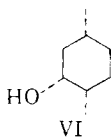
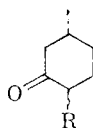


group of VA would have to make a molecular amplitude contribution of  $+3200^\circ$  (opposite to that of VIII), but the axial methyl group would lower<sup>3</sup> this value appreciably because of its situation in a negative octant. Experimentally (Fig. 1), a positive Cotton effect of  $+4800^\circ$  was obtained, which requires that another conformation play an important or exclusive role. If the twist form<sup>15</sup> (of the boat VB) is written as in VC, it will be seen that two of the ring carbons (C-3 and C-5) now make positive contributions,<sup>16</sup> as does the C-5 methyl group, thus being in qualitative agreement with the observed curve. The driving force for this conformational change from VA toward VC is almost certainly the relief of the buttressing to which the axial C-3 hydrogen in VA is exposed on the part of the C-5 methyl function as well as one of the equidistant methyl groups of the *t*-butyl moiety.

- |     |   |
|-----|---|
| I   | R = $-\text{CH}(\text{CH}_3)_2$                       |
| II  | R = $\dots\text{CH}(\text{CH}_3)_2$                   |
| III | R = $=\text{C}(\text{CH}_3)_2$                        |
| IV  | R = $-\text{C}(\text{CH}_3)_3$                        |
| V   | R = $\dots\text{C}(\text{CH}_3)_3$                    |
| VII | R = H   |
| IX  | R = $-\text{C}(\text{CH}_3)_2\text{CO}_2\text{H}$     |
| X   | R = $\dots\text{C}(\text{CH}_3)_2\text{CO}_2\text{H}$ |



Addition<sup>17</sup> of cyanide to (+)-pulegone (III) and then hydrolysis gives two isomeric acids, m.p. 92 and m.p. 121°. Rotatory dispersion measurements on these acids and their methyl esters together with equilibration experiments yielded results very similar to those reported above, thus demonstrating that the lower melting isomer should be represented by IX and the higher one by X.

All of the new substances in this communication were fully characterized and gave satisfactory analyses.

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(15) See W. S. Johnson, V. J. Bauer, J. L. Margrave, M. A. Frisch, L. H. Drieger and W. N. Hubbard, *J. Am. Chem. Soc.*, **83**, 606 (1961).

(16) Consideration of such "asymmetric" ring forms in applications of the octant rule to stereochemical problems concerning six-membered rings—similar to W. Klyne's treatment (*Bull. Soc. Chim. France*, 1396 (1960)) of cyclopentanones—will be covered in a forthcoming paper with Prof. Klyne.

(17) A. Lapworth and R. W. L. Clarke, *J. Chem. Soc.*, **89**, 1869 (1906), isolated only one acid (m.p. 121°).

## A NEW PYROLYTIC OLEFIN SYNTHESIS<sup>1</sup>

Sir:

Michaelis and v. Gimborn<sup>2</sup> found that  $(\text{C}_6\text{H}_5)_3\text{P}^+\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5\text{Cl}^-$  decomposes slowly at  $100^\circ$  to give triphenylmethylphosphonium chloride. In a somewhat similar experiment Piaux<sup>3</sup> reported that  $\text{C}_6\text{H}_5(\text{CH}_3)_2\text{N}^+\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5\text{I}^-$  yields phenyltrimethylammonium iodide on heating. Neither authors reported the isolation of any other products. It seemed reasonable to suspect, as was suggested by Michaelis and v. Gimborn,<sup>2</sup> that carbon dioxide and ethylene were formed.

