

volumes of the chlorides (or bromochlorides), di-*tert*-butyl peroxide, and triethylsilane were diluted with sufficient cyclopropane to give a final ratio of approximately 1:1:1:4 (v/v).

All samples were thoroughly degassed using a freeze-pump-thaw cycle. When spectra were of low intensity, the relative amounts of the reactants were varied to maximize the signal.

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$(\text{CCH}_3)_6^{2+}$, an Unusual Dication^{1,2}

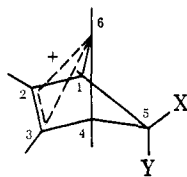
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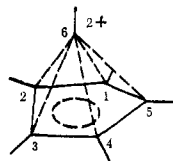
Abstract: The $(\text{CCH}_3)_6^{2+}$ dication (**2**) has been prepared in strongly acidic solution from a variety of precursors. Several reactions of this species are reported. A number of possible structures for the dication are considered and found to be not in agreement with the structure of the quenching products and/or the pmr spectrum. Two alternatives remain for further consideration: a rapid degenerate rearrangement of structures **5** and the nonclassical structure **2**, involving a hexacoordinated carbon atom. Pmr and cmr spectral data, the rates of deuterium exchange and of carbonylation, and the thermal stability together with the reported *ab initio* calculations provide strong evidence for the nonclassical structure **2**.

The idea that in some cations the carbon atom might have a coordination number higher than four was first suggested by Wilson^{3a} and was later developed by Winstein.^{3b,c} Nonclassical ions with a pentacoordinated carbon atom like norbornyl and norbornenyl cations have become common phenomena in the literature since then. Examples of ions with an electronic structure strongly related to that of the norbornenyl cation are the nonclassical 1,2,3,4,5,6-hexamethylbicyclo[2.1.1]hexenyl cations **1**.⁴ These ions are im-

bond.^{4,5} Examples of more extended delocalization are found in the larger aromatic and homoaromatic cations, but in these cases the coordination number of carbon does not exceed 4.^{3c} In recent literature, however, one encounters some nonclassical ions in which a description in terms of a two-electron, three-center bond was judged to be not adequate and a more complex electronic structure was proposed. Among these is the $(\text{CH})_5^+$ cation proposed by Stohrer and Hoffmann⁶ to have a square-pyramidal configuration **3** involving a



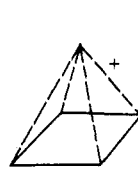
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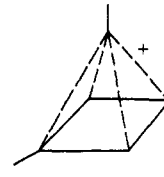
2

- a, X = H; Y = CH₃
- b, X = CH₃; Y = H
- c, X = CH₃; Y = Cl
- d, X = CH₃; Y = Br
- e, X = OH; Y = CH₃
- f, X = CH₃; Y = OCH₃

portant in this context as precursors and intermediates in the preparation and reactions of the title compound, dication **2**. In **1** and in the norbornenyl cation there is not much charge delocalization toward the bridgehead carbon atoms and therefore the electronic structure can be described making use of a two-electron, three-center



3



4

pentacoordinated carbon atom. Recent calculations⁷ agree with these results insofar that **3** is considered to be an energy minimum. Experimental evidence concerning this type of ion was obtained in the case of the dimethyl-substituted species **4**⁸ and some bishomo- $(\text{CH})_5^+$ cations.⁹

In the case of dication **2** one deals with an analogous delocalized electronic structure; this time, however, a hexacoordinated carbon atom is involved. Hexa-

(1) Chemistry and spectroscopy in strongly acidic solutions XL. For part XXXIX, see ref 2a.

(2) For preliminary communications, see (a) H. Hogeveen and P. W. Kwant, *Tetrahedron Lett.*, 1665 (1973); (b) *ibid.*, 3747 (1973).

(3) (a) T. P. Nevell, E. de Salas, and C. L. Wilson, *J. Chem. Soc.*, 1188 (1939); (b) S. Winstein and D. S. Trifan, *J. Amer. Chem. Soc.*, 71, 2953 (1949); (c) for a review, see S. Winstein, *Quart. Rev., Chem. Soc.*, 23, 1411 (1969).

