

## The Dipole Moments of Some Aliphatic Ethers

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Dipole moments of eight ethers were measured in benzene solution. Table I gives the experimental data and the calculated results. The symbols  $f_2$ ,  $d$  and  $e$  refer to mole fraction of ether, density and dielectric constant, respectively. The molar refraction  $MR_D$  was calculated in each case from the atomic refractions.<sup>2</sup> The dipole moment  $\mu$  calculated by the method of Hedestrand<sup>3</sup> is given in Debye units. The moment of 1.28  $D$  for diethyl ether in benzene is in good agreement with the value of 1.27  $D$  given by Hassel and Uhl.<sup>4</sup> The values of 1.26 and 1.22  $D$  obtained for di-*n*-butyl ether and ethyl *n*-butyl in benzene, respectively, are to be compared with the values 1.22 and 1.24  $D$  obtained by Li and Terry.<sup>5</sup> Groves and Sugden<sup>6</sup> give the value 1.18  $D$  for the moments of the normal symmetrical ethyl, propyl and butyl ethers in the vapor state. There is a considerable solvent effect in benzene, and the variation of moments reported here may be due to this effect alone. It is perhaps signifi-

cant, however, that the average of the moments of the symmetrical ethers (1.28  $D$ ) is larger than that of the unsymmetrical ethers (1.21  $D$ ). Symmetry in ethers might be expected to stabilize hyperconjugation structures which represent polarization of the alkyl groups by oxygen.

### Experimental

Capacitances were measured by the heterodyne-beat method.<sup>7</sup> A modification of the electronic circuit<sup>8</sup> described by Müller, Garman and Droz<sup>9</sup> was used. The dielectric constant of benzene was assumed to be 2.276 at 25°.<sup>10</sup>

**Benzene and the Normal Symmetrical Ethers.**—Commercial products were purified by refluxing over sodium and distillation. Physical constants are as follows: benzene, b. p. 80.3–80.5°,  $d_{25}^4$  0.8736; diethyl ether, b. p. 34.5–34.6°,  $d_{25}^4$  0.7079; dipropyl ether, b. p. 90.5–91.0°,  $d_{25}^4$  0.7416; dibutyl ether, b. p. 141–142°,  $d_{25}^4$  0.7637.

**Asymmetric Ethers.**—Sodium was dissolved in an excess of alcohol and an equivalent amount of alkyl halide was added dropwise. After six hours of refluxing the ether was distilled off, treated with sodium over a prolonged period, and redistilled. The following physical constants were obtained: ethyl *n*-propyl ether, b. p. 63.0–63.4°,  $d_{25}^4$  0.7270; ethyl *n*-butyl ether, b. p. 92.0°,  $d_{25}^4$  0.7452; methyl *n*-propyl ether, b. p. 38.3–39.0°,  $d_{25}^4$  0.7230; methyl *n*-butyl ether, b. p. 70.5–71.0°,  $d_{25}^4$  0.7393; *n*-propyl *n*-butyl ether, b. p. 116.5–117.0°,  $d_{25}^4$  0.7531.

TABLE I

DENSITIES, DIELECTRIC CONSTANTS AND DIPOLE MOMENTS AT 25°

$f_2$	$d$	$\epsilon$	$f_2$	$d$	$\epsilon$
Diethyl ether			Ethyl <i>n</i> -propyl ether		
0.006168	0.8726	2.295	0.007026	0.8728	2.297
.01818	.8710	2.327	.01224	.8715	2.300
.04983	.8652	2.372	.03065	.8681	2.331
.08879	.8591	2.442	.05600	.8634	2.352
$MR_D$ 23.00	$\mu$ 1.28		$MR_D$ 27.63	$\mu$ 1.16	
Di- <i>n</i> -propyl ether			Methyl <i>n</i> -butyl ether		
0.009158	0.8722	2.295	0.009977	0.8719	2.298
.02006	.8701	2.315	.01305	.8717	2.300
.03587	.8672	2.344	.02713	.8688	2.328
.05300	.8631	2.376	.05846	.8636	2.374
$MR_D$ 31.66	$\mu$ 1.31		$MR_D$ 27.06	$\mu$ 1.25	
Di- <i>n</i> -butyl ether			Ethyl <i>n</i> -butyl ether		
0.005780	0.8721	2.293	0.003695	0.8731	2.285
.008948	.8710	2.295	.009879	.8718	2.293
.01881	.8696	2.315	.01905	.8701	2.307
.03748	.8660	2.343	.03682	.8662	2.333
$MR_D$ 41.03	$\mu$ 1.26		$MR_D$ 31.76	$\mu$ 1.22	
Methyl <i>n</i> -propyl ether			<i>n</i> -Propyl <i>n</i> -butyl ether		
0.009180	0.8714	2.292	0.004597	0.8727	2.293
.01622	.8701	2.304	.009947	.8714	2.296
.03334	.8665	2.336	.02434	.8686	2.317
.06385	.8607	2.365	.04277	.8647	2.340
$MR_D$ 22.35	$\mu$ 1.24		$MR_D$ 36.33	$\mu$ 1.17	

