

*dl*-3,5-Dimethyl-1,7-dicyanoheptane (VIIb).—From 22.3 g. of *dl*- $\beta$ , $\beta'$ -dimethylpimelic acid, by the method described for the preparation of VIa, 12 g. of *dl*-isomer VIIb was obtained; b.p. 138–139° (2 mm.),  $n_D^{25}$  1.4582. This material was converted to the dinitrile in an over-all yield of 57% by the procedure described for the preparation of VIIa; b.p. 173–174° (3 mm.),  $n_D^{25}$  1.4550.

*Anal.* Calcd. for  $C_{11}H_{18}N_2$ : C, 74.10; H, 10.24. Found: C, 74.07; H, 10.18.

*trans*-4,6-Dimethylcyclooctanone (VIIIb).—From 6.5 g. of dinitrile VIIb was obtained 5.0 g. of crude VIIIb by the cyclization method described for the synthesis of VIIa. One gram of this material was converted to its semicarbazone derivative, which after two crystallizations from aqueous alcohol gave 0.6 g. of white plates, m.p. 176–178°.

*Anal.* Calcd. for  $C_{11}H_{20}NO$ : C, 62.52; H, 10.01. Found: C, 62.64; H, 9.90.

Two grams of purified semicarbazone was hydrolyzed by the method described for the *cis* isomer, and after distillation under vacuum the product was obtained; wt. 0.6 g.,  $n_D^{25}$  1.4631.

*Anal.* Calcd. for  $C_{10}H_{18}O$ : C, 77.80; H, 11.76. Found: C, 78.20; H, 11.59.

*trans*-1,3-Dimethylcyclooctane (IXb).—Ketone VIIIb was converted to the hydrocarbon as described for the *cis* isomer. From 1.5 g. of pure ketone there was obtained 0.8

g. (59%) of the pure hydrocarbon, b.p. 181.5–182.0°,  $n_D^{25}$  1.4564,  $d_4^{25}$  0.8192.

*Anal.* Calcd. for  $C_{10}H_{20}$ : C, 85.62; H, 14.22. Found: C, 85.57; H, 13.99.

**Equilibration Experiments.**—Samples of about 100 mg. of the isomeric hydrocarbons IX were sealed in small tubes with about 20 mg. of palladium-on-carbon catalyst. The tubes were heated in a furnace at the desired temperature for 2 weeks. At 260° it was found that equilibration had occurred since the same mixture (by infrared analysis) was obtained from both isomers. At 299° extra bands appeared in the infrared spectrum, and it was clear that a reaction other than equilibration was taking place. At 230° the equilibration was incomplete.

Vapor phase chromatography of the pure hydrocarbons IX and synthetic mixtures of them on various columns gave no separation. The analysis was therefore done by the infrared method. The *trans* isomer gave bands at 8.45, 10.4 and 11.1 $\mu$  which were suitable for analysis. The *cis* isomer likewise gave suitable bands at 8.56, 9.1, 10.3 and 11.35 $\mu$ . From these bands the *trans* isomer in the equilibrated mixture was found to be 53, 55 and 51%. Similarly, the *cis* was 42, 36, 49 and 40%. After normalization the composition of the mixture is 56% *trans* and 44% *cis*, with a probable error of about  $\pm 3\%$ . From the equilibrium constant and temperature (533°K.) it was found that for the reaction  $\text{trans} \rightleftharpoons \text{cis}$ -1,3-dimethylcyclooctane,  $\Delta F = +0.25$  kcal./mole.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY, AMES, IOWA]

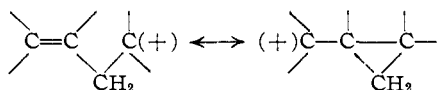
## The Solvolysis of *exo*- and *endo*-7-Isopropylidene-dehydronorbornyl Tosylates

By C. H. DEPUY, I. A. OGAWA AND J. C. MCDANIEL

RECEIVED OCTOBER 17, 1960

The tosylates of *exo*- and *endo*-7-isopropylidene-dehydronorborneol have been solvolyzed in glacial acetic acid containing sodium acetate. Both isomers solvolyzed with anchimeric assistance of the appropriate homoallylic unsaturation, the *exo* isomer with the 5,6- and the *endo* isomer with the 7,8-double bond. *Despite the fact that in both reactions a carbonium ion is generated at position 2, the two homoallylic ions are completely independent, the ion from the endo-tosylate giving exclusively endo-acetate, the ion from the exo-tosylate giving exclusively rearranged acetate.* Similar results were obtained on solvolysis of the dihydro compounds *exo*- and *endo*-7-isopropylidene-norborneol. The limits which these results place on the structure of homoallylic cations are discussed.

