[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Elimination Reactions of the 1,2-Dimethylcyclohexyl System

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RECEIVED NOVEMBER 30, 1953

The pyrolysis of *cis*- and *trans*-1,2-dimethylcyclohexyl acetates leads to the formation of large amounts of 2-methylmethylenecyclohexane. However, the *cis* isomer gives 5–10% 1,2-dimethylcyclohexene which is specifically absent from the products from the *trans*-acetate. In comparison experiments it was found that 1-methylcyclohexyl acetate gives about 86% methylenecyclohexane and 14% 1-methylcyclohexene. The isomeric 1,2-dimethylcyclohexyl bromides undergo second-order elimination with sodium hydroxide in 98% ethanol at rates which differ by a factor of twelve. The *trans* structure has been assigned to the fast isomer. The *trans*-bromide is stoichiometrically converted to 1,2-dimethylcyclohexene under conditions favorable for second-order elimination, but the *cis* isomer gives largely 2-methylmethylenecyclohexane.

In connection with another study it became necessary to assign structures to derivatives of the 1,2-dimethylcyclohexyl system. Since extensive studies have established the preferred steric course of the bimolecular elimination reaction[1,2] and of the pyrolytic elimination of carboxylic acids from their esters,[3–5] these reactions were utilized in establishing the structure of the compounds in question. The results form a picture which is in most respects consistent with previous speculations concerning the mechanisms of the reactions.

Experimental

***cis*- and *trans*-1,2-dimethylcyclohexanol** were prepared by the method of Chiurdoglu.[6] The addition of methylmagnesium bromide to 2-methylcyclohexanone was carried out in the usual manner. Care must be taken to maintain the reaction mixture at reflux temperature to prevent the formation of cakes by the insoluble product of the reaction. The mixtures were hydrolyzed with aqueous ammonium chloride, extracted with ether, washed, concentrated and distilled. Crude yields were about 90%.

A small amount of remaining ketone was best removed by warming the crude product with *p*-nitrophenylhydrazine for several hours before the final distillation. Fractionation of the isomeric alcohols at pressures of 25–55 mm. through a glass center-rod column (70 plates at atmospheric pressure) afforded a clean separation. Less than 1 ml. of mixed alcohols was obtained in the distillation of 100-g. batches. The yield of *cis*-alcohol varied somewhat in different batches but always constituted 7–10% of the crude mixture. No noticeable increase in the yield of the *cis* isomer was observed when methyllithium was used instead of the Grignard reagent in the preparation. The physical constants of the alcohols agree well with those previously reported.[8] The properties of materials used in this study are shown in Table I.

TABLE I

PROPERTIES OF *t*-ALCOHOLS (ROH) AND ACETATES (ROAc)

R	Alcohol B.p., °C.	Alcohol B.p., Mm.	Alcohol n^{25}_D	Acetate B.p., °C.	Acetate B.p., Mm.	Acetate n^{25}_D	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
cis-1,2-Dimethylcyclohexyl	95.7	53	1.4628	84	18	1.4440	70.5	69.9	10.6	10.6
trans-1,2-Dimethylcyclohexyl	86.8	52	1.4588	78	20	1.4401	70.5	69.4	10.6	10.3
1-Methylcyclohexyl	68	24	1.4582	74	20	1.4435	69.2	69.8	10.3	10.8

1-Methylcyclohexanol was prepared by the reaction of methylmagnesium bromide with cyclohexanone. The crude product was fractionated through the center rod column. The yield was 90%. The physical constants of material used in our study are included in Table I.

Acetates were prepared from the alcohols by the following procedure. About 0.05 mole of alcohol was mixed with 30 ml. of dimethylaniline and the solution was cooled in an ice-bath. About 0.10 mole of acetyl chloride was added to the stirred solution. The mixture was allowed to stand at room temperature for one hour and then was heated on the steam-bath for 3–4 hours. After cooling, the mixture was poured into ice-water containing 10% hydrochloric acid and extracted with pentane. The pentane solution was dried over potassium carbonate and distilled. Yields were virtually quantitative. Physical constants are shown in Table I.

