

ment in the C-Cl bond in a more SN₂ like transition state and a similar argument would apply.

The most reassuring observation supporting the solvent reorganization argument is the behavior of the entropy of activation. It has been argued above that the inversion of the net molecular dipole vector direction in the activation process for *p*-nitrobenzyl chloride should result in considerable reorganization of the solvation shell compared with the *p*-methyl case. Although the activation entropies shown in Table II are only approximate in view of the fact that rates and activation energies at the same temperature are not available, there can be little doubt that the greater degree of reorganization in the *p*-nitro case is reflected in the very much larger negative ΔS^* value compared with *p*-methyl. Had the solvent shell change in the activation process been merely one of enhanced electrostriction of a shell of essentially initial state composition due to enhanced polarity of the C-Cl bond, a greater $-\Delta S^*$ value for the *p*-methyl would have been expected.

The comparison of the activation parameters in the two systems and consideration of the various dipole vector changes therefore lend strong support to the argument that solvation shell composition changes do take place in the activation process as assumed in the specific solvation model.

Conclusion

The observed temperature dependence of activation energy behavior for the solvolysis of benzyl chloride in ethanol-water mixtures and the effect of *p*-substitution both lend support to the argument that specific solvation by one or other of the components of the binary solvent system plays an important role in determining the activation parameters associated with reactions in mixed solvents.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO, BOULDER, COLO.]

Hydrolysis Reactions of Halogenated Cyclobutene Ethers: Synthesis of Diketocyclobutenediol^{1a}

BY J. D. PARK, S. COHEN^{1b} AND J. R. LACHER

RECEIVED MARCH 5, 1962

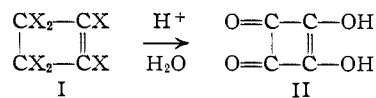
The hydrolysis reactions of 1,2-diethoxy-3,3,4,4-tetrafluorocyclobutene and 1,3,3-triethoxy-2-chloro-4,4-difluorocyclobutene were studied under acidic and basic conditions. Complete hydrolysis of the above compounds resulted in the isolation and identification of diketocyclobutenediol, a new dibasic acid with interesting properties. The anion of this dibasic acid is a member of a series of symmetrical electron delocalized anions, C_nO_n⁻², representing a new class of aromatic substances. This paper is an extension of a study first reported earlier.²

Recently, much interest has been shown in compounds possessing the cyclobutadienoquinone structure since they represent stable molecules with the same formal degree of strain as in the elusive cyclobutadiene, since all four carbon atoms have sp² bonding. Cyclobutadiene, however, has never been prepared although its brief existence has been erroneously reported³ and later shown to be a dimer of cyclobutadiene.⁴ Blomquist and Maitlis have recently reported the synthesis of 3,4-dimethylene cyclobutene.⁵ Sharts and Roberts⁶ have reported cyclohexenyl derivatives of cyclobutadienoquinone.

Prior to this time, only aromatic-substituted derivatives of cyclobutadienoquinone had been prepared.⁷

Roberts has estimated from heat of combustion data that the cyclobutadienoquinone ring system should have a resonance energy (or discrepancy energy using Doering's nomenclature) of 31–60 kcal. per mole.^{7b,8} This being true, it would therefore seem that cyclobutadienoquinone-type structures should be stable even without resonance stabilization contributions from aromatic substitution.

If this is the case, then diketocyclobutenediol would be the logical end product obtainable from the complete hydrolysis of the cyclobutene ethers according to the scheme where X = halogen and/or alkoxy¹



Both Roberts^{7a,7b} and Blomquist^{7c} prepared their phenylcyclobutadienoquinone compounds by hydrolyzing with concentrated sulfuric acid the fluorine atoms which were allylic to a phenyl group. This also becomes simple chemistry, since $\text{CF}_2\text{CH}=\text{C}(\text{C}_6\text{H}_5)\text{CF}_2$ is a vinylog of $-\text{CF}_2-\text{C}_6\text{H}_5$. Ben-

(1) (a) This paper represents part of a thesis submitted by S. Cohen to the Graduate School, University of Colorado, in partial fulfillment of the requirements for the Ph.D. degree, Aug., 1959. (b) Continental Oil Co. Fellow, Ponca City, Okla., 1957–1958.

