[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF DELAWARE]

Isomerism in the Diels–Alder Reaction. IV. Directive Influences in Addition Reactions of the Double Bond in Bicyclic Adducts[1,2]

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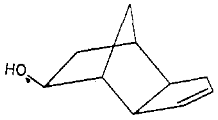
Distinction between alternative structures for the product of bromination of the *endo* Diels–Alder adduct of cyclopentadiene and maleic anhydride is provided by two lines of evidence reported here. The influence of the bicyclic substituent on the steric course of the addition reaction is briefly considered.

Introduction

In an earlier paper in this series[1b] we have shown that on the basis of dipole moment measurements the structure of the bromination of the *exo*-cyclopentadiene–maleic anhydride Diels–Alder adduct I was uniquely consistent with a *trans*-2,3-dibromide formulation II, but the structure of the dibromide obtained from the *endo*-adduct III was consistent with both the 2,7-rearranged product IV and the *cis*-2,3-vicinal dibromide formulation V. At that writing we preferred the structure IV in line with many demonstrations of the course of Wagner–Meerwein rearrangement accompanying addition to the double bond in bicyclic systems. Thus, for example, Bartlett and Schneider[3] have shown that the Diels–Alder adduct VI (dicyclopentadiene) underwent addition of the elements of water through a course of rearrangement that resulted in product VII. A similar course of rearrangement was observed in these laboratories in the addition of bromine[1c] and the elements of hydrogen peroxide[4] to norbornylene. We are reporting here structural evidence that indicates an entirely different course of reaction is involved with addition to the double bond in III than was observed in the apparently similar cases of dicyclopentadiene and norbornylene.

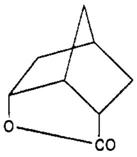


VII

Proof of the Structure of the Bromination Product from III.—Consider the two possibilities consistent with the observed dipole moment[1b] of this product, *viz.*, IV and V. Solution of the dibromide in dilute base produces[5] a bromolactonic acid which could be formulated as VIIIa or VIIIb, resulting from displacement of bromine ion by carboxylate anion with Walden inversion. Only one such displacement is possible leading to VIIIa without epimerization of the second carboxylate anion to the *endo* configuration. Two such inversions occurring successively with equal facility might have been expected leading from V to the dilactone IXb. However, the reaction producing the dilactone requires stronger base and higher temperatures, in which procedure the epimerization of VIIIa depicted in the reaction diagram has been readily effected in entirely similar structures.[6] These alternative structures, IXa and IXb, for the dilactone, are readily distinguishable by dipole moment measurements. Agreement between the calculated moment of structure IXb and the observed moment of the dilactone may be noted in the results summarized in Table I. Though the discrepancy between the observed moment and the moment calculated for structure IXb is slightly greater than the ordinarily acceptable deviation,[1b] in the present instance it is to be expected that the dipole interaction of the two lactone groups in the *endo* configuration would produce a small lowering of the observed from the calculated moment, with some attendant spreading of the bond angles.[7] A similar interaction effect in IXa would also be expected to produce a lowering of the moment and a corresponding increase in the discrepancy (2.6 *D*) between its calculated moment and that observed for the dilactone.

TABLE I

DIPOLE MOMENTS OF THE LACTONES

	μ Calcd., *D*	μ Obsd., *D*
IXa	6.2	
IXb	9.4	8.8
	..	4.7

From this line of evidence it was concluded that V was the more probable of the two alternative structures for the dibromide obtainable from III. A second line of evidence confirming this assignment was obtained by dehydrohalogenation of the bromolactonic acid with potassium *t*-butylate in *t*-butyl alcohol. The strongly basic *t*-butylate anion has almost no nucleophilic properties to complicate the elimination reaction and the dehydrobromination, under these circumstances, was accomplished with very little accompanying displacement products, obtainable with use of other bases, *i.e.*, potassium hydroxide in methanol. Formulation of the bromolactonic acid as VIIIa predicts the formation of the olefin Xa on dehydrobromination, whereas VIIIb would be expected to yield Xb (and/or its ketone tautomer). The product actually obtained showed properties consonant with Xb, affording readily a 2,4-dinitrophenylhydrazone different from the derivatives of the two other known

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(1) For previous papers in this series see (a) THIS JOURNAL, **74**, 3044 (1952); (b) **75**, 3356 (1953); (c) **76**, 4072 (1954).