It is now well established that resonance interaction may take place between an electron-deficient center and a double bond not directly attached to the same carbon. When the site of unsaturation and the carbonion are separated by a single, saturated carbon atom, the system is known as "homoallylic," and the interaction as "homoallylic resonance." The interaction was first noted for cholesteryl cations,<sup>1</sup> and has been extensively investigated there, in the dehydronorbornyl system,<sup>2</sup> and with cyclopropylcarbinol compounds.<sup>1b</sup> Reactions involving such homoallylic participation are often characterized by an abnormally rapid rate of solvolysis relative to the



corresponding dihydro compound,<sup>3</sup> by the isolation of products containing a cyclopropane ring, and by stereochemical criteria (*e.g.*, solvolyses

(1) For recent, comprehensive discussions see (a) S. Winstein and E. M. Kosower, *J. Am. Chem. Soc.*, **81**, 4399 (1959), and (b) R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver and J. D. Roberts, *ibid.*, **81**, 4390 (1959).

(2) S. Winstein, H. M. Walborsky and K. Schreiber, *ibid.*, **73**, 5795 (1950).

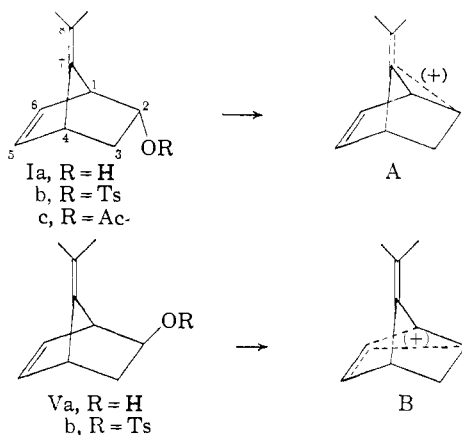
(3) If the participation makes itself felt in the rate-determining step.

occurring with retention of configuration). Despite the extensive amount of work which has been published on homoallylic systems, a number of important problems dealing with the nature of the intermediate ions remain unsettled.<sup>1</sup> In particular, the type of bonding involved in these ions is unclear, as well as the possible participation of classical carbonium ions in some of their reactions. In this paper we report studies which place important restrictions on the type of bonding in some homoallylic ions, and which also demonstrate, in a convincing manner, that classical ions cannot be involved in their reactions.

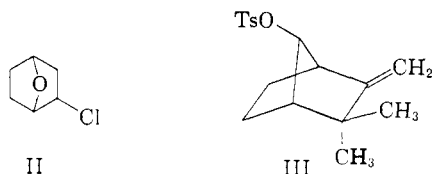
We recently reported methods for the synthesis of *endo*-7-isopropylidene-dehydronorborneol (Ia) from 6,6-dimethylfulvene and  $\alpha$ -acetoxyacrylonitrile.<sup>4</sup> The alcohol group in this interesting molecule is dihomallylic, being separated from both the 7,8- and 5,6-double bonds by a single saturated carbon atom. Participation is then possible, at least in theory, with either of the two double bonds. On stereochemical grounds, interaction with the 5,6-double bond would not be expected to be detectable kinetically in this system but, if important, could be demonstrated by the nature of the products resulting from the reaction. At the

(4) C. H. DePuy and P. R. Story, *J. Am. Chem. Soc.*, **82**, 627 (1960).

same time, participation with the 7,8-double bond, if it occurred, would provide another example of homoallylic interaction of a type hitherto unknown. Previous attempts to demonstrate participation in analogous systems have been unsuccessful. Thus Martin and Bartlett<sup>5</sup> failed to detect any anchimeric assistance during the solvolysis of II, and



van Tamelen and Judd<sup>6</sup> found no kinetic evidence for participation in III.