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zal-type halogens are very prone to hydrolysis and many synthetic procedures have been built up on this reaction to give C_6H_5COR compounds. It is evident that many simple reactions of organic chemistry can be used on substituted cyclobutene systems to give a variety of interesting cyclobutenones.

The Hydrolysis of the Cyclic Ethers.—The method giving the highest yield of diketocyclobutenediol was found to be the hydrolysis of the diether, 1,2-diethoxy-3,3,4,4-tetrafluorocyclobutene. Although the triether, 1,3,3-triethoxy-2-chloro-4,4-difluorocyclobutene, gave substantial amounts of diketocyclobutenediol merely by reflux in water, there is a greater weight loss and other products result. The diketocyclobutenediol is quite stable so that by simply heating a stirred mixture of the diether with three times its weight of 50% aqueous sulfuric acid at 100° for approximately 12 hours, almost quantitative hydrolysis is effected.

The hydrolysis of the triether with water is much more interesting and complex although a poorer synthetic method for diketocyclobutenediol itself. The triether, which is a vinylog of an orthoester, was hydrolyzed under initially mild conditions—merely a water reflux. On working up the products, the following compounds were found: $CF_2C(OH)=CClCO$, $COC(OH)=C(OH)CO$, $CF_2C(OEt)_2-CHClC(OEt)_2$, HF, HCl, SiO_2 and EtOH.

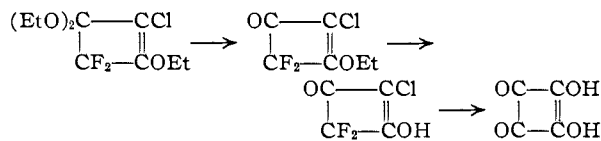
The acid, $CF_2C(OH)=CClCO$, is easily accounted

for as being the product of hydrolysis of the ethoxy functions in the triether ortho-type ester: $CF_2C(OEt)=CClC(OEt)_2 \rightarrow CF_2C(OEt)=CClCO \rightarrow CF_2C(OH)=CClCO$. The infrared spectrogram of

this acid showed a carbonyl absorption at 5.6μ , a $C=C$ conjugate absorption at 6.2μ , and a broad absorption in the acid hydrogen-bonding range. Upon esterifying with ethanol the cyclobutenone structure $CF_2C(OEt)=CClCO$ was obtained which is identical

with that prepared by ketalization of the triether. Upon standing with dilute nitric acid, the solution of the cyclobutenol shows a fluoride ion test but no test for the Cl^- ion. After boiling a few minutes, the chloride ion starts appearing. This would indicate that in the hydrolysis reaction, the enol first converts into $COC(OH)=CClCO$ which being an acid chloride

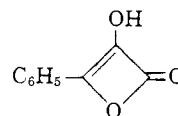
further hydrolyzes to diketocyclobutenediol. The most reasonable path of hydrolysis of the triether therefore would be



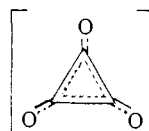
A small amount of the tetraether, $CF_2C(OEt)_2-CClHC(OEt)_2$ was obtained: this probably arose from the addition of ethanol to the initial triether.

In acidic solutions, fluorinated olefins can add ethanol across the double bond.⁹

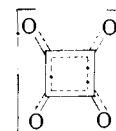
Due to its acid strength (pK_2 of 3.0) diketocyclobutenediol should exist entirely as the dienolate. Roberts' extremely strong acid, 4-hydroxy-3-phenylcyclobutene-1,2-dione with a pK_a of 0.37 also exists entirely as the enolate.^{7b}



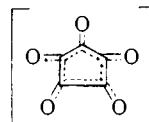
The dienolate $C_4O_4^{2-}$ is a symmetrical electron delocalized anion. It is a member of a general series of symmetrical resonance stabilized anions $C_nO_n^{2-}$, whose salts have been considered as a new class of aromatic substances.¹⁰ In the infrared



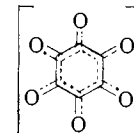
$C_3O_3^{2-}$
unknown as yet



$C_4O_4^{2-}$
"squarate"



croconate



rhodizinate

spectrogram of the anhydrous dipotassium salt, $K_2C_4O_4$, the carbonyl and the carbon double bond absorptions of the acid have vanished and instead an extremely intense absorption from 6.5 to 6.75μ appears. This is in the accepted range for $C-O$ vibration in acid salts¹¹ and represents the breathing vibration of the anion as a whole. The infrared spectrograms of the dipotassium salts of croconic acid and rhodizonic acid are similar to $K_2C_4O_4$ in that there is no infrared absorption in the usual carbonyl region and a strong broad band appears around 6.6μ .