(2) This work was sponsored by the Office of Naval Research under Contract Nonr-567(00).

(3) P. D. Bartlett and A. Schneider, THIS JOURNAL, **68**, 6 (1946).

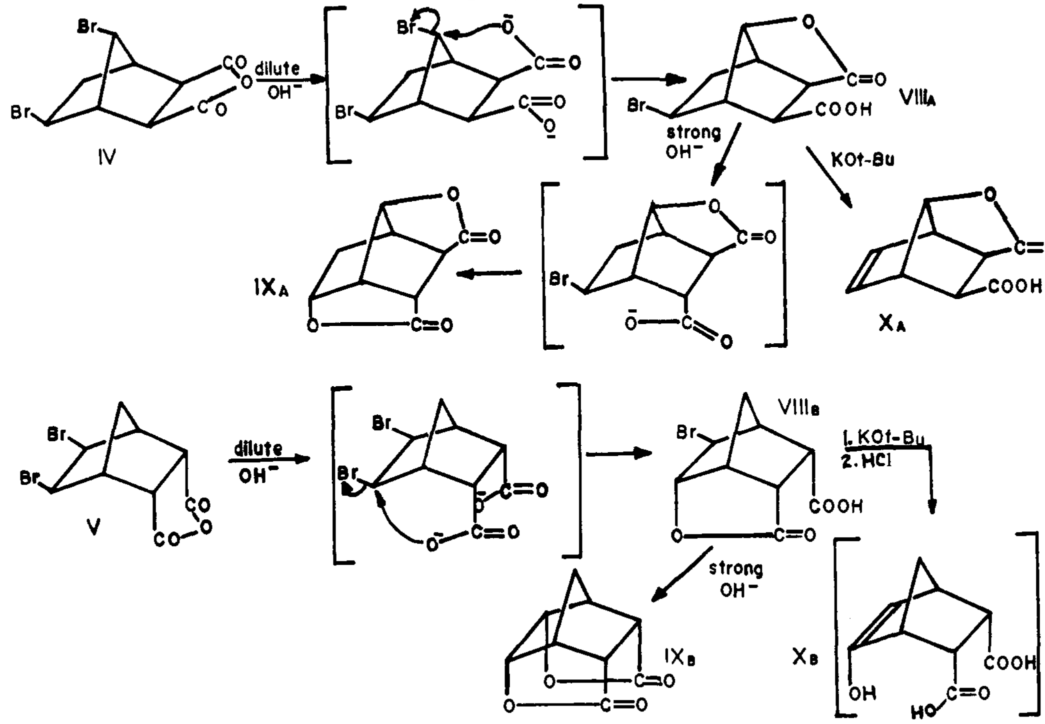
(4) Unpublished results from these laboratories.

(5) Unpublished results from these laboratories.

(6) K. Alder and G. Stein, *Ann.*, **504**, 216 (1933).

(7) C. P. Smyth, *Chem. Revs.*, **6**, 574 (1929); H. M. Smallwood and K. F. Herzfeld, THIS JOURNAL, **52**, 1919 (1930).

REACTION DIAGRAM



XI, R = hydrogen, X = Br
XII, R = anhydride, X = Br
XIII, R = hydrogen, X = OH

isomeric keto dibasic acids reported by Alder and Stein.[8,9]

Discussion of Results

The *exo-cis* dibromide configuration V, established by the above considerations, indicates an entirely different course of reaction than observed for norbornylene.[1c] We have attributed the formation of the 2,7-rearranged dibromide from norbornylene to the directive influence of the bromine atom in the bridged ion intermediate XI. The fact that *none* of the 2,7-rearranged product IV is obtained from bromination of III would appear to indicate that in an intermediate such as XII the bromine atom is without influence in determining the transition state leading to dibromide product. The result with norbornylene suggests, to the contrary, that the bromine atom has a profound effect in determining the direction of collapse of the bridged ion XI. Similarly in perhydroxylation of norbornylene, a pronounced influence of the hydroxyl group in the intermediate XIII is also observed and the product is exclusively the non-vicinal diol.[4] We have concluded, therefore, that the intermediate XII does *not* obtain (or is of little importance) in the mechanism of bromination of III.