***trans*-1,2-Dimethylcyclohexyl bromide** was prepared by the reaction of hydrogen bromide with 1,2-dimethylcyclohexene in pentane. About 0.05–0.10 mole of the olefin was dissolved in 10 ml. of pentane which had been purified by distillation from phosphorus pentoxide in a vacuum line. The solution was cooled in an ice-bath and hydrogen bromide, which had been redistilled and stored in another part of the line, was admitted to the flask. Gas was adsorbed rapidly by the solution and the pressure became constant after about 15 minutes. Stirring was continued for 45 minutes and then the reaction vessel was removed from the line and the product was worked up. The pentane solution was washed with aqueous bicarbonate and water and was dried over Drierite. The pentane was removed by distillation. The residual bromide always underwent some decomposition on distillation and was, therefore, purified for analysis by flash distillation. However, the raw product gave the theoretical amount of acid in solvolysis experiments and solvolyzed at a uniform rate in experiments which were carried to 95–98% completion.

Anal. Calcd. for $C_8H_{15}Br$: C, 50.3; H, 7.9; Br, 41.9. Found: C, 51.2; H, 7.6; Br, 41.2; n^{20}_D 1.4940; d^{25}_{25} 1.2318.

***cis*-1,2-Dimethylcyclohexyl bromide** was never obtained pure, but mixtures with the isomeric bromide were obtained by a number of methods. The highest yields of the *cis* isomer were obtained by the reaction of hydrogen bromide with *cis*-1,2-dimethylcyclohexanol at −78°.[7] The mixed bromide was worked up as described above and was shown by solvolytic analysis to yield the theoretical amount of acid. The composition of the mixture rich in *cis* bromide was determined by the kinetic method described below.

Pyrolysis of the acetates was carried out by dropping the material to be cracked through a 10-mm. Pyrex tube packed with $^1/_{16}$ inch Pyrex helices and heated by a vertically mounted Fischer micro-combustion furnace. A plug of glass wool was used to keep the packing in place. The ester was delivered from a dropping funnel with a by-pass. The receiver was immersed in an ice–salt-bath. A slow stream of nitrogen was passed through the apparatus throughout a run. The acetates were introduced into the pyrolysis tube at a rate of 2–3 drops per minute. The products were collected in pentane over aqueous sodium bicarbonate, washed with water and dried. The pentane was distilled off care-

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[1] W. Hückel, W. Tappe and G. Legutke, *Ann.*, **543**, 191 (1940).

[2] S. J. Cristol and A. Begoon, THIS JOURNAL, **74**, 5025 (1952), and earlier papers in the series.

[3] C. D. Hurd and F. Blunk, *ibid.*, **60**, 2419 (1938).

[4] D. H. Barton, *J. Chem. Soc.*, 2174 (1949).

[5] E. R. Alexander and A. Mudrak, THIS JOURNAL, **72**, 1810, 3194 (1950).

[6] G. Chiurdoglu, *Bull. soc. chim. Belg.*, **47**, 241 (1938).

[7] T. D. Nevitt and G. S. Hammond, unpublished observations.

fully. Operating with 1-g. samples it was found that conversion to olefins was essentially quantitative in one pass at 450°. The olefin mixtures were analyzed as a three component system by examination of their infrared spectra in a 0.073 mm. cell. The spectra were compared with those of synthetic mixtures of 1,2-dimethylcyclohexene, 2,3-dimethylcyclohexene and 2-methylmethylenecyclohexane.[8] There is considerable overlapping of characteristic bands and no characteristic peaks were found which gave a close fit to Beer's law in the ternary mixtures. Compositions were estimated by graphical interpolation among the spectra of control mixtures which were made up to bracket closely the compositions of the product mixtures. The results are summarized in Table II. The infrared characteristics of the olefins which were utilized in the analyses are given in Table III.

TABLE II

PYROLYSIS OF ACETATES (ROAc) AT 450°

	Product composition, %		
R[a]	1,2-Dimethylcyclohexene	2,3-Dimethylcyclohexene	2-Methylmethylenecyclohexane
Trans	0	7 ± 3	93 ± 5
Trans	0	12 ± 3	88 ± 5
Cis	4 ± 3	5 ± 3	91 ± 5
Cis	9 ± 3	5 ± 3	86 ± 5
	Methylenecyclohexane		1-Methylcyclohexene
MC	86 ± 5		14 ± 5
MC	87 ± 5		13 ± 5

[a] *Trans* and *cis* refer to 1,2-dimethylcyclohexyl, MCH is 1-methylcyclohexyl.