(1) Department of Chemistry, University of Maryland, College Park, Md.

(2) Landolt-Börnstein, "Physikalisch-chemische Tabellen," Fifth Edition, Julius Springer, Berlin, 1936.

(3) G. Hedestrand, *Z. physik. Chem.*, **B2**, 428 (1929).

(4) O. Hassel and A. H. Uhl, *ibid.*, **B8**, 187 (1930).

(5) N. C. C. Li and T. D. Terry, *This Journal*, **70**, 344 (1948).

(6) L. G. Groves and S. Sugden, *J. Chem. Soc.*, 1779 (1937).

(7) C. P. Smyth, "Dielectric Constant and Molecular Structure," The Chemical Catalog Co., Reinhold Publ. Co., New York, N. Y., 1931.

(8) The electronic parts of the apparatus were assembled by Mr. Iwao Miyake of the Physics Department.

(9) R. H. Müller, R. L. Garman and M. E. Droz, "Experimental Electronics," Prentice-Hall, Inc., New York, N. Y., 1942, p. 280.

(10) C. P. Smyth and W. S. Walls, *This Journal*, **53**, 527 (1931).

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RECEIVED MAY 10, 1950

## Chemical Properties of Californium

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### Introduction

In the course of the production and identification of a radioactive isotope of californium (atomic number 98)<sup>1</sup> some evidence as to the chemical nature of this transuranium element was obtained. This isotope was prepared by the bombardment of Cm<sup>242</sup> with 35-Mev. helium ions in the 60-inch cyclotron of the Crocker Radiation Laboratory and is believed to have the mass number 244. The Cf<sup>244</sup> has a half-life of about 45 minutes and decays at least partially by the emission of alpha-particles of 7.1-Mev. energy.

It should be pointed out that the first successful identification of the new element depended on the quite accurate prediction of some of its nuclear and chemical properties. The anticipation of the nuclear properties (principally half-life and radiation characteristics) was necessary in order to design adequate chemical procedures of sufficiently short duration and to use suitable instruments for the detection of its radiations. The predic-

(1) S. G. Thompson, K. Street, Jr., A. Ghiorso and G. T. Seaborg *Phys. Rev.*, **78**, 298 (1950).

tion of the nuclear properties of isotopes of element 98 will be discussed more completely in another report<sup>2</sup>; however, it should be mentioned that the isotope expected to be most easily detected in the bombardments contemplated was Cf<sup>244</sup> with an anticipated half-life of from 30 minutes to several hours and emitting alpha-particles with an energy in the range 7.0 to 7.3 Mev. and it was on this basis that the chemical procedure was designed.

The necessity for predicting some of the chemical properties arises principally because of the large amount of radioactivity associated with the Cm<sup>242</sup> target material. The few micrograms of Cm<sup>242</sup> available for the target emitted approximately 10<sup>10</sup> alpha-particles per minute. With the yields expected for the isotopes of element 98 that could be produced by helium-ion bombardment, one could hope to make only a few hundred disintegrations per minute of the new element. Thus it is obvious that after bombardment a very substantial chemical separation from the target material had to be made before any attempt to detect the new element could possibly be successful.

These problems are of the same type as those encountered in the first production and isolation of berkelium<sup>3,4</sup> using Am<sup>241</sup> as the target material. The smaller amount of Cm<sup>242</sup> and its higher specific activity (about 1000 times that of Am<sup>241</sup>) made the problem of isolation from the target material more difficult. On the other hand, the additional data furnished by the chemical properties of berkelium made the prediction of the chemical properties of element 98 much more certain.