Failure to observe such a reaction path is attributed to the reduced electron density at C$_5$, resulting from the presence of the electron-attracting carbonyl substituent, which tends to prevent delocalization of the C$_4$–C$_5$ electron pair. When the car-

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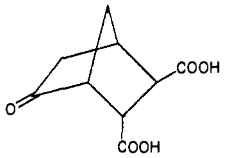
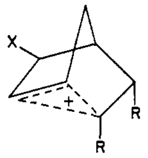
[8] K. Alder and G. Stein, *Ann.*, **525**, 183 (1936).

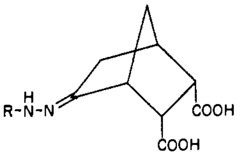
[9] We have considered the possibility that the 2,4-dinitrophenylhydrazine derivative was an acid hydrazide of structure (D), resulting



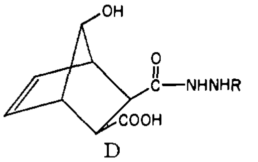
A



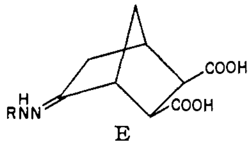
B



C



D

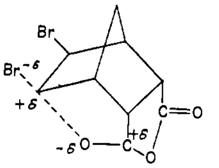


E

from hydrolytic cleavage of the lactone Xa. If this were the case we would expect major differences in the infrared spectrum compared to that of the known *trans*-keto acid (A) and its 2,4-dinitrophenylhydrazone (B). The close similarity of the spectra of (B) and (C) eliminates, in our estimation, structure (D) and consequently Xa. It should be noted that acid hydrazide formation in the preparation of the 2,4-dinitrophenylhydrazone of the known *trans*-keto acid (A) is also ruled out, since the spectrum of the resulting compound (B) does not exhibit an absorption band for a ketone carbonyl at 5.9–6.0 μ present in the parent compound A.

It is possible that structure (E) is a suitable description for the 2,4-dinitrophenylhydrazine derivative of Xb. Since (E) is also a *keto* dibasic acid it could only have resulted from the dehydrohalogenation of a vicinal dibromide, thereby also eliminating the dibromide IV from consideration. The only possible precursor of (E) is V and thus (E) could only have arisen in a reaction series involving base-catalyzed epimerization of the *endo*-carboxyl groups to the *exo* configuration. A vicinal dibromide with *exo-cis*-carboxyl groups could not yield the bromolactonic acid intermediate used in the above transformations.

bonyl is in the *exo* configuration the normal *trans*[10] course of bromination has been noted.[1b] The *cis* bromination, occurring when the carbonyl substituent is in the *endo* configuration, may be a consequence of two factors: (1) a large non-bonded interaction[11] between bromine and carbonyl in the *endo* configuration provides a large steric factor opposing formation of a *trans* bromination product. (2) The developing vacancy in the *p* orbital at C_3 (which obtains when the positive end of the polarized bromine attacks at C_2) is supported by the negative end of the carbonyl dipole. The resulting transition state is strongly suggestive of the displacement reaction (in which bromide$^{-\delta}$---$C_3^{+\delta}$ ----$^{-\delta}$ π-orbital of the carbonyl constitute a line of centers) as represented in XIV.



XIV

We are engaged in studies of the rates of bromination of Diels–Alder adducts in continuing these investigations of the influence of substituent nature (electronic) and geometry (*endo, exo*) on the kinetics and mechanism of addition in bicyclic systems.

Experimental

Preparation of the *endo*-Adduct.—The procedure of Diels and Alder[12] was followed using one mole of freshly distilled cyclopentadiene and one mole of maleic anhydride. The product was recrystallized from low-boiling petroleum ether. A 95% yield of the *endo*-adduct, m.p. 161–162°, was obtained.

Bromination of the *endo*-Adduct.—The procedure of Bartlett and Schneider[3] was followed. From 1 mole (164 g.) of the *endo*-adduct and 1.2 moles (192 g.) of bromine there was obtained 220 g. (68%) of the dibromoanhydride, m.p. 205–206°.