When Ib was allowed to solvolyze in glacial acetic acid containing sodium acetate and the rate of the reaction followed acidimetrically, it was immediately obvious that the ionization was strongly assisted by the presence of the 7,8-double bond. The rate constants for this solvolysis are reported in Table I, along with constants for several other bicyclic compounds for comparison. It can be seen from the data that the *endo*-tosylate Ib is about 2000 times more reactive than *endo*-dehydronorbornyl tosylate (VII) which displays no anchimeric assistance to solvolysis, and that it approaches *exo*-dehydronorbornyl tosylate (VIII) in reactivity. In the absence of participation the 7,8-double bond would be expected to be rate-depressing due to its inductive effect.

The demonstration of a rate enhancement in solvolysis is good evidence for participation in the transition state, but tells nothing about the fate of the homoallylic ion once formed. For instance, both *exo*- and *endo*-norbornyl tosylates give many of the same products on solvolysis, showing that participation may become important after the rate-determining step. Consequently, a study of the products of the acetolysis was indicated. The acetate formed in the reaction was carefully isolated, hydrolyzed to the corresponding alcohol and chromatographed. An 87% yield of pure, crystalline, unrearranged *endo*-7-isopropylidene-dehydronorborneol (Ia) was obtained. Even more

(5) J. C. Martin and P. D. Bartlett, *J. Am. Chem. Soc.*, **79**, 2533 (1957).

(6) E. E. van Tamelen and C. I. Judd, *ibid.*, **80**, 6305 (1958).

TABLE I  
RATES OF ACETOLYSIS OF SOME BICYCLO[2,2,1]HEPTYL  
TOSYLATES

Compound	Temp., °C.	Rate	Ref.
Ib	50	$7.70 \pm 0.28 \times 10^{-5}$	
	30	$7.25 \pm 0.20 \times 10^{-6}$	
	(25)	$(3.70 \times 10^{-6})^a$	
IV	50	$3.24 \pm 0.11 \times 10^{-4}$	
	30	$3.90 \pm 0.09 \times 10^{-5}$	
	(25)	$(2.26 \times 10^{-5})^a$	
Vb	30	$6.27 \pm 0.10 \times 10^{-5}$	
VI	30	$1.76 \pm 0.05 \times 10^{-4}$	
VII	25	$2 \times 10^{-9}$	7
VIII	25	$1.5 \times 10^{-5}$	7
IX	25	$8.4 \times 10^{-8b}$	8
X	25	$2.36 \times 10^{-5}$	9

<sup>a</sup> Calculated from the data at higher temperatures.

<sup>b</sup> Calculated with the assumption that tosylates react at one-third the rate of brosylates.

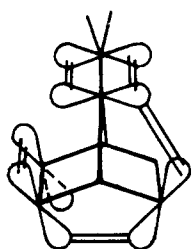
strikingly, when the crude reaction mixture from the acetolysis was examined with the aid of gas chromatography, only a single, sharp peak characteristic of the *endo*-acetate was observed under conditions in which *exo*- and rearranged acetates (*vide infra*) were cleanly separable. Obviously the solvolysis had proceeded with a very high degree of specificity.

The most likely conclusion to be drawn from the stereospecificity of the solvolysis is that the two homoallylic ions A and B are independent of one another, and that no interconversion takes place under the conditions of the reaction. Two alternate explanations are possible, however. In the first of these, it could be imagined that for some reason participation with the 7,8-double bond is so much more favorable energetically than with the 5,6-double bond that, in an equilibrium between ions A and B, A predominates by a large factor. In the second possibility, A and B might be imagined to be resonance structures, the actual intermediate having, simultaneously, interaction between the cationic center and both double bonds, as in XII. This intermediate might, in theory, react with solvent *endo*-acetate Ic exclusively. Both of these possibilities would be ruled out if it could be shown that the ion B, formed by solvolysis of the *exo*-tosylate Vb, gave entirely different products.

(7) S. Winstein and M. Shatavsky, *ibid.*, **78**, 593 (1956).

(8) S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan and H. Marshall, *ibid.*, **74**, 1127 (1952).

