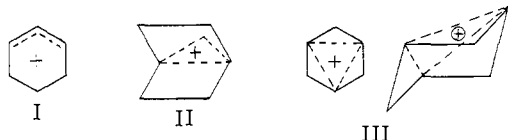


of the CH_2 and CH^+ lines together with the practically 2:1 peak area ratio virtually constitutes proof for the non-classical nature of the C_6H_9^+ ion. However, data so far do not allow unanimous differentiation as to whether the ion has a simple allylic structure (I) or a stabilized homoallylic structure (II). In 3-cyclohexenyl bromide the double bond can not get far away from the ionization center as it can in open chain compounds. It therefore has an ability to interact with the developing carbonium ion center. This consideration lends plausibility that a stabilized homoallylic cation (II) is preferentially formed with some of the character of a bicyclo[2,2,0]hexyl cation and some of a bicyclo[3,1,0]hexyl cation. Hydrogen shift and π -electron delocalization leading to Winstein's homoaromatic trishomocyclopropenyl ion¹ (III), as suggested earlier,² still should be considered, but



seems more unlikely. 2-Cyclohexenyl bromide on the other hand preferentially gives the allylic ion (I). Resolution of the fine structure of the proton spectrum was not sufficiently good at room temperature. Taking the spectrum at -60° still has not enabled sufficient differentiation. The classical, asymmetric carbonium ion structure however definitely must be eliminated, since it cannot be in agreement with present observations.

No definite solvolysis products were obtained so far in treatment of the cyclohexenyl complexes with water or D_2O . However, in the gas-liquid chromatographic investigation of the products there is indications of presence of small amounts of not yet identified alcohols. From the rather complex products (similarly to products of thermal decomposition of the complexes) two crystalline substances were isolated in small amounts (less than 10% of over-all products). The first, melting at 145° , $\text{C}_{12}\text{H}_{16}$, is octahydrobiphenylene. Dehydrogenation with selenium gave biphenylene (m.p. 110° and identical with an authentic sample of biphenylene). The other product, melting at $\sim 230^\circ$, $\text{C}_{18}\text{H}_{24}$, was identified as dodecahydro-tri-*o*-phenylene (m.p. $199-200^\circ$, identical with an authentic sample of tri-*o*-phenylene). The identified products obviously are cyclalkylation products of the cyclohexenyl ion with cyclohexadiene. The bulk of the decomposition products is, however, polymeric material. Deprotonation of the cyclohexenyl carbonium ion must give preferentially cyclohexadiene-1,3, a conjugated diolefin which readily undergoes Diels-Alder addition leading ultimately to high molecular weight polycyclohexadienes.³ Cyclohexadiene-1,4, being a nonconjugated diolefin, shows no similar ability.

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SECONDARY DEUTERIUM ISOTOPE EFFECTS IN
BIMOLECULAR ELIMINATION OF
2-PHENYLETHYL-1,1- d_2 BROMIDE AND
2-PHENYLETHYLDIMETHYLSULFONIUM-1,1- d_2
BROMIDE

Sir:

In a previous publication¹ it was reported that in $\text{S}_{\text{N}}1$ -type solvolysis the β -deuterium isotope effect is much greater for alkyl halides than for alkyl sulfonium salts. Similar effects now have been obtained in the elimination of 2-phenylethyl-1,1- d_2 bromide and the corresponding dimethylsulfonium ion. Both reactions show second-order kinetics.² Skell and Hauser have shown that during the conversion of 2-phenylethyl bromide to styrene with sodium ethoxide in ethanol-*O-d* the unreacted bromide does not accumulate deuterium, which was taken as an evidence that hydrogen and bromine are lost simultaneously.³ On the other hand it was shown that in the reaction of 2-phenylethyldimethylsulfonium bromide with sodium hydroxide in aqueous solution the C-S bond is stretched very little in the transition state, as manifested by a small ^{34}S isotope effect.⁴ It still seems rather unlikely that a carbanion of appreciable stability is involved. It is possible to envision that the mechanism of this reaction is also "concerted" in the sense of having no detectable intermediate, and that the transition state possesses some carbanion character.

2-Phenylethyldimethylsulfonium-1,1- d_2 bromide was prepared (containing 1.91 atoms of deuterium per molecule) and the rate of elimination in aqueous alkali at 79.95° was followed by potentiometric titration. The rate was found equal to that of the non-deuterated sulfonium salt. It was also found that 75% of the original quantity of deuterium exchanged prior to the reaction. In spite of this difficulty it seems that if there had been an appreciable isotope effect it would have been still noticeable.

The rate of the reaction of 2-phenylethyl-1,1- d_2 bromide (containing 1.90 atoms of deuterium per molecule) with sodium ethoxide in absolute ethanol was followed by measuring the absorption of styrene at $248 \text{ m}\mu$ and an α -deuterium isotope effect of 17.0% was found ($k_{\text{H}}/k_{\text{D}} = 1.17$). The rate constant at 59.8° for the undeuterated compound (k_{H}) amounted to $(1.015 \pm 0.008) \times 10^{-2}$ (mean of

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1.018, 1.048, 0.985, 1.006, 1.017 and 1.015×10^{-2}) and for the deuterated compound (k_D) (0.867 ± 0.010) $\times 10^{-2}$ (mean of 0.891, 0.877, 0.844, 0.877 and 0.844×10^{-2}) $\text{sec.}^{-1} \text{mole}^{-1}$ (0.008 and 0.010 are standard deviations of the mean).

