

2'-bromo analog, m.p. 186–190° (dec.), $[\alpha]_D^{26} +15^\circ$ (water), was prepared in 46% yield by the reaction of IV with anhydrous hydrogen bromide in trifluoroacetic acid. (Anal. Calcd. for $C_9H_{11}N_2O_5Br$: C, 35.19; H, 3.61; N, 9.12; Br, 26.02. Found: C, 35.28; H, 3.45; N, 9.50; Br, 26.68.)

It is probable that this synthesis of 2'-halogeno nucleosides from 2,2'-anhydro derivatives can be extended to halogeno nucleosides of other bases. Inasmuch as the requisite intermediates have been prepared in this laboratory, the method is being applied to the thymidine series.

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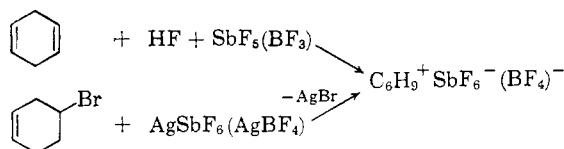
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NON-CLASSICAL CYCLOHEXENYL CARBONIUM ION

Sir:

Protonation of cyclohexadiene-1,4 with $HF + BF_3$ or $HF + SbF_5$ (either by the acids or by *in situ* treatment with $AgBF_4 + HCl$ or $AgSbF_6 + HCl$) gave in liquid SO_2 at -30° deep brown to red colored homogeneous solutions. After distilling off the solvent in a vacuum line system, solid tetrafluoroborate and hexafluoroantimonate complexes of the composition $C_6H_9^+BF_4^-$ and $C_6H_9^+SbF_6^-$, respectively, were obtained. In the strong acid media side reactions, leading to coupling and polymeric products, also take place and purification of the complexes represented difficulty.

The difficulty of the acid catalyzed side reactions was overcome when 3-cyclohexenyl bromide was treated in liquid SO_2 solution at -30° with anhydrous $AgBF_4$ and $AgSbF_6$. Quantitative silver halide elimination takes place and again colored solutions were obtained, with considerably less intense color, however, than in the case of protonation of cyclohexadiene-1,4. The precipitated



silver bromide was filtered and part of the solvent distilled off (all operations were carried out preferentially in a closed vacuum line system). Solid tetrafluoroborate (m.p. $\sim 56^\circ$ sealed tube) and hexafluoroantimonate (m.p. $\sim 115^\circ$ sealed tube) complexes were obtained with the composition corresponding to $C_6H_9^+BF_4^-$ (calcd.: C, 42.81; H, 5.36; F, 45.24. Found: C, 44.51; H, 6.17; F, 43.2) and $C_6H_9^+SbF_6^-$ (calcd.: C, 25.87; H, 2.84; F, 35.96. Found: C, 28.17; H, 3.13; F, 33.2). The complexes are light brown, highly sensitive compounds. Recrystallization from liquid SO_2

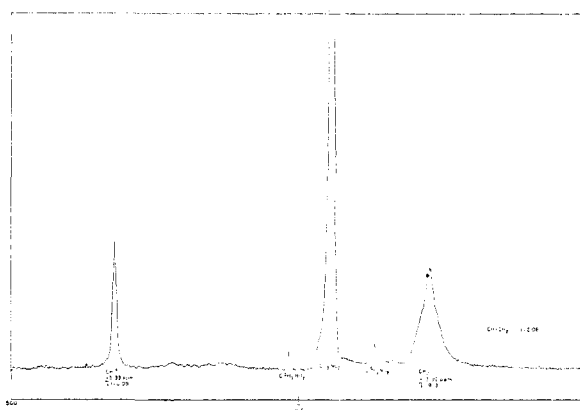


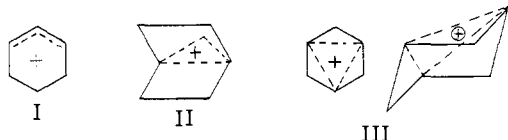
Fig. 1.— H^1 magnetic resonance of $C_6H_9^+SbF_6^-$ in CH_3NO_2 solution at 60 mc.

yielded only very lightly colored compounds, the pure salts being most probably colorless. The complexes must be rigorously protected from moisture and from oxygen. They dissolve to some extent in solvents such as nitromethane, sulfur dioxide and dioxane (in the latter, however, there is a fast observable color change and obvious reaction). The solutions are colored (brown to red in SO_2 , blue in nitromethane and dioxane) but the color may arise from impurities still present.

In considering the nature of the isolated complexes, we must assign them carbonium salt structures, $C_6H_9^+BF_4^-$ and $C_6H_9^+SbF_6^-$, as it is difficult to consider any covalent structure for BF_4^- and SbF_6^- complexes. The tetrafluoroborate and hexafluoroantimonate nature of the complexes was proved beside elementary analyses by the characteristic infrared bands and by n.m.r. proton and fluorine resonance investigations, giving proof of the symmetrical anions. (a) Infrared bands, $C_6H_9^+BF_4^-$: 3041 vw, 2927 vs, 2858 s, 1603 w, 1445 m, 1348 w, 1072 vs, br(BF_4^-), 1012 sh, 889 w, 840 w, 792 vw, 765 w, 720 m; $C_6H_9^+SbF_6^-$: 3012 vw, 2925 vs, 2865 s, 1601 w, 1430 m, 1260 w, 1150 m, 1070 w, 1015 w, 970 m, 890 w, 865 w, 795 w, 720 vs, 655 s (SbF_6^-) (spectra were obtained as Nujol-Fluorolube mixed mulls). (b) Ultraviolet absorption maxima, $C_6H_9^+SbF_6^-$: (in dioxane) λ_{max} m μ (E) 307 (234), 242 (1350), 250 (shoulder (1248)). (The solvent is interfering with the complexes after a few minutes, thus fresh solutions must be used immediately and even so the data, as a result of solvent interference, are not considered entirely reliable). (c) Nuclear magnetic resonance: The proton resonance spectrum of $C_6H_9^+SbF_6^-$ (Fig. 1) in nitromethane solution at room temperature (60 Mc., water as external reference) indicates only two types of hydrogens. The corresponding tau values (using the correction factor of 5.21 p.p.m. for water-tetramethylsilane) are 9.13 and -0.09 , respectively. The relative peak areas observed are 2.06:1. The fluorine resonance spectra of the compounds at 56.46 Mc. gave evidence only of the symmetrical anions BF_4^- and SbF_6^- .

The observed CH peak at so low field ($\tau = -0.09$, giving a negative value on the Tiers scale) indicates a positively charged "acidic" CH^+ . The presence of only two types of protons, the position

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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