(4) H. Hogeveen and P. W. Kwant, *J. Amer. Chem. Soc.*, 95, 7315 (1973).

(5) S. Yoneda, Z. Yoshida, and S. Winstein, *Tetrahedron*, 28, 2395 (1972).

(6) W. D. Stohrer and R. Hoffmann, *J. Amer. Chem. Soc.*, 94, 1661 (1972).

(7) (a) H. Kollmar, H. O. Smith, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 95, 5834 (1973); (b) M. J. S. Dewar and R. C. Haddon, *ibid.*, 95, 5836 (1973); (c) W. J. Hehre and P. v. R. Schleyer, *ibid.*, 95, 5837 (1973).

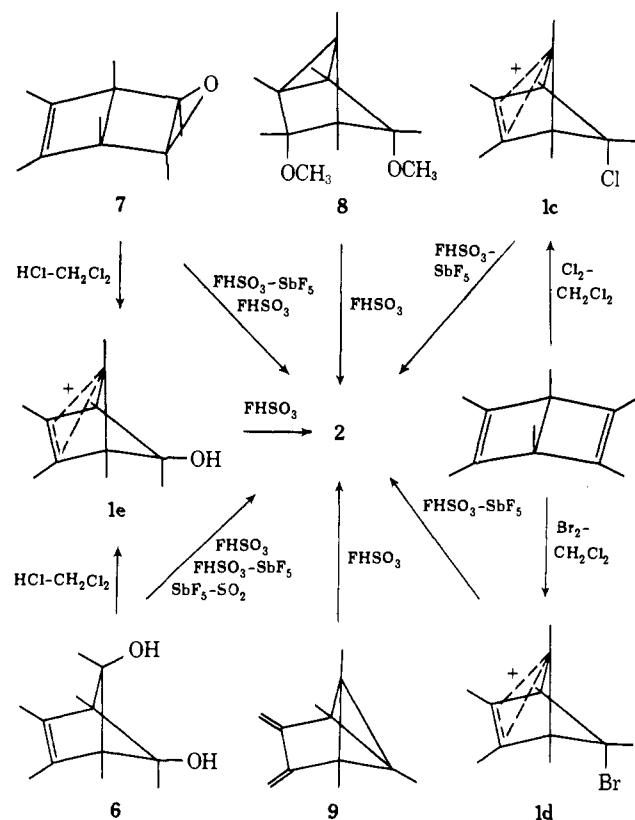
(8) (a) S. Masamune, M. Sakai, and H. Ona, *J. Amer. Chem. Soc.*, 94, 8955 (1972); (b) S. Masamune, M. Sakai, H. Ona, and A. L. Jones, *ibid.*, 94, 8956 (1972).

(9) (a) H. Hart and M. Kuzuya, *J. Amer. Chem. Soc.*, 94, 8958 (1972); (b) S. Masamune, M. Sakai, A. V. Kemp-Jones, H. Ona, A. Venot, and T. Nakushima, *Angew. Chem.*, 85, 829 (1973); (c) H. Hart and M. Kuzuya, *Tetrahedron Lett.*, 4123 (1973).

coordinated carbon atoms are not encountered in organic chemistry. Only in the field of organometallic chemistry, e.g., carboranes, is such a high coordination number observed.¹⁰ The bonding situation in carboranes, involving penta- and hexacoordinated carbon atoms, is analogous to that of the carbonium ions: sometimes it is sufficient to use two-electron, three-center bonds, but in other cases one preferably uses a more delocalized description.¹¹

In this paper we present the results of our studies concerning the chemistry and spectroscopy of the $(CCH_3)_6^{2+}$ dication and we present the arguments which prompt us to propose nonclassical structure **2** rather than a system of rapidly equilibrating structures **5** as depicted in Figure 1.