TABLE III

INFRARED CHARACTERISTICS OF THE OLEFINS

Compound	Optical density (pure liquid)	Frequency, cm.$^{-1}$
1-Methylcyclohexene	0.592	1262
	.630	1140
	.612	760
Methylenecyclohexane	.450	1110
	.554	981
	.270	833
1,2-Dimethylcyclohexene	.473	1350
	.354	1260
	.297	1230
2,3-Dimethylcyclohexene	.542	1300
	.718	980
	1.137	800
2-Methylmethylenecyclohexane	0.588	1248
	.438	951
	.412	928

The composition of the olefin mixture was determined by comparison with the spectra of synthetic mixtures of 1,2-dimethylcyclohexene, 2,3-dimethylcyclohexene and 2-methylmethylenecyclohexane as described above. The results of the experiments are summarized in Table II.

The reaction of *trans*-bromide with lithium aluminum hydride was carried out by adding an ether solution containing an excess (3:1) of lithium aluminum hydride to a solution of the bromide in ether. The mixture was allowed to stand at room temperature for three days, hydrolyzed with sodium potassium tartrate solution, extracted with pentane and worked up as usual. The spectrum of the product was identical with that of the pure 1,2-dimethylcyclohexene.[9,10]

The reaction of the *trans*-bromide with heterocyclic bases was carried out by allowing a solution of the bromide in the base (pyridine, 2-picoline and 2,6-lutidine) to stand at room temperature for 4 days. The mixture was then heated to 60° for three hours and worked up by adding pentane, washing with dilute sulfuric acid and water, drying and stripping off the pentane. The progress of the reactions could be observed in a qualitative manner because the amine hydrobromides crystallized from the reaction mixtures. It was quite evident that pyridine reacted more rapidly than 2-picoline which in turn was faster than 2,6-lutidine. Further evidence was obtained by examination of the spectra of the products. It was evident that the reaction with lutidine had not gone to completion as strong bands characteristic of the bromide appeared in the spectrum of the residue after removal of pentane, whereas essentially quantitative yields of olefins were obtained with the less hindered bases.

The accuracy of the analytical method was poor but it was found that *trans*-bromide gives immeasurably small amounts of olefins other than 1,2-dimethylcyclohexene in all of the reactions described above. When treated with the heterocyclic bases at 100° the yield of symmetrical olefin was decreased (about 86% with lutidine) and more of the exocyclic isomer was produced.

TABLE IV

ELIMINATION FROM 1,2-DIMETHYLCYCLOHEXYL BROMIDES WITH SODIUM LYATE IN 98% ETHANOL AT 25°

	Product, %	
Composition of bromide mixture	1,2-Dimethylcyclohexene	2-Methylenemethylcyclohexane
22% *cis*	87 ± 5	13 ± 5
63% *cis*	50 ± 5	50 ± 5
100% *trans*	100	0

Solvolysis rates were measured in 55.4 mole per cent. water–methyl ethyl ketone, in 98% methanol and in 98% ethanol. The reaction was followed by periodically removing aliquots which were titrated with a standard solution of triethylamine in benzene or toluene. Brom phenol blue was employed as an indicator and ionic strength was controlled by the addition of varying amounts of lithium perchlorate.

The rates of second-order elimination reactions were measured in dry methanol and in 98% ethanol. Exactly 100 ml. of standard solution, prepared by dissolving clean sodium metal in the alcohol, was introduced into the reaction flask and allowed to come to equilibrium in the constant temperature bath. Then approximately 0.4 ml. of the bromide was added by means of a pipet. Five-ml. aliquots were removed periodically for analysis. Samples were quenched by delivery from the pipet into 25 ml. of cyclohexane. The cyclohexane solution was then extracted twice with 20-ml. portions of 3 *N* nitric acid. The extracts were combined and ionic bromide was determined by the Volhard method.[13] The original concentration of alkyl bromide was determined by adding a 5-ml. aliquot to 20–25 ml. of water, allowing the mixture to stand for 24 hours in a stoppered flask and then determining its acid titer. The same procedure was used for determination of the solvolysis equivalent of weighed samples of the bromides.