Since berkelium had taken its place as the eighth member of the actinide transition series of elements, there was every reason to believe that element 98 should be an "eka-dysprosium." The fact that the Bk(III)–Bk(IV) couple had a potential of *ca.* –1.6 volts made it extremely likely that element 98 would have a stable plus three oxidation state in aqueous solution and that higher states would be attained with difficulty if at all. Thus element 98 should follow the rare earth elements in its precipitation chemistry.

The most satisfactory method up to the present for separating the heavy actinide elements from each other consists of selectively eluting them from a column of cation exchange resin with ammonium citrate solution<sup>4,5</sup> and hence it was necessary to anticipate the position of elution of element 98. That element 98 should elute ahead of berkelium was obvious from the behavior of the rare earths<sup>6</sup>

and the preceding actinides, but it was necessary to make a more quantitative estimate of its position of elution relative to the other actinides in order to devise the most efficient chemical procedure possible. A comparison of relative rates of elution of the lanthanide triad europium–gadolinium–terbium with the actinide triad americium–curium–berkelium<sup>4</sup> had disclosed a remarkable similarity in the change in ionic size (and consequently rate of elution) on filling in the 4f and 5f electrons. The break in change of radius that is encountered after the half-filling of the 4f shell and which results in the large separation of terbium from gadolinium on elution with ammonium citrate solution occurs again at the half-filling of the 5f shell and results in the large separation of berkelium from curium. The most obvious difference between the lanthanide and actinide elements is the more rapid change in ionic radius and consequent greater differences in rate of elution of the actinides. Thus, although the relative spacing in the triad americium–curium–berkelium is very similar to that of europium–gadolinium–terbium, the separation between adjacent actinides is about 1.2 times that of the analogous rare earths. Using this relationship between the actinides and the rare earths one felt quite confident that the position of elution of element 98 could be predicted quite accurately from the position of dysprosium in relation to terbium. The top half of Fig. 2 shows the relative rates of elution of the rare earth elements europium, gadolinium, terbium and dysprosium. This figure was constructed by combining data from several different sources.<sup>4,7,8,9</sup> Using this information it was predicted that element 98 would be eluted at about 1.4 times the rate of elution of berkelium.

#### Experimental

With these nuclear and chemical predictions in mind, a bombardment was made in which the chemistry was designed to allow the detection of long range alpha-particles of half-life as short as 20 minutes. The chemical procedure consisted essentially of dissolving the curium oxide target in 6 *M* HNO<sub>3</sub>, adding 200 micrograms of La<sup>+++</sup> carrier, and precipitating the lanthanum hydroxide with ammonium hydroxide. Lanthanum hydroxide carries the heavy actinides and many fission products. The hydroxide precipitate was dissolved in 0.5 *M* perchloric acid, adsorbed on a small amount of ammonium form Dowex-50 cation exchange resin, and placed on top of a column 2 mm. in diameter and 17 cm. long packed with the same resin. The eluting agent was ammonium citrate buffered with citric acid to a pH of 3.5 (total citrate concentration 0.25 *M*). In order to decrease the time of separation, the elution was carried out at an elevated temperature of 87°. The flow rate of the eluting agent was held at one drop (*ca.* 0.030 cm.<sup>3</sup>) about every two minutes. In this elution experiment 7.1-Mev. alpha-particles were found very close to the expected position (drop numbers 24 to 28) of elution of element 98. At this same elution position there were approximately 10<sup>4</sup> alpha-disintegrations per minute of Cm<sup>242</sup> which came from column break through of some of the large amount of activity in the curium elu-

(2) S. G. Thompson, K. Street, Jr., A. Ghiorso and G. T. Seaborg, *Phys. Rev.*, to be published.

(3) S. G. Thompson, A. Ghiorso and G. T. Seaborg, *ibid.*, **77**, 838 (1950); *ibid.*, in press.

(4) S. G. Thompson, B. B. Cunningham and G. T. Seaborg, *THIS JOURNAL*, **72**, 2798 (1950).

(5) B. B. Cunningham, E. R. Tompkins and L. B. Asprey, unpublished work (1947).