Since the cerate cleaved all four $C-C$ bonds and only CO_2 was produced, this proves that each carbon atom was substituted only with an oxygen function. This solid acid analyzed for $H_2C_4O_4$ and the potassium salt, which crystallized with one molecule of water of hydration, analyzed exactly for $K_2C_4O_4 \cdot H_2O$. Diketocyclobutenediol in our laboratory has been given the trivial name "squaric acid" (first suggested by Dr. G. V. D. Tiers of the 3M Company).

Experimental

1,3,3-Triethoxy-2-chloro-4,4-difluorocyclobutene¹² and 1,2-diethoxy-3,3,4,4-tetrafluorocyclobutene¹³ were prepared according to previously described methods.

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1,3,3-Triethoxy-1,2,2-trichloro-4,4-difluorocyclobutane.—Into a glass cylinder fitted with a sintered-glass frit and a reflux condenser was placed 101.5 g. (0.40 mole) of the triether and 50 ml. of carbon tetrachloride. Chlorine gas was passed through the solution for 4 hours during which time the cylinder was immersed in a salt-ice cooling bath and covered with black cloth. Although 58 g. of chlorine had passed into the solution, the gain in weight was only 4 g. Excess chlorine in solution as well as hydrogen chloride was removed by warming and shaking the product under slight vacuum. The clear, colorless oil was first distilled under vacuum in a Todd column. From 56 g. of the product mixture, two pure materials were obtained: 11 g. of low boiling compound, 58–60° (4 mm.), n_D^{25} 1.4452, d_4^{25} 1.340 with a sharp penetrating odor; and 34 g. of a viscous, sweet smelling oil, b.p. 100–101° (4 mm.), m.p. 26°, n_D^{25} 1.4492, d_4^{25} 1.325. The low boiling fraction was subsequently shown to be cyclobutenone corresponding to the hydrolysis of the ketal group of the triether: 2-chloro-3-ethoxy-4,4-difluoro-2-cyclobutenone. The infrared spectrogram showed a carbonyl absorption at 5.6 μ and a C=C absorption at 6.1 μ ; the curve was identical with that of the authentic material. The high boiling fraction was the chlorine addition product 1,3,3-triethoxy-1,2,2-trichloro-4,4-difluorocyclobutane. Infrared showed no unsaturation of any kind.

Anal. Calcd. for $C_{10}H_{16}Cl_2F_2O_3$: C, 36.7; H, 4.61; Cl, 32.4; F, 11.6; M.R., 66.0. Found: C, 36.84; H, 4.74; Cl, 32.2; F, 11.8; M.R., 66.1.

2-Chloro-3-ethoxy-4,4-difluorocyclobutenone. A. HCl Ketalysis.—The vinyl ketone was prepared by the ketalysis of the triether using anhydrous hydrogen chloride in diethyl ether. A mixture of 25.5 g. (0.1 mole) of the triether and 150 ml. of anhydrous diethyl ether was treated with anhydrous hydrogen chloride for 12 hours. The reaction mixture was poured into ice and the ether layer then dried over anhydrous sodium sulfate. After the removal of the ether solvent, the product was rectified on the Todd column. The cyclobutenone was obtained in 60% yield, 11.0 (0.06 mole), b.p. 76° (7 mm.), n_D^{25} 1.4469, d_4^{25} 1.346. This liquid with a very penetrating odor was identical with the low boiling fraction from the above chlorination reaction as was shown by the infrared spectrogram and analysis. The unreacted triether was recovered (9.1 g.).

Anal. Calcd. for $C_8H_8F_2ClO_2$: C, 39.47; H, 2.76; Cl, 19.42; F, 20.81; ethoxyl, 24.6; sapon. equiv., 182.5. Found: C, 39.47; H, 2.98; Cl, 19.37; F, 19.62; ethoxyl, 23.9; sapon. equiv., 180.