Hydrolysis of the Dibromoanhydride (m.p. 205–206°).—The anhydride was hydrolyzed according to the method of Alder and Stein.[13] One hundred and sixty-two grams (0.5 mole) of the dibromoanhydride yielded 160 g. (94%) of the dicarboxylic acid (m.p. 181–182° dec.).

Preparation of the *trans*-bromolactonic acid (m.p. 186°) was accomplished by the procedure of Alder and Stein.[8]

4-Keto-*endo*-3,6-methylenehexahydro-*trans*-phthalic Acid (A).—The keto acid was prepared from the *trans*-bromolactonic acid (m.p. 186°) according to the procedure of Alder and Stein.[8]

The 2,4-dinitrophenylhydrazone (B) was prepared by adding the calculated amount of the keto acid to a solution of 2,4-dinitrophenylhydrazine hydrochloride in boiling aqueous methanol. The yellow dinitrophenylhydrazone precipitated out on cooling. Recrystallization from methanol gave yellow plates melting at 157.5–159.5°.

Anal. Calcd. for $C_{15}H_{14}O_8N_4$: N, 14.81. Found: N, 14.73.

Preparation of the Bromolactone Acid, m.p. 157°.—Thirty-two and four tenths g. (0.1 mole) of the *endo*-dibromoanhydride (m.p. 205–206°) was added to a solution of 31.8 g. of sodium carbonate in 500 cc. of water. The mixture was stirred until almost complete solution occurred and filtered through a plug of glass wool to remove any undissolved dibromoanhydride. The filtrate was acidified with dilute nitric acid to precipitate the bromolactone acid, which upon recrystallization from boiling water gave needles melting at 113–116°.[14] After drying in a vacuum oven at 80–90°, 10.5 g. of the bromolactone acid was obtained, melting at 155.5–157°.

Dehydrohalogenation of the Bromolactone Acid. M.p. 157°.—Thirteen and five-hundredths grams (0.05 mole) of the bromolactone acid suspended in 100 cc. of boiling *t*-butyl alcohol was added to a solution of 0.15 mole (5.85 g.) of potassium in 100 cc. of *t*-butyl alcohol. There was an immediate precipitation of the potassium salt of the acid. The mixture was then refluxed for 72 hours, cooled to room temperature, and poured into an excess of cold dilute sulfuric acid. The solution was saturated with ammonium sulfate and thoroughly extracted with ether. After drying over sodium sulfate, the ether and *t*-butyl alcohol were removed on a hot-plate and the brown viscous oil that remained was stored in a vacuum desiccator over calcium chloride to remove final traces of water and *t*-butyl alcohol. On the assumption that this product was a mono-*t*-butyl ester of Xb it was simultaneously hydrolyzed with boiling mineral acid and converted to its 2,4-dinitrophenylhydrazone (C) as follows. To 1.0 g. of non-crystallizable ester was added 100 ml. of 0.05 *M* solution of 2,4-dinitrophenylhydrazine in 0.5 *M* aqueous methanolic hydrochloric acid and the resulting clear solution brought to reflux. Water was added through the condenser to the point of cloudiness. The solution clarified again on being brought to a boil and was held under reflux for approximately 10 to 15 minutes. On cooling, the product came out as a light yellow precipitate. Additional crops were obtained on further dilution of the filtrate with water. On recrystallization from chloroform–*n*-pentane the final product was obtained in the form of yellow crystals melting at 211–214° dec.

Anal. Calcd. for $C_{15}H_{14}O_8N_4$: N, 14.81. Found: N, 14.69.

