the end of the reaction when a tetrahydrofuran solvent had been employed the mixtures were concentrated under reduced pressure to about 10 ml. and poured into 150 ml. of methanol to precipitate the polymer. Polymeric products were purified by dissolving them in a minimum amount of benzene and reprecipitating in 150 ml. of methanol and by lyophilizing from benzene solution.

A. In Nitrobenzene.—A solution of 1.6 g. of 2,6-dimethyl-*p*-benzoquinone diazide in 100 ml. of nitrobenzene was irradiated for 24 hours at 0°. The solution was concentrated under reduced pressure to 10 ml. and poured into 150 ml. of methanol to precipitate a small amount of polymeric material (0.1 g.). The green distillate, b.p. 110° (10 mm.), from this concentration showed a maximum in the ultraviolet spectrum at 743 m μ which was identical to the maximum for a solution of nitrosobenzene in nitrobenzene.¹³

Similarly, the decomposition of both *p*-benzoquinone diazide and 2,6-dimethyl-*p*-benzoquinone diazide by irradiation in nitrobenzene at 0° afforded nitrosobenzene as shown by the ultraviolet spectra. These solutions also showed maxima in the 440–480 m μ region, characteristic of *p*-benzoquinone and 2,6-dimethyl-*p*-benzoquinone. In the case of the *p*-benzoquinone diazide, 3.3 g. (0.05 mole) of freshly cracked cyclopentadiene was added to the distillate obtained from the decomposition of 1.2 g. (0.01 mole) of diazide in 50 ml. of nitrobenzene. The solution was stirred for 4 hours and the solvent was removed under reduced pressure. The residue, 0.62 g. (26%), was recrystallized from ethanol to yield 1,4,4a,5,8,8a,9a,10a-octahydro-1,4,5,8-dimethano-9,10-anthraquinone, m.p. 156–157°, reported^{29,30} 157–158°. The melting point of a mixture of this sample and an authentic sample was undepressed.

B. In Benzene.—Photodecomposition of 2.0 g. of 2,6-dibromo-*p*-benzoquinone diazide in 200 ml. of benzene gave 1.4 g. (63%) of 2,6-dibromo-4-hydroxybiphenyl, m.p. 93.0–93.5°, reported¹¹ 96°. *Anal.* Calcd. for C₁₂H₈Br₂O: C, 43.93; H, 2.44. Found: C, 43.65; H, 2.65.

The photodecomposition of 1.0 g. of anhydrous *p*-benzoquinone diazide in benzene afforded 0.90 g. (64%) of crude *p*-phenylphenol. Four recrystallizations of the crude material from a benzene-hexane mixture gave pure product, m.p. 165°, reported¹¹ 164°.

C. In 2,2,5,5-Tetramethyltetrahydrofuran.—Irradiation of a solution of 0.82 g. of *p*-benzoquinone diazide in 400 ml. of 2,2,5,5-

TABLE II

DECOMPOSITION OF DIAZIDES IN TETRAHYDROFURAN						
Monomer	Concn. ^a	T, °C.	Time, hr.	Light	Conv., ^b %	$[\eta]^c$
I 4H ₂ O	75	0	16	Yes	38	0.18
	75	66	14	Yes	65	.12
	75	66	24	No	53	.08 ^d
	60	0	36	Yes	68	.11
I	25	0	36	Yes	76	.12 ^e
	75	0	12	Yes	45	.10 ^f –0.30
II	55	66	36	No	8	.12
	20	0	36	Yes	45	.13 ^e
	225	0	24	Yes	35	.05
III	225	66	24	No	43	.03

^a Numbers refer to ml. solvent/g. monomer. ^b Calculated on the basis of a 1:1 copolymer with solvent. ^c Inherent viscosities: 0.25 g. of polymer/100 ml. of benzene, 25°. ^d A number average molecular weight, 3118, of this sample was obtained in chloroform on a Mechrolab 301A vapor pressure osmometer. ^e In chloroform. ^f \bar{M}_n of the $[\eta] = 0.10$ sample was 2245 as measured in *d*.

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TABLE III

ANALYSIS OF COPOLYMERS

Monomer	Calcd. for homopolymer, %		Calcd. for copolymer, %		Found, %		
	C	H	C	H	C	H	N
I	78.26	4.38	73.15	7.37	72.44	6.64	..
II	79.97	6.67	74.97	8.39	73.95	7.99	1.00
III	28.84	0.80	37.30	3.13	35.98	2.16	..

TABLE IV

ULTRAVIOLET SPECTRA OF POLYMERS AND MODEL COMPOUNDS^a

Compound	λ_{\max} , m μ	log ϵ
Poly-(1,4-phenylene oxide)	295	2.93 ^b
Anisole	277	3.15
Diphenyl ether	278	3.26
4-Hydroxydiphenyl ether	281	3.48
4-Methoxydiphenyl ether	280	3.43
Poly-(2,6-dimethyl-1,4-phenylene oxide)	287	2.84 ^b
2,6-Dimethylanisole	265	2.78

^a In chloroform. ^b Extinction coefficient calculated on the basis of a 1:1 copolymer.

tetramethyltetrahydrofuran³¹ at 0° afforded 0.16 g. (25%) of yellow polymer, 74% of which was soluble in benzene and had an intrinsic viscosity of 0.059. Subjecting 2,6-dimethyl-*p*-benzoquinone diazide to similar treatment afforded only a trace of

(31) L. Henry, *Compt. rend.*, **143**, 496 (1906).