The above analytical sample, as well as all liquids analyzed, were purified by vapor phase gas chromatography.

B. Phosphorus Pentachloride Ketalysis.—A mixture of 12.5 g. (0.06 mole) of solid phosphorus pentachloride and 15.5 g. (0.06 mole) of the cyclobutene triether was heated in an oil-bath. At 70° light foaming began; the temperature was maintained at 70 to 80° for 3 hours. At the end of this foaming period, the temperature was raised to 90°. Meanwhile, ethyl chloride collecting in a Dry Ice trap (b.p. 10–11°) was identified by means of its infrared spectrogram.

The mixture was poured onto ice and some sodium carbonate was cautiously added to complete the hydrolysis of the phosphorus oxychloride by-product. The product was taken up in methylene dichloride and dried over anhydrous sodium sulfate. After removal of the solvent, the resulting oil was vacuum distilled to give 9.0 g. (82% yield) of the cyclobutenone, b.p. 65° (4.5 mm.), n_D^{25} 1.4471. The infrared spectrogram was identical with that obtained from the hydrogen chloride procedure. In other preparations with phosphorus pentachloride, the phosphorus oxychloride was removed by distillation and the cyclobutenone product then distilled.

Diketocyclobutenediol. The Hydrolysis of the Triether.—A two-phase mixture of 18.53 g. (0.07 mole) of 1,3,3-triethoxy-2-chloro-4,4-difluorocyclobutene, n_D^{25} 1.4280, and 50 ml. of distilled water was stirred and heated in an oil-bath; no visible reaction was evident after 4 hours at 95°. At 101° slow reaction began and the lower triether layer started to hydrolyze while a gentle reflux occurred. After 5 hours the lower layer had disappeared and the reaction mixture was clear, one phase, and light yellow in color. The temperature in the flask at the end of this reaction was 84°, while the oil-bath was 102°, due to the refluxing ethanol formed during hydrolysis. Upon cooling a light yellow solid had crystallized out of the strongly acidic reaction solution.

The solid (2.53 g.) was removed by filtration of the reaction mixture and combined with a second fraction obtained after ice cooling. It was triturated with hot ethanol to remove any coprecipitated material. The strongly acidic solid was then purified by recrystallization from hot water. Upon cooling 2.0 g. (0.018 mole) of white diketocyclobutenediol with a decomposition point about 293° was obtained. Purification is quite simple since diketocyclobutenediol is about 7% soluble in boiling water and 2% soluble at room temperature. It does not appear to be soluble in acetone or ether and so can be dried quickly using these solvents as rinses; the solid is not hygroscopic.

The compound gives an intense purple color with ferric chloride solution characteristic of enols; it decolorizes permanganate solution, bromine water, and ceric nitrate which oxidizes it quantitatively to CO_2 . It titrates easily as a dibasic acid giving a neutralization equivalent of 57.9; calcd. 57.1. The acid gives a strong periodic acid test characteristic of adjacent oxygen-carbon linkages. It does not give a phenylhydrazone test since the carbonyls are not ketonic acid carbonyls. The infrared spectrogram of the solid showed a broad absorption at 4.3 μ characteristic of strong hydrogen bonding and chelation. The carbonyl absorption occurred at 5.5 μ and the C=C conjugation system absorbed at 6.1 μ . The ultraviolet absorption of a 10⁻⁴% aqueous solution was broad λ_{max}^{25} 269.5 m μ , ϵ 37,000. The infrared spectrogram of the dipotassium salt shows a very intense absorption band from 6.5 to 6.75 μ whereas the carbonyl and C=C absorptions of the acid disappear; this shows the equivalence of all four oxygens due to resonance.

Anal. Calcd. for $C_4H_2O_4$: C, 42.11; H, 1.78. Found: C, 42.21; H, 1.85.

1,1,3,3-Tetraethoxy-2-chloro-4,4-difluorocyclobutane.—The coprecipitated solid was dissolved in the hot ethanol used in triturating the original solid of the hydrolysis reaction. It was purified by crystallization from 80% ethanol solution. Beautiful white crystals amounting to 0.20 g. of 1,1,3,3-tetraethoxy-2-chloro-4,4-difluorocyclobutane, m.p. 85–85.5°, were obtained. The infrared spectrogram showed no absorption in the unsaturated regions and strong absorption at 8.95 and 9.55 μ characteristic of ethers. This tetraethoxy ether appears quite stable as it can be heated to boiling without decomposition. There was no reaction upon heating with ethanolic potassium hydroxide. A negative chloride test on the solution showed that no dehydrochlorination took place.