The product furthermore gave the characteristic burgundy color test for 2,4-dinitrophenylhydrazones with methanolic potassium hydroxide distinguishing it from an acid hydrazide and from the hydrazine reagent. The analysis and properties, it was noted, were very similar to that of the

TABLE II

DIPOLE MOMENT DATA[16]

Concn., moles × 10^3	$\epsilon - n^2$	Concn., moles × 10^3	$\epsilon - n^2$
Dilactone		*endo*-2,5-Methylene-1,2,5,6-tetrahydrobenzoic acid, monolactone[17]	
2.78	0.082	9.19	0.078
4.69	.093	11.99	.083
6.58	.116	20.56	.105
9.04	.133	31.86	.133
10.53	.145	44.47	.164
$\mu = 8.8\ D$		$\mu = 4.7\ D$	

SPECTRAL DATA

Comparison of the carbonyl absorption bands in the infrared spectra of 4-keto-3,6-methylenehexahydro-*trans*-phthalic acid (A) and its 2,4-dinitrophenylhydrazone (B) with the 2,4-dinitrophenylhydrazone (C) obtained from the dehydrohalogenation of the 157° bromolactone acid gave the following results:

Compound	Max. of carbonyl bands, μ
A	5.8, 5.9–6.0 (broad)
B	5.8
C	5.8

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[10] See, for example, M. J. S. Dewar, "Electronic Theory of Organic Chemistry," Oxford Press, New York, N. Y., 1949, p. 143.

[11] For a general discussion of this factor see D. H. R. Barton, The Tilden Lecture, *J. Chem. Soc.*, 1027 (1953).

[12] O. Diels and K. Alder, *Ann.*, **460**, 98 (1928).

[13] K. Alder and G. Stein, *Ann.*, **504**, 247 (1933).

[14] The bromolactone acid apparently forms a hydrate. This compound melts at the same temperature as the bromohydrin described by Alder and Stein (*Ann.*, **504**, 216 (1933)).

[15] K. Alder and G. Stein, *Ann.*, **514**, 1 (1934).

[16] For procedures see reference 1b. Dioxane was used as the solvent in these determinations. These measurements were made by D. Pascale.

[17] This compound was prepared according to the method of K. Alder and G. Stein (*Ann.*, **514**, 197 (1934)).

isomeric compound (B) prepared above. Distinction was verified by infrared spectral differences (see Spectral Data) and mixed melting point depression.

4,5-Dihydroxy-3,6-methylenehexahydrophthalic Acid Dilactone (IXB).—The procedure of Alder and Stein[15] was followed. From 16 g. of the bromolactone acid (m.p. 157°) there was obtained 8 g. of the dilactone melting at 264–266°.

In compound A, the broad band at 5.9 to 6.0 μ is due to the 4-keto group while the sharper band at 5.8 μ is due to the carbonyl functions of the carboxylic acid groups. Compounds (B) and (C) did not display the first absorption band mentioned above, but they both absorbed strongly at 5.8 μ. This is identical with the carbonyl absorption of the carboxylic acid functions in compound (A). Compound (C) could possibly be the corresponding anhydride, but since only one absorption band is present in the carbonyl region (typical aliphatic anhydrides display two carbonyl absorption bands at 5.4 and 5.6 μ) we prefer the dicarboxylic acid structure consistent with the chemical analysis.

The spectra of compounds (B) and (C) were identical in the region of 2–8 μ and only slight differences existed in the region between 8–16 μ. These latter differences could be ascribed to the respective *cis–trans* relationships of the carboxyl groups.

Acknowledgment.—We are indebted to Dr. Harold C. Beachell for interpreting the infrared spectra of these compounds. We also wish to express our gratitude to the Office of Naval Research for their generous grant which supported this research.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

The Low Reactivity of Cyclopropane Derivatives toward Free Radicals

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Cyclopropyl cyanide, methyl cyclopropyl ketone and phenylcyclopropane have been found to be unreactive toward a variety of free radicals despite the fact that their olefinic analogs undergo radical propagated polymerization with ease.

Various authors have pointed out similarities between olefins and cyclopropanes with respect to both their chemical and physical properties.[1] Since these correlations are based upon reactivity toward electrophilic and nucleophilic reagents and physical properties it was of interest to consider extension of the observations to include reactivity toward free radicals.

Other work has supplied interesting but fragmentary evidence on the subject. Roberts and Dirstine[2] have carried out the photochemical chlorination of cyclopropane. Although the rate of the reaction was somewhat slow the results show that at least one radical, the chlorine atom, attacks the hydrocarbon by hydrogen abstraction rather than by attack on carbon to effect ring opening. Similarly, Brown and Borkowski[3] observed that in the chlorination of methylcyclopropane only hydrogen abstraction from the methyl group occurred despite the presence of a tertiary structure at one of the ring atoms. Trotman-Dickenson and Steacie[4] have reported that the rate of hydrogen abstraction from cyclopropane by the methyl radical is slower than are the rates of the corresponding reactions with cycloalkanes of larger ring size.