Numerous examples of α -deuterium isotope effect in a carbonium ion solvolysis reaction have been reported,⁵ but not in a bimolecular elimination (E_2). The effect is explained in terms of the reduction in the force constant for the bending of the C-H bond in the sp^2 -bonded activated complex.⁶

The difference in the α -deuterium effects between 2-phenylethyl bromide and the corresponding sulfonium ion most probably results from the same reason as the old established difference in bimolecular eliminations between alkyl halides and alkyl sulfonium or ammonium ions governed by Saytzeff and Hofmann rules. A larger electron transfer from carbon to halogen is needed to give the transition state than in C-S heterolysis. Thus there should be more unsaturation in the transition state and the α -carbon should be closer to sp^2 hybridization.

The authors thank Sir Christopher Ingold and Professor W. H. Saunders for helpful discussions.

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RECEIVED OCTOBER 12, 1961

A NEW COÖRDINATION TYPE AROUND FLUORINE ATOM

Sir:

In connection with the studies carried on from a long time in our Institute on metalloorganic complexes containing bridge bonds,^{1,2,3} we have undertaken the X-ray structural study of the compound $\text{KF} \cdot 2\text{Al}(\text{C}_2\text{H}_5)_3$ (I), for the first time synthesized and studied by Ziegler *et al.*⁴

A $\text{KF} \cdot 2\text{Al}(\text{C}_2\text{H}_5)_2$ solution is obtained by reaction of finely ground KF with a stoichiometric quantity of $\text{Al}(\text{C}_2\text{H}_5)_3$ dissolved in toluene, at about 60° . We then have obtained good crystals of (I) by slow evaporation of toluene from the solution at room temperature.

Our X-ray analysis has confirmed that the complex (I) has the ionic structure $\text{K}^+[(\text{C}_2\text{H}_5)_3\text{Al-F-Al}(\text{C}_2\text{H}_5)_3]^-$; moreover we have surprisingly obtained definite evidence of colinearity among Al-F-Al atoms. In fact, the ordinary Patterson analysis led us to the conclusion that the rhombo-

hedral unit cell of (I), containing only one molecule, is centrosymmetrical, so that K^+ ion and F atom are bound to lay on two crystallographic centers of symmetry, while the Al-F distance, successively determined by Fourier methods ($1.80 \pm 0.06 \text{ \AA}$), clearly indicates that the atoms are bonded together.

The unit cell of (I) has the constants: $a = b = c = 8.95 \pm 0.05 \text{ \AA}$; $\alpha = \beta = \gamma = 55^\circ 20' \pm 1'$, space group $R\bar{3}$; $N = 1$.

At this point of the refinement, we can assign fractional coordinates of first approximation to all the atoms (excepting hydrogen atoms). The present satisfying accordance between observed and calculated structure factors on the (111) and (110) projections ($R = 0.17$) allows us to conclude that: (1) the Al-F-Al axis is a threefold axis, with inversion center, for the $[(\text{C}_2\text{H}_5)_3\text{Al-F-Al}(\text{C}_2\text{H}_5)_3]^-$ ion; (2) the coordination type around the aluminum atom is tetrahedral, with normal Al-C⁶ and C-C distances, while the Al-F distance appears to be close to that observed for instance in $\text{Na}_3\text{-AlF}_6$.⁷ It is to be noted that this datum is in contrast with the fact that usual bridge bond distances are somewhat longer ($0.20 \div 0.30 \text{ \AA}$) than the corresponding single bond distances.^{1,6,8}

If we suppose a sp hybridization for the fluorine atom, a partial π -bond character on the Al-F bond may arise from a certain overlap between the $2p_y$ and $2p_z$ filled fluorine orbitals and the $3d$ empty aluminum orbitals. This hypothesis seems to us particularly supported by recent studies, which demonstrate the ability of F^9 and C^{10} coordinated atoms to reduce the size of the $3d$ orbitals of second row elements.

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RECEIVED OCTOBER 21, 1961

STEREOSPECIFIC REARRANGEMENT OF NEOPENTYL ALCOHOL-1-*d*^{1,2}

Sir:

Neopentyl alcohol-1-*d* (I, 9.0 g.; acid phthalate, $[\alpha]^{25}_D - 1.10$, $C = 12$, acetone), which was optically active by virtue of isotopic substitution and which was obtained *via* asymmetric reduction of trimethylacetaldehyde-1-*d* by actively fermenting yeast,³ has been rearranged by treatment with bromoform (200 g.) and aqueous potassium hydroxide (412 g., 56%) for four hours under reflux by the method for dehydration of alcohols investigated by

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(2) We wish to acknowledge with gratitude, support of this research by Grant 5248 from the U. S. Public Health Service and Grant 495 from the Petroleum Research Fund.

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