Anal. Calcd. for $C_{12}H_{21}ClF_2O_4$: C, 47.59; H, 6.99; Cl, 12.55; F, 11.78. Found: C, 47.37; H, 6.97; Cl, 12.70; F, 11.74.

3-Keto-2-chloro-4,4-difluorocyclobutenol.—In order to isolate without extensive decomposition the remaining hydrolysis products, which were in solution, the reaction medium was concentrated by vacuum drying. The solution (after removal of the above solids) was concentrated to 15 ml. by evacuating to 30 mm. pressure. The solvent caught in a cold trap was an aqueous ethanol solution from which 6.5 g. (0.14 mole) of ethanol was isolated. Some buff-colored solid crystallized out of the strongly acidic concentrated solution. The remaining liquid was evaporated to dryness at 0.5 mm. pressure. The material caught in the cold trap was a mixture of fairly concentrated aqueous hydrofluoric and hydrochloric acids from which silica, due to glass etching, settled out.

The residual solid amounting to 4.5 g. was difficult to recrystallize due to some decomposition. It was dissolved in water and extracted continuously with ether, in which it is very soluble. The solid (m.p. 114–119°) which is highly acidic, was found to contain fluorine and chlorine. The infrared spectrogram showed carbonyl and C=C conjugate absorptions at 5.6 and 6.2 μ , respectively. The neutralization equivalent found was 147 whereas the theoretical value corresponding to $CF_2C(OH)=CClCO$, which would result

from hydrolysis of the ethoxyl group, is 154. Upon refluxing with ethanol and benzene the acid was re-esterified to give $CF_2C(OEt)=CClCO$, identical with the previously prepared 2-chloro-3-ethoxy-4,4-difluorocyclobutenone.

Best Preparation of Diketocyclobutenediol.—The desired diketocyclobutenediol was prepared by the hydrolysis of the diether with 50% sulfuric acid.

A mixture of 250 ml. of aqueous 50% sulfuric acid solution and 80 g. (0.373 mole) of the diether was heated in an oil-bath for 12 hours at 100°. At the end of this time all the diether which was initially in the upper layer had been hydrolyzed and the flask was filled with white solid. Extensive etching occurred due to the reaction of hydrogen fluoride with glass. The solid was filtered and dissolved in 800 ml. of boiling water. Upon cooling the first fraction, 31 g. of diketocyclobutenediol crystallized. A total of 40 g. (0.35 mole) of white diketocyclobutenediol was obtained. It was dried by acetone-ether rinses and placed in an evacuated phosphorus pentoxide desiccator. The 40 g. represent a 94% yield based on the diether. The neutralization equivalent was 57.8; calcd. for the dibasic acid is 57.1. The infrared spectra of the solid acid and potassium salt were identical with that previously prepared from the hydrolysis of the triether. The cyclobutadienoquinone acid appeared to be stable up to 294° at which point it decomposed but did not melt. The diketocyclobutenediol showed the same chemical tests as the previously prepared material; a positive enol test with ferric chloride, oxidation by cerate, permanganate, periodic acid, and bromine water solutions. The dipotassium salt crystallized with one molecule of water of hydration.

Anal. Calcd. for $K_2C_4O_4 \cdot H_2O$; C, 23.07; H, 0.96; H_2O , 8.64. Found: C, 23.32; H, 0.99; H_2O , 8.53.

Quantitative Oxidation with Cerate Solution.— $H_2C_4O_4 + 10 Ce^{++} + 4 H_2O \rightarrow 4 CO_2 + 10 Ce^{+3} + 10 H^+$.

A 0.118 N ceric sulfate solution was made from hexanitratotriammonium cerate according to the procedure of G. Frederick Smith. Ten ml. of an aqueous 0.114 molar solution of diketocyclobutenediol was titrated with the standard cerate solution using the Beckman Zeromatic meter with a platinum indicating electrode and a calomel reference. The curve showed a very steep rise in potential at the equivalence point; 0.55 volt within 2 drops of cerate. The volume of cerate required was 95.2 ml.; *i.e.*, 1.14 ml. of compound required 11.2 meq. of cerate. This, therefore, showed the equivalent weight of the diketocyclobutenediol in oxidation to be 11.4 g. or 1/10 the molecular weight.