Several examples of what appear to be ring opening by atoms or radicals have been reported. Probably the most conclusive of these is the photosensitized polymerization of cyclopropane.[5] Opening by halogen atoms is probably involved in the photochemical conversion of cyclopropane and bromine to 1,3-dibromopropane[6] and the thermal and photochemical synthesis of 1,3-diiodopropane from cyclopropane and iodine.[7]

Experimental

Cyclopropyl cyanide was prepared in 55–66% yield by the method of Cloke and co-workers.[8] The product was distilled through a 40-plate glass center rod column and material boiling at 131.5–132.0°, n^{20}_D 1.4161, was used throughout the study.

Cyclopropyl methyl ketone, Matheson Co., was distilled through the center rod column and material boiling at 110–111° was taken for use.

Phenylcyclopropane was prepared by an adaptation of the method of Kishner.[9] A mixture of 118 g. of 5-phenyl-3-pyrazoline, prepared by the method of Lardelli and Jeger,[10] 30 g. of pulverized potassium hydroxide and 2.5 g. of platinized asbestos[11] was heated in a one-liter, three-necked flask equipped with a stirrer and a Claisen distillation head. The temperature was raised slowly by means of a Glas-Col mantle and the heat was shut off at the first sign of reaction. When the exothermic reaction ceased the temperature was again raised and the product was distilled. Both the distillate and the residue were steam distilled and the steam distillate was taken up in ether and dried first with sodium sulfate and then with sodium and redistilled. The product was collected at 60–63° (11 mm.) and was finally redistilled giving a colorless oil, wt. 11.5 g. (12%), b.p. 173.5° (740 mm.), n^{20}_D 1.5320.

β-Methylstyrene was prepared by the dehydration of phenylethylcarbinol with phosphoric acid.[12] The product was a colorless liquid, b.p. 53–56° (11 mm.).

Decomposition of Benzoyl Peroxide in Cyclopropyl Cyanide.—A solution of 0.529 g. of benzoyl peroxide in 10.58 g. of cyclopropyl cyanide was degassed by evacuation to 1 mm. at −78°, sealed and heated at 82° for 24 hours. The contents of the tube were distilled giving essentially quantitative recovery of the nitrile.

In another experiment a solution of 20.13 g. of peroxide and 11.10 g. of nitrile in 250 cc. of carbon tetrachloride was degassed, sealed and heated at 82° for 24 hours.

The product mixture was fractionally distilled through

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(1) For a general summary see R. A. Raphael, "Chemistry of Carbon Compounds," Vol. IIA, "Alicyclic Compounds," Elsevier Press, Houston, Texas, 1953, pp. 25–28.

(2) J. D. Roberts and P. H. Dirstine, THIS JOURNAL, **67**, 1281 (1945).

(3) H. C. Brown and M. Borkowski, *ibid.*, **74**, 1894 (1952).

(4) A. F. Trotman-Dickenson and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 329 (1951).

(5) H. E. Gunning and E. W. R. Steacie, *ibid.*, **17**, 351 (1949).

(6) M. S. Kharasch, M. Z. Fineman and F. R. Mayo, THIS JOURNAL, **61**, 2139 (1939).

(7) R. A. Ogg and W. J. Priest, *J. Chem. Phys.*, **7**, 736 (1939).

(8) J. B. Cloke, R. J. Anderson, J. Lachmann and G. E. Smith, THIS JOURNAL, **52**, 2791 (1921).

(9) N. Kisbner, *J. Russ. Phys. Chem. Soc.*, **45**, 949 (1913); *C. A.*, **7**, 3965 (1913).

(10) G. Lardelli and O. Jeger, *Helv. Chim. Acta*, **32**, 1817 (1849).

(11) D. O. Shelis, *J. Phys. Chem.*, **33**, 1167 (1929).

(12) W. M. Dehn and K. E. Jackson, THIS JOURNAL, **55**, 4285 (1933).