(6) See W. C. Johnson, L. L. Quill and F. Daniels, *Chem. Eng. News*, **25**, 2494 (1947), for references.

(7) J. O. Rasmussen, unpublished work (1949).

(8) B. H. Ketelle and G. E. Boyd, *THIS JOURNAL*, **69**, 2800 (1947).

(9) G. H. Higgins and K. Street, Jr., *ibid.*, **72**, in press (1950).

tion peak; under these conditions a maximum decontamination factor from curium of about  $10^6$  can be obtained. The high energy alpha-particles were detected in the presence of the  $\text{Cm}^{242}$  alpha-particles by means of a 48-channel differential pulse analyzer and decay of these alpha-particles was followed by taking successive pulse analyses. The 7.1-Mev. alpha-particles decayed with a half-life of about 45 minutes. This single experiment probably offers sufficient evidence for the discovery of element 98. The possible exception to this conclusion is that the activity could conceivably be another isotope of berkelium if the position of elution had been miscalculated, since the  $\text{Cm}^{242}$  break-through prevented the location of the known  $\text{Bk}^{243}$  activity (formed by deuteron contamination in the alpha-particle beam) at its expected position.

In order to eliminate this latter possibility, in a later bombardment the length of the column was shortened to about 15 cm. and instead of attempting to locate elements 97 and 98 immediately all of the fractions up to and including approximately  $10^6$  counts per minute (c./m.) of  $\text{Cm}^{242}$  were combined. This combined fraction which should have contained element 98 and berkelium, as well as part of the curium, was acidified with hydrochloric acid, reabsorbed on a small volume of resin, placed on another column, and eluted again under the same conditions. The results of this elution are shown in Fig. 1. Three distinct

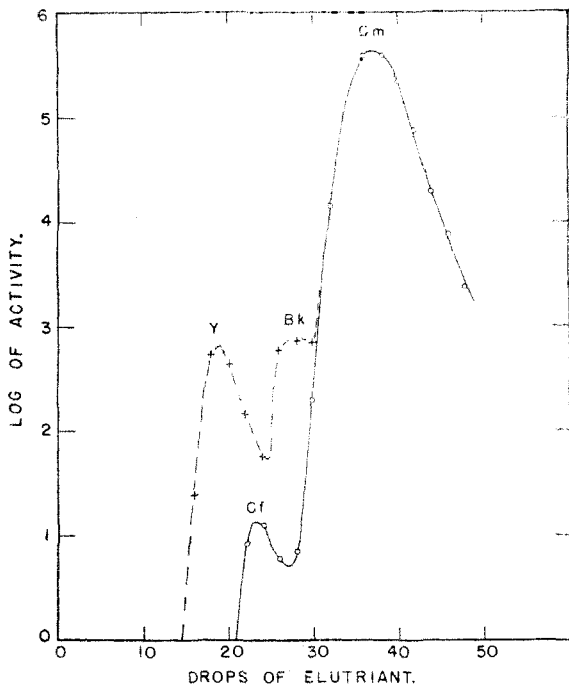


Fig. 1.—Elution of combined curium, berkelium and californium fraction with ammonium citrate. Solid curve indicates alpha-particle counts per minute; dashed curve, Auger and conversion electrons and beta-particles (and alpha-particles).

peaks labeled californium, berkelium and curium are evident. Pulse analysis of the activity in the californium peak showed the 7.1-Mev. alpha-particles and these decayed with a 45-min. half-life. The berkelium peak was identified by the 4.6-hr. half-life of the electron and electromagnetic radiation and the three characteristic alpha-particle groups<sup>2</sup> of  $\text{Bk}^{243}$ . The first peak is due to beta-particle emitting fission product yttrium which would not have been separated up to this point. This elution demonstrates conclusively that the new alpha-emitter is not an isotope of berkelium.

#### Additional Chemical Experiments

In subsequent bombardments small amounts (ca. 50 c./m.) of the new alpha-emitter were isolated and further tracer chemical experiments performed in order to characterize somewhat more closely its chemical properties. It is interesting to note that the amount of californium (ca. 50 c./m.) which it has been possible to produce for these experiments corresponds to *only a few thousand atoms of the element*. In these experiments the activity was first separated by carrying on lanthanum fluoride and lanthanum hydroxide and by the use of ion exchange columns as described above. Because of the small amount of activity produced and the short half-life only a few chemical experiments could be performed after each bombardment. The results of these tracer experiments are given below. In all cases the course of the californium in the experiments was followed by performing pulse analyses for the 7.1-Mev. alpha-particle.