TABLE V

RATE OF PHOTODECOMPOSITION OF A 3.108×10^{-4} M SOLUTION OF 2,6-DIMETHYLBENZOQUINONE-4-DIAZIDE

Time $\times 10^{-2}$, sec.	ln (C_0/C)	Time $\times 10^{-2}$, sec.	ln (C_0/C)
2.1	0.193	9.0	0.982
3.9	.367	11.4	1.344
5.7	.510	13.8	2.064
7.2	.677		

polymer. Thermal decomposition of 0.5% solutions of the two monomers at reflux temperature (111.0°) produced only traces of polymer.

D. In Tetrahydrofuran.—Summarized in Table II are the results of decompositions in tetrahydrofuran. Tables III and IV give analytical and ultraviolet spectral data, respectively. The products from *p*-benzoquinone diazide are slightly yellow and those from 2,6-dimethyl-*p*-benzoquinone diazide are white. Polymer samples prepared from the hydrated monomers only showed weak bands at 1695 cm.⁻¹ (C=O str., conj.) in the infra-red region while all polymers showed maxima at 1195–1200 cm.⁻¹ (C–O–C str.).

Kinetics.—Tetrahydrofuran solutions 2.325×10^{-3} M (Fig. 1) and 3.108×10^{-4} M (Table V) in 2,6-dimethyl-*p*-benzoquinone diazide were placed in a flask equipped with a mechanical stirrer, and blanketed by an atmosphere of nitrogen. This apparatus was partially immersed in a bath maintained at 0°. During irradiation with a G.E. AH-4 mercury vapor lamp, 1-ml. aliquots were withdrawn, diluted to 10 ml. in the dark and placed in a Beckman DU spectrophotometer at 0° to determine optical density at 357 m μ . The quantum yield was obtained by using both uranyl nitrate and oxalic acid as standards.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, NEW YORK 27, N. Y.]

The Acid Dissociation Constants of Some 1,2-Cyclopropanedicarboxylic Acids. Some Comments Concerning Acid Dissociation Constants of Dicarboxylic Acids¹

BY LAYTON L. MCCOY² AND GUENTER W. NACHTIGALL

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The acid dissociation constants of twenty-three substituted 1,2-cyclopropanedicarboxylic acids are reported. Some of the trends in the relationships between structure and dissociation constants are pointed out and discussed. A general discussion of some problems connected with acid dissociation constants, especially for dicarboxylic acids, is given.

As a result of previous studies on the preparation of polysubstituted cyclopropanes,³⁻⁶ we have accumulated a number of sets of substituted isomeric 1,2-cyclopropanedicarboxylic acids. Many of the compounds were new, and others were not readily accessible previously. Earlier studies of the physical and chemical properties of substituted cyclopropanes often have been limited to readily available alkyl-substituted compounds. As the result of our work making cyclopropanes with carboxyl, ester, nitrile groups and halogen available, we have considered it desirable to investigate the physical properties of these cyclopropanes substituted with electron-withdrawing groups. The present report gives an initial survey of the acid dissociation constants of most of the 1,2-diacids available to us. Because our compounds comprise a rather heterogeneous group, we have not aimed for extremely refined results, but rather we have tried to obtain adequate data for the following purposes: (1) To observe any trends in the relationships between structure and acid dissociation constants, and if such trends were discernible to see if they matched similar trends in related succinic acids or maleic-fumaric acids. (2) To use

any empirical relationships observed in (1) to help assign configurations to some of the new diacids.

Experimental

Materials.—The diacids used are listed in Table I with references to their source. In all cases, the samples titrated were those for which analyses are reported in the references, or they are samples prepared in an identical manner. All of the acids titrated to better than 99% of theoretical equivalence.

Titrations.—These were carried out with type SBR 2/SBU/TTT 1 automatic titration equipment of the Radiometer Corporation, with Radiometer type G-202 B glass electrode and type K 4312 calomel electrode. A jacketed container of about 100-ml. capacity, the jacket connected to a temperature-controlled water-bath, which permitted temperature control at $20.0 \pm 0.1^\circ$, was used as the titration vessel. During each titration, the access of air (carbon dioxide) was prevented by maintaining a nitrogen blanket over the solution. Titrant, 0.100 N sodium hydroxide, was added by means of a 2.5-ml. syringe buret to 100.0 ml. of a 0.00100 M solution of the acid in carbon dioxide-free distilled water. Before each titration, the pH meter was standardized against buffer solutions (Fisher Scientific) over the range pH 3.00 to pH 6.50. At least two titrations were run on each acid, the first of which was automatically recorded, while during the second titration direct readings were taken from the micrometer arrangement of the syringe buret and from the pH meter. Automatically recorded data were found to be unsuitable for the desired evaluation because the chart could not be read with sufficient accuracy. Agreement between titrations of the acid was generally within 0.03 pH unit.

Determination of Acid Dissociation Constants.—The data were treated by the method of Speakman⁷ and by Ebersson's modification thereof.⁸ All *trans*-acids, where K_1/K_2 was about 50 or less, were treated according to Speakman's graphical

(1) Part of this report is taken from a senior honors project by G. W. Nachtigall.

(2) To whom inquiries should be sent. Present address: Department of Chemistry, University of Kansas City, Kansas City 10, Mo.

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