With this in mind a series of phosphonium and ammonium salts,  $\text{R}_3\text{Z}^+\text{CH}_2\text{CO}_2\text{R}'\text{X}^-$ ; Z = P, N; X = Br, Cl; R =  $\text{C}_6\text{H}_5, \text{C}_4\text{H}_9$ , have been prepared and pyrolyzed at temperatures ranging from  $136$ – $200^\circ$ . In all cases an olefin, carbon dioxide and the appropriate onium salt were formed. The best yields and mildest reaction conditions were found with salts,  $(\text{C}_4\text{H}_9)_3\text{P}^+\text{CH}_2\text{CO}_2\text{R}'\text{X}^-$ . Several representative yields of olefins are: R', cyclohexyl (57%); 2-octyl (76%); 1-octyl (62%); 2-heptyl (76%); 1-decyl (67%); cyclohexylcarbonyl (54%); 1-menthyl (43%); *d*-neomenthyl (45%); *trans*-2-phenylcyclohexyl (73%); *cis*-2-phenylcyclohexyl (85%) and *trans*-stilbene (90%).

A quantitative study of the isomer distributions obtained with R' = 1-butyl, 1-octyl, 2-butyl, *t*-amyl revealed that both 1-butyl and 1-octyl give 1-butene and 1-octene of high purity (>95%) and high yield. Isomerization of the initially formed terminal olefin can occur if it is not removed from the reaction mixture as it is formed. For example the 1-octyl salt gave 60% 1-octene and 40% isomers when the decomposition was conducted at  $170^\circ$  and the olefin was distilled at atmospheric pressure. Under the same conditions except for reduced pressure (110 mm.) the olefin was >95% 1-octene. Pyrolysis of the 2-butyl salt at  $170^\circ$  yielded a mixture of butenes; 1-butene (33%), *trans*-2-butene (48%) and *cis*-2-butene (19%). Decomposition of the *t*-amyl salt proceeded smoothly at *ca.*  $140^\circ$  to give a mixture of methylbutenes; 2-methyl-1-butene (32%) and 2-methyl-2-butene (68%).

This synthetic procedure has the advantage over the more conventional ester pyrolysis in the lower temperature required for olefin formation. This is particularly the case for the formation of terminal olefins from primary alcohols.<sup>4</sup> The drastic reduction in temperatures required for effective synthesis suggests a mechanistic change from that for the usual ester pyrolysis.<sup>4</sup> An intriguing possibility involves a transition state in which hydrogen is being transferred to carbon rather than oxygen. Work on this aspect of the reaction and its synthetic extension is being continued.

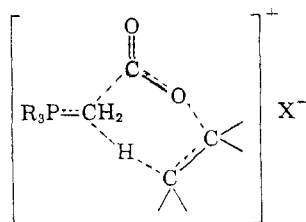
A typical procedure is given: 2-octyl bromoacetate, 23.0 g., 0.10 mole, and tributylphosphine, 20.0 g., 0.10 mole, were mixed with cooling. The mixture was heated to  $190^\circ$  (bath) and maintained

(1) Research supported by the National Science Foundation.

(2) A. Michaelis and H. V. Gimborn, *Ber.*, **27**, 272 (1894).

(3) L. Piaux, *Compt. rend.*, **190**, 645 (1930).

(4) C. H. DePuy and R. W. King, *Chem. Revs.*, **60**, 431 (1960).



at this temperature until no more olefin distilled (3 hr.). The distillate was fractionated through a semi-micro spinning band column to give 8.3 g. (76%) of mixed octenes, b.p. 46–47° (48 mm.).

(5) National Science Cooperative Graduate Fellow, 1960–1961.

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### ON THE VOLUME EXPANSION OF SODIUM-IN-AMMONIA SOLUTIONS

Sir:

We have investigated the expansion accompanying the dissolution of sodium to form dilute solutions in ammonia. The extraordinary results obtained are shown in Fig. 1, where  $\Delta V$  is defined as,  $\Delta V = (\text{volume of solution} - \text{volume of constituents})/\text{g. atoms Na}$ .

We offer a qualitative explanation for the behavior of  $\Delta V$ . At infinite dilution dissociation of metal is complete into "solvated" or "trapped" electrons and metal ions, and the expansion is large. As the concentration is increased, ions and electrons associate forming "atoms" and "molecules," and  $\Delta V$  decreases. This would suggest that the latter species may not be the highly expanded types suggested by Becker, Lindquist and Alder.<sup>1</sup> The minimum in  $\Delta V$  occurs in the concentration range where the conductance also passes through a minimum.<sup>2</sup> This result, together with measurement of transport numbers<sup>3</sup>, indicate that incipient metal properties are commencing to show up in this region. In essence, electrons are now being released to solvent, and  $\Delta V$  increases again.