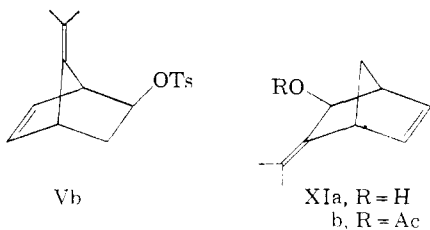
(9) P. von R. Schleyer, private communication.



XII

The *endo*-alcohol Ia was readily available from the reduction of the corresponding ketone, but this reaction was highly stereospecific and gave only small, unisolable amounts of the *exo* isomer.<sup>4</sup> Equilibration of the crude hydride reduction product with aluminum isopropoxide in isopropyl alcohol gave an approximately 50-50 mixture of the two alcohols. These could not be separated by crystallization or column chromatography, but were readily separable by isolative gas chromatography using a 20% THEED<sup>10</sup>-on-Celite column one meter long. When prepared in this way the *exo*-alcohol was a crystalline solid which was converted to its tosylate and solvolyzed under the same conditions as for the *endo*-tosylate. As expected, the rate of the acetolysis of Vb was rapid at 30°, again indicating anchimeric assistance. The rate constant for the solvolysis is given in Table I. The reaction was carried out on a larger scale and the products were isolated. Gas chromatographic analysis of the crude acetate showed it to be a single compound, with a different retention time on g.p.c. from either the *exo*- or *endo*-acetate. Cleavage of the ester with LiAlH<sub>4</sub> afforded a white, crystalline alcohol, m.p. 102-103°, which was different from either *exo*- or *endo*-7-isopropylidenedehydronorborneol. It displayed infrared absorption bands at 6.36 and 13.8 μ, characteristic of a double bond in the norbornyl system<sup>11</sup> and, by analogy with the type of rearrangement taking place with *exo*-norbornyl tosylate, it was assigned structure XI.

These results make it very clear, then, that the two homoallylic cations A and B are neither identical nor interconvertible under the conditions of the reaction. Hence, *there are at least two distinct carbonium ions capable of existence at position 2, their formation depending upon the stereochemistry of the original tosylate.* The most striking of the two would seem to be A, since it appears likely that rearrangement to give the allylic carbonium ion analogous to XI would be favored thermodynamically. These results rule out classical character

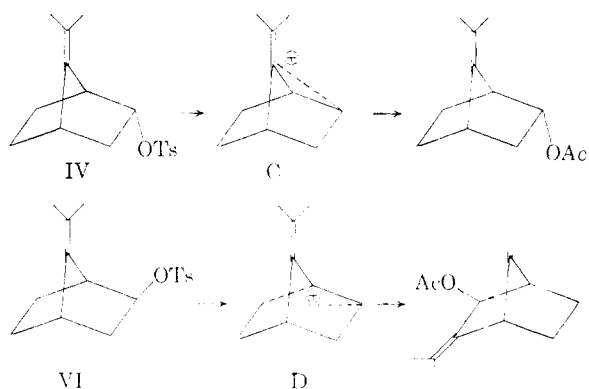


(10) Tetra-(hydroxyethyl)-ethylenediamine.

(11) L. Kaplan, H. Kwart and P. von R. Schleyer, *J. Am. Chem. Soc.*, **82**, 2341 (1960).

to the carbonium ion, and demand an activation energy for the conversion of A to B.

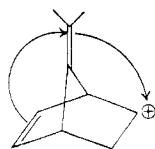
It next seemed pertinent to investigate the analogous solvolyses in the 5,6-dihydro compounds, *exo*- and *endo*-7-isopropylidene-norbornyl tosylates, IV and VI. Here the analogous intermediates would be, from IV the homoallylic cation C, and from VI the non-classical cation D, resulting from



participation of the saturated β-carbon. The results in these cases were completely in accord with those reported above. Both tosylates solvolyzed rapidly compared to analogous tosylates which could not have anchimeric assistance to ionization. Again the *endo*-acetate was the exclusive product from acetolysis of the *endo*-tosylate (as evidenced by the appearance of only a single peak on g.p.c. analysis and the isolation, in 89% yield, of the corresponding alcohol after saponification and chromatography). The *exo*-tosylate gave none of the *endo*-acetate, but again formed a rearranged acetate. The alcohol produced upon saponification of this acetate was identical with that formed by partial hydrogenation of the rearranged alcohol XIa from the *exo*-dehydrotosylate above. Again no interconversion could be detected between the homoallylic and the non-classical ions.