A small amount of the californium tracer (with  $10^4$  alpha c./m.  $\text{Cm}^{242}$ ) was placed on a cation exchange column packed with hydrogen form Dowex-50 resin and eluted with 13 *M* HCl solution. The californium was eluted at essentially the same position as the curium as are the other heavy actinides<sup>4,10</sup> americium and berkelium, and well ahead of the rare earth elements.

Several attempts were made to oxidize Cf(III) to a higher oxidation state. Carrying on zirconium phosphate was used as a test for oxidation to the (IV) state and lack of carrying on lanthanum fluoride as a test for Cf(IV) on the basis of analogy with the behavior of other actinide elements in tracer experiments.

Experiments performed after oxidation with 0.2 *M* ammonium persulfate for 10 min. at 70° in a solution 1 *M* in nitric acid and 0.2 *M* in sulfate showed less than 10% carrying on zirconium phosphate and greater than 80% carrying on lanthanum fluoride precipitated by adding  $\text{La}^{+++}$  and making the supernatant 1 *M* in hydrofluoric acid.

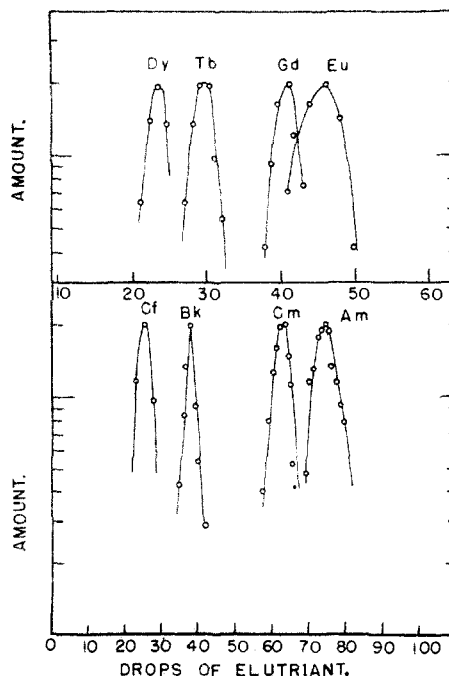


Fig. 2.—Comparison of the rates of elution of californium, berkelium, curium and americium with their homologs dysprosium, terbium, gadolinium and europium. One free column volume has been subtracted.

(10) K. Street, Jr., and G. T. Seaborg, *THIS JOURNAL*, **72**, 2700 (1950).

Similar experiments after oxidation with sodium bismuthate for 5 min. at 60° in 5 *M* nitric acid also showed less than 10% carrying on zirconium phosphate and greater than 80% carrying on lanthanum fluoride from the supernatant made 3 *M* in hydrochloric acid and 1 *M* in hydrofluoric acid.

Although there are uncertainties in the tracer experiments, due largely to the small amount of californium available, it can be concluded that the oxidation of Cf(III) to the (IV) or (VI) states in aqueous solution even with these strong oxidizing agents is not possible or that the oxidation is slow.

### Discussion

The chemical properties of californium all indicate that it fits in well as the ninth actinide element. Perhaps the best evidence for this is a comparison of the relative rates of elution with ammonium citrate of the actinide elements californium-berkelium-curium-amerium and their rare earth homologs dysprosium-terbium-gadolinium-europium. To facilitate this comparison the elution data for the rare earths and actinides are plotted together in Fig. 2. Here the ordinates are normalized to show equal amounts of activity. The relative spacing for californium, berkelium, curium and amerium were taken from Fig. 1 and from an elution experiment in which berkelium, curium and amerium were present. The curves for the rare earths were taken from the previously mentioned sources.