Prior to this study reliable data for  $\Delta V$  were not available much below 1 *N* where  $\Delta V$  is approximately 42 cc.<sup>4</sup> In making estimates of the size of the trapped electron, it had been assumed that this value of  $\Delta V$  probably would not be too different from its value at infinite dilution.<sup>3</sup> Judging by our results, the value for infinite dilution appears to be approximately 41.5 cc. It is interesting to note that the two values of  $\Delta V$ , taken where the states of the system are vastly different, are very nearly the same.

In our study, volume changes were measured directly using a dilatometer technique. We esti-

(1) E. Becker, R. M. Lindquist and B. J. Alder, *J. Chem. Phys.*, **25**, 971 (1956).

(2) C. A. Kraus, *J. Am. Chem. Soc.*, **43**, 749 (1921).

(3) J. L. Dye, G. E. Smith and R. F. Sankuer, *ibid.*, **82**, 4803 (1960).

(4) C. A. Kraus, G. S. Carney and W. C. Johnson, *ibid.*, **49**, 2206 (1927).

(5) W. N. Lipscomb, *J. Chem. Phys.*, **21**, 52 (1953).

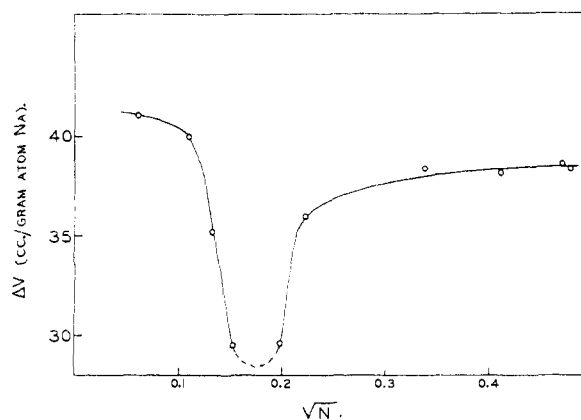


Fig. 1.—Expansion vs.  $\sqrt{N}$  for solutions of sodium in ammonia at  $-45^\circ$ .

mate that the maximum error in  $\Delta V$  in our experiments does not exceed three per cent.; most certainly it is less than this normally. We shall present additional data and describe our experimental method in detail in a paper to be presented soon.

Support for this research from the Office of Ordnance Research, U. S. Army, is gratefully acknowledged.

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### MECHANISM OF ELECTRICAL CONDUCTIVITY IN FUSED SALTS

Sir:

We wish to make a preliminary report on some recent work pertinent to the mechanism of electrical conductivity in fused salts. The attempts to correlate diffusion, electrical migration and fluidity data, and isotope separations by electrical migration in fused salts may all be affected by these findings.<sup>1</sup>

Mixtures of  $\text{LiNO}_3$  and  $\text{KNO}_3$  were placed in the anode compartment and pure  $\text{NaNO}_3$  in the cathode compartment of a U-shaped cell,<sup>2</sup> the compartments being separated by ultrafine Pyrex or in some cases quartz porous plate. Electrolysis was allowed to proceed and the total amount of cation and the ratio of Li:K passing from anode to cathode compartment were measured. The results, listed in Table I, show that within experimental error the ions move at the same rate in all mixtures. The transport number of the cation is indicative of which ion the mixture resembles most. The transport numbers of the cations in pure  $\text{KNO}_3$  and  $\text{LiNO}_3$  are 0.60 and 0.84, respectively.<sup>3</sup>

(1) G. J. Janz, C. Solomons and H. J. Gardner, *Chem. Revs.*, **58**, 461 (1958).

(2) F. R. Duke and R. A. Fleming, *J. Electrochem. Soc.*, **106**, 130 (1959).

(3) F. R. Duke and B. B. Owens, *ibid.*, **105**, 548 (1958).