Two additional points of interest seem worthy of mention. The similarity between the rate constants for the solvolysis of the *exo*-7-isopropylidene-norbornyl (IV) and dehydronorbornyl (Ib) tosylates and those for *exo*-norbornyl (X) and dehydronorbornyl (VIII) tosylates indicates that the potential allylic character of the rearranging carbonium ion has little effect on the rate of the reaction. This may prove to be general, or may be due to unfavorable orientation of the π-electrons of the 7,8-double bond in this particular system. A second interesting comparison is between the rates of acetolysis of *endo*-7-isopropylidene-norbornyl tosylate (IV) and *endo*-7-isopropylidenedehydronorbornyl tosylate (Ib). Since electron donation from 5,6-unsaturation to the 7-position is known,<sup>12</sup> it might have been anticipated that the transition state for the solvolysis of the dehydronorbornyl system could be stabilized by an interaction such as that shown in XIII. Actually, however, the diene is less reactive than the mono-ene, and it

(12) S. Winstein, M. Shatavsky, C. Norton and R. B. Woodward, *ibid.*, **77**, 4183 (1955).



XIII

seems unlikely that this type of interaction is important.

### Experimental

Melting points are uncorrected. Analyses were performed by Weiler and Strauss, Oxford, England. Gas chromatographic analyses were performed using a Perkin-Elmer model 154-C vapor Fractometer. The column used for the analysis of the alcohols was a 1 m.  $\times$  6 mm. Pyrex tube packed with 9% by weight THEED (tetra-(hydroxyethyl)-ethylenediamine) on 60-80 mesh Celite. The column used in preparative runs was a 1 m.  $\times$  15 mm. tube packed with 20% by weight THEED on Celite.

*endo*-7-Isopropylidene-bicyclo-(2,2,1)-5-hepten-2-ol (Ia), m.p. 74-75°, was prepared by the method of DePuy and Story.<sup>4</sup>

*exo*-7-Isopropylidene-bicyclo-(2,2,1)-5-hepten-2-ol was obtained by equilibration of Ia. The *endo*-alcohol (5 g., 0.03 mole), aluminum isopropoxide (6.8 g., 0.03 mole) and acetone (0.1 ml.) were dissolved in 100 ml. of dry isopropyl alcohol and the solution heated under reflux for 72 hours. Dilute acid was added, the products extracted with ether, the extracts washed and dried over anhydrous MgSO<sub>4</sub>. The solvent was carefully removed (the alcohols are very volatile) and the resulting oil analyzed by g.p.c. It contained about 43% *exo*-alcohol. The mixture was dissolved in pentane and as much *endo*-alcohol as possible allowed to crystallize, leaving a mixture containing about 60% *exo*-alcohol. A single pass through the preparative column was sufficient to separate about 200 mg. of the oil into two crystalline alcohols. Recrystallization from pentane gave the *exo*-alcohol in the form of long white needles, m.p. 56-57°.

*Anal.* Calcd. for C<sub>10</sub>H<sub>14</sub>O: C, 79.95; H, 9.39. Found: C, 79.65; H, 9.27.

*endo*-7-Isopropylidene-bicyclo-(2,2,1)-2-heptanol, m.p. 81-82°, was prepared by the method of DePuy and Story.<sup>4</sup>

*exo*-7-Isopropylidene-bicyclo-(2,2,1)-2-heptanol was prepared by equilibration of the corresponding *endo*-alcohol as described above. After isolation by g.p.c. and recrystallization from pentane it had a m.p. 62.5-63°.

*Anal.* Calcd. for C<sub>10</sub>H<sub>16</sub>O: C, 78.89; H, 10.59. Found: C, 78.64, 78.02; H, 9.07, 10.13.

**Tosylates.**—All tosylates were prepared from the alcohols by the method of Tipson.<sup>13</sup> The *endo*-tosylates have been described earlier.<sup>4</sup> The *exo*-tosylates decomposed on standing or heating and accurate melting points could not be obtained.