Pseudo-unimolecular rate constants were determined using the integrated form of the first-order law. Constants were calculated between successive points and averaged. In order to determine the bimolecular rate constants, runs were carried out in which the initial concentration of base was varied. The pseudo first-order constants, k', were then fitted to the standard expression, $k' = k_2[\mathrm{B}] + k_1$ where k_2 is the bimolecular rate constant, [B] the average concentration of base varied 10% or less during the course of individual runs.

The rate of elimination from the *cis*-bromide was determined in runs with mixtures containing 60–70% of that isomer. The reaction in solutions in which the initial concentration of base was 0.2–0.5 *N* was followed carefully from the point at which it was calculated that 99% of the *trans*-bromide had been consumed to the time at which a

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(8) G. S. Hammond and T. D. Nevitt, THIS JOURNAL, **76**, 4121 (1954).

(9) It is interesting to note that *trans* elimination is apparently the preferred course with lithium aluminum hydride here as it was in a case previously reported by Cram.[11]

(10) Letsinger and Bobko have recently reported[12] that a somewhat similar reagent, butyllithium, shows a preference for *cis* elimination of the elements of phenol from a pair of stereoisomerically related phenyl ethers.

(11) D. J. Cram, THIS JOURNAL, **74**, 2149 (1952).

(12) R. L. Letsinger and E. Bobko, *ibid.*, **75**, 2649 (1953).

(13) H. H. Willard and N. H. Furman, "Elementary Quantitative Analysis," 2nd Ed., D. Van Nostrand Co., Inc., New York, N. Y., 1935, p. 139.

like fraction of the *cis*-bromide had been consumed. Extrapolation of a first-order plot of these points to zero time gave the initial concentration of *cis*-bromide. The concentration of *trans*-bromide was determined as the difference between the initial concentration of *cis*-bromide and the total base consumed at infinity.

The kinetic data are summarized in Tables V and VI.

TABLE V

RATES OF SOLVOLYSIS OF CYCLOALKYL BROMIDES (RBr) AT 25.3°

R[a]	Medium	$LiClO_4$, *N*	$k_1 \times 10^6$, sec.$^{-1}$
trans	98% EtOH	0.000	6.0 ± 0.1
trans	98% EtOH	.059	6.8 ± .1
trans	98% EtOH	.118	7.8 ± .1
trans	98% EtOH	.177	8.8 ± .1
trans[b]	98% EtOH	.236	9.7 ± .2
trans	98% EtOH	.100	7.6 ± .1
trans + *cis*[c]	98% EtOH	.100	7.5 ± .1
trans	Methanol	.100	51.1 ± .6
trans	H_2O–MEK[e]	.098	34.7 ± .6
trans + *cis*[d]	H_2O–MEK	.098	35.3 ± .6
MCH	H_2O–MEK	.098	31.7 ± .6

[a] *trans* and *cis* refer to 1,2-dimethylcyclohexyl, MCH is 1-methylcyclohexyl. [b] Value given is average over the course of a run. [c] Mixture containing 62% *cis*. [d] Mixture containing 71% *cis*. [e] 55.4 mole % water in methyl ethyl ketone.

TABLE VI

RATES OF BIMOLECULAR ELIMINATION REACTIONS

R	Base, *N*	Pseudo first-order rate constant × 10^5, sec.$^{-1}$	Second-order rate constant × 10^4, liter mole sec.$^{-1}$
		In methanol	
trans	None	6.0 ± 0.1	....
trans	0.0151	7.0 ± .1	(6.6 ± 2.3)
trans	.0303	7.7 ± .2	5.3 ± 0.08
trans	.0605	9.0 ± .2	5.0 ± .06
trans	.158	11.1 ± .2	3.3 ± .05
		In ethanol	
trans	None	0.60 ± .01	....
trans	0.0395	2.0 ± .07	3.3 ± 0.5
trans	.0790	2.7 ± .1	2.5 ± .2
trans	.345	8.7 ± .2	2.3 ± .2
trans	.520	14.7 ± .5	2.5 ± .1
cis	.000	0.60 ± .01	....
cis	.345	1.63 ± .03	0.17 ± 0.06
cis	.520	2.43 ± .07	.20 ± .04