The inorganic reactions of the acid are quite interesting as colored precipitates are formed with many metal ions and relatively weak oxidizing agents like ferricyanide are reduced.

Acknowledgment.—We gratefully acknowledge the help of the Continental Oil Company of Ponca City, Okla., for a fellowship grant to one of us and to the Minnesota Mining and Manufacturing Co., St. Paul, Minn., for its partial support of this work.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BRIGHAM YOUNG UNIVERSITY, PROVO, UTAH]

Thermal Decomposition of 1,1'-Azobutane, 1,1'-Azoisobutane, 2,2'-Azobutane and 2,2'-Azoisobutane¹⁻³

BY ANGUS U. BLACKHAM AND NORMAN L. EATOUGH

RECEIVED MARCH 20, 1962

Four azobutanes have been prepared, each above 99 mole % in purity: 1,1'-azobutane, 1,1'-azoisobutane and 2,2'-azobutane from the appropriate aldehyde or ketone *via* the azine and dialkylhydrazine, and 2,2'-azoisobutane from *N*-bromo-*t*-butylamine and silver oxide. A flow system, designed so that during the sampling period the reaction products flow directly into a gas chromatographic column, was used to measure the rates of thermal decomposition in a small borosilicate glass reactor tube. Helium and hydrogen were used as carrier gases. Concentrations of approximately 1 and 5% of azo compound in the carrier gas were used. The rate of decomposition was determined by measurement of the nitrogen produced. The decomposition reaction of these azobutanes is first order. The activation energies for R—N=N—R in helium in which R, respectively, is *n*-butyl, isobutyl, *sec*-butyl and *t*-butyl are 53.2, 49.0, 48.4 and 43.0 kcal./mole. For each of the first three, the activation energy determined in hydrogen is less than that in helium. For 2,2'-azoisobutane the values are the same. The gaseous products of the thermal decomposition have been determined for each azobutane in both hydrogen and helium. These data indicate the relative extent of the coupling, disproportionation and decomposition reactions of the four butyl radicals.

Introduction

Free alkyl radicals are transitory species in the thermal decomposition of azoalkanes. In the initial step a molecule of azoalkane decomposes to a molecule of nitrogen and two alkyl radicals.⁴⁻⁶

This study was made to provide information concerning azobutanes as sources of four isomeric butyl radicals in the temperature range 200–400°. The kinetics of decomposition of four symmetrical azobutanes have been determined and the gaseous products of decomposition have been analyzed.

Experimental

2,2'-Azobutane.—Methylethyl ketazine was prepared in two ways: (1) by mixing 95% hydrazine and cold ethanol

at 0°, then slowly adding freshly distilled butanone, and refluxing for 6 hours⁷; and (2) by slowly adding hydrazine hydrate to twice the number of moles of butanone in diethyl ether at 0°, stirring at room temperature for 2 hours, distilling the ether, and drying with anhydrous potassium carbonate.⁸ Better yields were obtained by the second method. The methylethyl ketazine was hydrogenated⁹⁻¹² in an equivalent of glacial acetic acid dissolved in ethanol with platinum oxide and hydrogen at 60 p.s.i.g. The hydrogenation was complete in 5 to 7 days. The reaction mixture was filtered to remove platinum and made basic with 10 *M* sodium hydroxide. The ethanol was removed by extraction with water. The product was dried with potassium carbonate. Vacuum fractionation through a 25-inch Vigreux column gave 1,2-di-*sec*-butylhydrazine (b.p. 73–78° (25 mm.), 75% average yield).

This compound was oxidized by direct addition of an equivalent of mercuric oxide^{11,12} in small portions. The mixture was heated on a steam-bath for 1 hour and then let

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(2) Presented at the 140th Meeting of the American Chemical Society, Chicago, Ill., Sept. 7, 1961.

(3) Abstracted in part from a thesis submitted by Norman L. Eatough in partial fulfillment of the requirements for the degree of Master of Science, Brigham Young University.

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