**Kinetic Measurements.**—The technique used was that of Winstein.<sup>14</sup> The bath temperatures were 49.99  $\pm$  0.02° and 30.00  $\pm$  0.03°. The acetolyses were run in sealed tubes each containing 5 ml. of solution, approximately 0.035 *M* in tosylate and 0.040 *M* in sodium acetate. The reactions gave good first-order plots over at least 50% of the reaction, but some curvature was observed at long reaction times. Several infinity points checked with calculated values to within a few per cent.

**Product Analysis.**—About 1.5 g. of each of the tosylates was allowed to solvolyze at 50° for 24 hours in 40 ml. of dry acetic acid which was 0.2 *M* in sodium acetate. The reaction mixture was poured into cold water and extracted with pentane. The extracts were washed with water, dried and the pentane removed. The product in each case showed only a single peak on g.p.c. analysis, under conditions which readily separated mixtures of the acetates of all four compounds. The acetates were hydrolyzed, the hydrolysis products extracted with pentane, dried and the solvent carefully removed. In each case the products crystallized immediately, and the alcohol was obtained in 85-90% yield after chromatography or recrystallization. The *endo*-tosylates gave these high yields of the corresponding *endo*-alcohols, identified by their infrared spectra and mixture melting points with authentic samples. The *exo*-tosylates gave two new alcohols.

**Alcohol from Acetolysis of Vb.**—This alcohol melted at 102.5-103.5°. It readily absorbed hydrogen over palladium-on-carbon and had infrared peaks at 6.36 and 13.7  $\mu$ , characteristic of the dehydronorbornyl system.

*Anal.* Calcd. for C<sub>10</sub>H<sub>14</sub>O: C, 79.95; H, 9.39. Found: C, 80.22; H, 9.38.

After the uptake of one molar equivalent of hydrogen the resultant dihydro alcohol was identical with that described below from the solvolysis of VI.

The alcohol from the acetolysis of VI melted at 86-87°.

*Anal.* Calcd. for C<sub>10</sub>H<sub>16</sub>O: C, 78.89; H, 10.59. Found: C, 78.64; H, 10.80.

(13) R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

(14) S. Winstein, C. Hansen and E. Grunwald, *J. Am. Chem. Soc.*, **70**, 812 (1948).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE PENNSYLVANIA STATE UNIVERSITY, UNIVERSITY PARK, PENNA.]

## The Proton Nuclear Magnetic Resonance Spectra of Cyclohexane, *cis*- and *trans*-Decalin, *cis*- and *trans*-Hydrindan and *cis*-Bicyclo[3.3.0]octane

BY WILLIAM B. MONIZ AND JOSEPH A. DIXON

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The 40 mc. proton n.m.r. spectra of six alicyclic hydrocarbons have been studied over a range of temperatures. From changes in the spectrum of *cis*-hydrindan at low temperature, it has been possible to obtain an approximate value of 6.4 kcal./mole for the energy barrier to chair-chair interconversion of the molecule. The lack of change in the *cis*-decalin spectrum at low temperature indicates that the chair-chair interconversion energy barrier is lower than that of *cis*-hydrindan, presumably because of non-bonded proton interactions. The spectra of *trans*-decalin, *trans*-hydrindan and *cis*-bicyclo[3.3.0]octane change little with temperature. The unusually low-field absorption present in the last, and attributed to the bridgehead protons, is qualitatively explained in terms of C-C bond anisotropy.

### Introduction

For some time, much interest has centered around the preferred conformations of cyclohexane, the isomeric decalins and related compounds containing the six-membered ring. Conformational analysis has supplied some qualitative answers to the problems of carbon skeleton flexibilities and favored arrangements of the atoms in these systems.<sup>1-5</sup>

(1) D. H. R. Barton and R. C. Cookson, *Quart. Revs. (London)*, **10**, 44 (1956).

The use of n.m.r. techniques to obtain conformational information about some of these systems appeared promising because of the marked dif-

(2) W. G. Dauben and K. S. Pitzer in "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, Chap. 1.

(3) W. Klyne in "Progress in Stereochemistry," Vol. 1, Academic Press, Inc., New York, N. Y., 1954, Chap. 2.

(4) S. J. Angyal and J. A. Mills, *Revs. Pure and Appl. Chem. (Australia)*, **2**, 185 (1952).

(5) H. D. Orloff, *Chem. Revs.*, **54**, 347 (1954).