A remarkable analogy between these two groups of elements is apparent, indicating that the same sequence of changes in ionic radius is encountered on filling in the 5*f* electrons as occurs on filling the 4*f* shell. It seems quite clear that curium represents the midway point in the actinide transition series of elements in view of its position analogous to gadolinium. The most obvious difference between the two groups is the larger magnitude of the contraction found in the actinides. That this should be the case is quite reasonable when one considers that the more loosely bound 5*f* electrons of the actinides would certainly be less effective as shielding electrons.

The experiments with respect to oxidation of californium above the (III) state are incomplete and further work is necessary in order to establish whether such states can exist in aqueous solution. The difficulty of oxidizing berkelium to the (IV) state<sup>4</sup> indicates that such higher oxidation states may not be expected. However, as the second element beyond the midpoint of this transition series, the possibility of oxidation to a (V) state (CfO<sub>2</sub><sup>+</sup>) must be borne in mind, particularly in view of the great stabilizing influence of the two oxygen atoms found in these elements for the MO<sub>2</sub><sup>+</sup> (and MO<sub>2</sub><sup>++</sup>) type of ions.

**Acknowledgment.**—It is a pleasure to acknowledge the help and advice of A. Ghiorso, G. H. Higgins and E. K. Hulet. This work was performed under the auspices of the U. S. Atomic Energy Commission.

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RECEIVED AUGUST 4, 1950

## The Schmidt Reaction of Some *p*-Substituted Acetophenones

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In connection with another study, we had the opportunity to investigate the Schmidt reaction of a number of *p*-substituted acetophenones. In view of the current interest in the mechanism of the reactions of hydrazoic acid with ketones,<sup>1-3</sup> and in view of the fact that few reactions of this type involving acetophenones containing electron withdrawing substituents are recorded in the literature, we wish to report our results at this time.

### Experimental

It was hoped that a uniform procedure could be employed for all the compounds in this study, and a medium of acetic acid containing sulfuric acid catalyst was thus chosen (Procedure A). However, several compounds were recovered unchanged when subjected to the Schmidt reaction in the above mentioned medium, and in those cases a medium of higher acid strength was employed (Procedure B).

**Procedure A.**—The ketone, 0.05 mole, was dissolved in 30–50 cc. of glacial acetic acid containing 0.1 mole of concentrated sulfuric acid. To the stirred solution at 60–70° there was then added sodium azide (0.075 mole) in small portions at such a rate that the temperature did not rise above 70°. The mixture was stirred with heating until all the evolution of nitrogen subsided (2–6 hours), and was then allowed to stand overnight at room temperature. The reaction mixture was poured onto ice and the solid product was filtered off, washed with water, dried and its melting point was determined. Whenever the melting point of the crude product was relatively close to that reported for the substituted acetanilide, the product was simply purified by crystallization and in most cases the purified acetanilide was also hydrolyzed to the corresponding aniline. When, on the other hand, the melting point differed appreciably from the literature value, the crude product was hydrolyzed and an attempt was made to isolate the substituted benzoic acid or aniline by conventional means.

**Procedure B.**—This procedure differed from the above in that the reaction was carried out in 50 ml. of concentrated sulfuric acid, and the reaction temperature was lowered to 30°.

The results obtained in this study are summarized in Table I.

### Discussion

It is generally agreed that the Schmidt reaction of ketones is acid catalyzed, and the results of this study offer further evidence on this point. In the case of substituted acetophenones in which the electron withdrawing character of the substituents caused a decrease in the basicity of the carbonyl oxygen atom, the reaction failed when only a catalytic amount of sulfuric acid was employed in the acetic acid medium. The reaction, how-

(1) Sanford, Blair, Arroya and Sherk, *THIS JOURNAL*, **67**, 1942 (1945).

(2) Smith, *ibid.*, **70**, 320 (1948).

(3) Newman and Gildenhorn, *ibid.*, **70**, 317 (1948).

(4) Smith and Horwitz, *ibid.*, **72**, 3718 (1950).

(5) Shechter and Kirk, Abstracts of Papers, 117th Meeting of the American Chemical Society, Philadelphia, 1950, p. 49L.

(6) Wolf, in Adams, "Organic Reactions," v. III, John Wiley and Sons, New York, N. Y., 1946, p. 307.

(7) Dice and Smith, *J. Org. Chem.*, **14**, 179 (1949).

(8) Alexander, "Ionic Organic Reactions," John Wiley and Sons, New York, N. Y., 1950, p. 71.