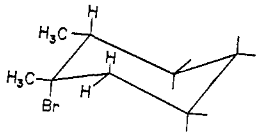
Discussion

Acetate Pyrolysis.—The results of the acetate pyrolysis are in reasonably good agreement with previous work. Bailey and King[14] found that the pyrolysis of a number of aliphatic acetates occurred in a highly structurally specific manner with a number of acyclic, unsymmetrical secondary and tertiary alkyl functions. It was found that in every case only the least substituted olefin was produced in detectable yield. A cursory examination shows a similar structural specificity in our study. However, it is disquieting to note that the endocyclic isomers are produced in appreciable yield despite the fact that a study of molecular models indicates that steric factors which may account in part for the preference for formation of methylene compounds should be of greater importance in the cyclic compounds. In order to ascertain that isomerization of products does not occur under the conditions of the experiment a mixture rich in 2,3-dimethylcyclohexene and an equivalent amount of acetic acid was passed through the furnace. The infrared spectrum of the olefin mixture was unchanged by this procedure.

The stereospecificity[3–7] of the pyrolysis reaction is demonstrated by the fact that the *cis*-acetate gives a few per cent. of 1,2-dimethylcyclohexene, whereas this olefin is specifically absent from the product mixture formed from the *trans* isomer. The contrast is clean-cut and constitutes strong confirmatory evidence for the structures assigned to the acetates and the parent alcohols. That no configurational changes occurred in the course of the acetate synthesis is demonstrated by the fact that the original alcohols are produced by cleavage of the esters with lithium aluminum hydride.

Elimination from the Bromides.—Qualitative observation of the infrared spectra of the products formed in a variety of reactions designed to produce 1,2-dimethylcyclohexyl bromides indicated considerable variation in the relative amounts of *cis* and *trans* isomers formed in the various reactions. The absence of structural isomers was established in several ways. The treatment of the mixtures with sodium lyate (hydroxide and ethoxide) in 98% ethanol or with sodium methoxide in methanol gave olefin mixtures which varied in composition but which were hydrogenated to give essentially pure *cis*-1,2-dimethylcyclohexane in nearly quantitative over-all yield. Furthermore, the solvolysis of the bromide mixtures gave clean first-order kinetics in runs which were carried to better than 95% completion. The rate of solvolysis of 1-methylcyclohexyl bromide was determined in one of the solvents, methyl ethyl ketone–water, and was found to be less than 10% lower than the one constant found for a variety of bromide mixtures. These observations make it seem rather certain that no skeletal rearrangements occurred during the course of any of the synthetic reactions.

It is also noteworthy that there is no kinetic evidence for an extra driving force in the solvolysis of the *trans*-bromide. Such an acceleration, had it been observed, could have been attributed to participation by neighboring hydrogens which are properly oriented for such interaction. It seems certain that the highly preferred conformation of this compound is I in which bromine is polar. In this structure there are two β-hydrogens which, with the bromine and two intervening carbon atoms, lie in a *trans*, coplanar configuration.



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This orientation would, however, be expected to appear highly favorable for the formation of the *trans*, coplanar transition state believed to be highly preferred for bimolecular elimination reactions. In accordance with this view it was found that a bromide, which was essentially pure *trans*, produced

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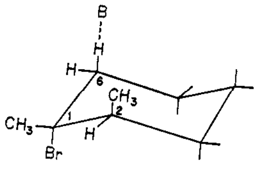
(14) W. J. Bailey and C. King, Abstracts of Meeting of the American Chemical Society, September, 1952, p. 8 M.

by the addition of hydrogen bromide to 1,2-dimethylcyclohexene in pentane, reacted very much more rapidly with strong bases than did mixtures. By kinetic analysis it was possible to show that the mixtures contained two components, one of which reacted approximately 12 times as fast as the other in second-order elimination reactions. The data reported in Table IV show furthermore that the fast component is converted exclusively to 1,2-dimethylcyclohexene, whereas the isomer gives relatively little of the symmetrical olefin. On this basis the assignment of the *trans* structure to the more reactive component seems unambiguous.

It is of interest to note that no more than trace amounts of 2,3-dimethylcyclohexene are formed from either bromide in bimolecular eliminations. While equilibration studies have not been carried out, it seems probable that the standard free energy of the exomethylene olefin is higher than that of the unsymmetrical endocyclic isomer.[15]

It is not difficult to rationalize the fact that the *cis*-bromide gives largely the exomethylene olefin in the E_2 reaction. Although *trans* elimination could go through a planar transition state much as II the methyl group at C_2 is so close to the *trans*-hydrogen on C_6 that some steric strain should exist between B and the methyl hydrogens.



II

The *trans*-bromide was allowed to react with a series of bases, pyridine, 2-picoline and 2,6-lutidine since it seemed possible that relatively large amounts of the exomethylene isomer might be formed as steric requirements were increased. No such trend was observed when the reactions were carried out at room temperature although the reaction rate was obviously decreased as the bulk of the base was increased. At 100°, picoline and lutidine, especially the latter, gave appreciable amounts of exomethylene compound. This may indicate that the activation energy of the E_2 reaction at the methyl group is becoming close enough to that of the reaction at the ring C–H to allow the former reaction to become competitive at the higher temperature. However, it is not possible to distinguish this from a similar increase in the competition from a carbonium ion mechanism at the higher temperatures.

Synthesis of Tertiary Acetates.—It is worth noting that highly efficient conversions of the tertiary alcohols to esters was achieved by acetylation with acetyl chloride in dimethylaniline as solvent. The more common procedure in which pyridine is used instead of dimethylaniline was found to be completely unsatisfactory.

Acknowledgment.—We are indebted to Miss Katherine Douglas for aid in the infrared spectroscopy and to the Iowa State Institute for Atomic Research for the use of the instrument. One of us (T.D.N.) is grateful for the partial support of this study by a fellowship grant from the Iowa State Research Institute.

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[15] This is based upon the assumption that the usual difference in the strain energy in endo- and exocyclic isomers[16] is not outweighed by repulsion between methyl groups.

[16] W. Hückel, "Theoretische Grundlagen der organischen Chemie," 2nd ed., Akademische Verlagsgesellschaft, Leipzig, 1934, p. 72.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OREGON STATE COLLEGE]

The Use of Monosubstituted Acetoacetic Esters in the Robinson Reaction[1]

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RECEIVED MARCH 15, 1954

A series of 2-oxo-3-alkyloctahydronaphthalenes has been prepared by Robinson's method using the methiodide of the Mannich base derived from cyclohexanone, formaldehyde and dimethylamine, and a series of substituted acetoacetic esters. Further substitution has been achieved by means of Grignard reaction with the keto group in the two position. The Robinson reaction has been shown to proceed reasonably well when alkyl-substituted acetoacetic esters are employed but to fail with aryl-substituted esters. Isomeric ketones were isolated when ethyl methylacetoacetate was used. A mechanism for the Robinson reaction is proposed.

It was originally shown by Robinson[3] that quaternary salts derived from Mannich bases may be employed conveniently for the alkylation of certain active-hydrogen containing molecules. The method has since found successful application,[4,5] and has been termed the α-acylethylation reaction by Lions.[5] With Mannich bases derived from cyclohexanone Robinson[3] was able to alkylate acetoacetic ester, the initial alkylation being followed by a ring closure of the aldol type. This process proved useful as a means for the synthesis of the decalin ring system.[3,6] However, there appears to be no record of any substituted aceto-

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[1] This work was supported by the Atomic Energy Commission under contract with Oregon State College and by a fellowship from E. I. du Pont de Nemours and Co., Inc., during 1952–1953 (R.L.P.). Published with the approval of the Monographs Publications Committee, Oregon State College, as Research Paper No. 246, School of Science, Department of Chemistry.

[2] This work was abstracted from theses submitted by Richard LaPore (du Pont Fellow in Chemistry 1952–1953) and David C. Bush in partial fulfillment of the requirements for the Doctor of Philosophy degree at Oregon State College.

[3] E. C. DuFeu, F. J. McQuillan and R. Robinson, *J. Chem. Soc.*, **53** (1937).

[4] H. R. Snyder and L. Katz, THIS JOURNAL, **69**, 3140 (1947); E. E. Howe, A. J. Zambito, M. R. Snyder and M. Tishler, *ibid.*, **67**, 38 (1945); H. R. Snyder and L. Hamlin, *ibid.*, **72**, 5082 (1950).

[5] N. S. Gill, K. B. James, F. Lions and K. T. Potts, *ibid.*, **74**, 4923 (1952).

[6] N. S. Gill and F. Lions, *ibid.*, **72**, 3468 (1950).