Preparation of Dication 2. Dication **2** can be generated in strongly acidic solutions from a variety of precursors. It was prepared by extraction of methylene chloride solutions of either monocation¹² **1c** or **1d** with $FHSO_3-SbF_5$ and by extraction of a solution of monocation^{12c,d} **1e** in $HCl-CH_2Cl_2$ with $FHSO_3$. The dication was also prepared directly from the precursors of ion **1e**: from diol **6**¹³ with either $FHSO_3$, $FHSO_3-$



SbF_5 , or SbF_5-SO_2 and from hexamethyldeazarbenzene epoxide (**7**)^{13a} with $FHSO_3$ or $FHSO_3-SbF_5$. Moreover dication **2** was obtained from diether **8**^{12b} and from diene **9**^{2b} with $FHSO_3$, presumably also by a two-step

(10) R. N. Grimes, "Carboranes," Academic Press, New York, N. Y., 1970.

(11) W. N. Lipscomb, *Accounts Chem. Res.*, **6**, 257 (1973).

(12) (a) R. Hüttel, P. Tauchner, and H. Forkl, *Chem. Ber.*, **105**, 1 (1972); (b) H. Hogeveen and P. W. Kwant, *Tetrahedron Lett.*, 423 (1973); (c) *ibid.*, 1351 (1973); (d) ref 4; (e) U. Burger and A. Delay, *Helv. Chim. Acta*, **56**, 1345 (1973).

(13) (a) H. N. Junker, W. Schäfer, and H. Nidenbrück, *Chem. Ber.*, **100**, 2508 (1967); (b) G. R. Krow and J. Reilly, *Tetrahedron Lett.*, 3129, 3133 (1972); (c) L. A. Paquette, S. A. Lang, Jr., S. K. Porter, and J. Clardy, *ibid.*, 3137, 3141 (1972).

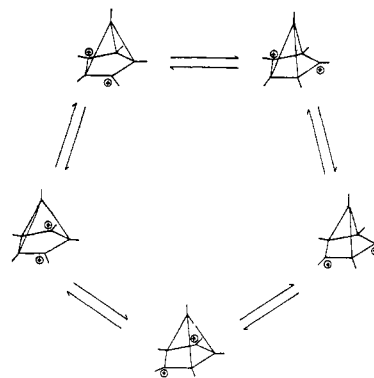
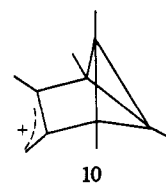


Figure 1. Degenerate rearrangement of ion **5**.

mechanism involving the monocations **1f** and **10**, respectively.



Pmr and Cmr Spectral Data. The pmr and cmr chemical shifts of dication **2** at -70° in $FHSO_3$ are given in Table I. The intensity ratios of the pmr signals

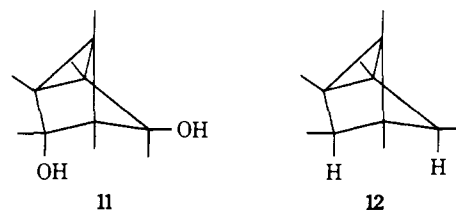
Table I. Pmr^a and Cmr^b Chemical Shifts of Dication **2** in $FHSO_3$ at -70°

| | C-1-C-5 | C-6 |
|---------------------|---------|------|
| Pmr, methyl protons | 2.65 | 1.96 |
| Cmr, methyl carbons | 10.6 | -2.0 |
| Cmr, ring carbons | 126.3 | 22.5 |

^a Relative to internal methylene chloride at δ 5.30. ^b Relative to external (capillary) TMS at δ 0.0.

and of the two types of cmr signals were 5:1. The pmr spectrum appeared to be temperature independent in the range from -140 to 100° , except for viscosity broadening in the lower temperature region.

Chemical Behavior of Dication 2. On quenching solutions of dication **2** in excess sodium methoxide in methanol, diether **8**^{12b} was found, whereas diol **11**^{12b}



was formed with excess potassium hydroxide in ethanol. When a solution of **2** in $FHSO_3$ was poured into a mixture of excess triethylamine and methylene chloride, diene **9**^{2b} was the major product and when poured into a suspension of excess lithium aluminum hydride in ether compound **12**^{12c,14} was obtained.

Dication **2** reacted in strongly acidic solutions under uptake of a hydride ion. In this way a monocation is formed which subsequently rearranges intramolecularly

(14) P. Tauchner and R. Hüttel, *Tetrahedron Lett.*, 4733 (1972).

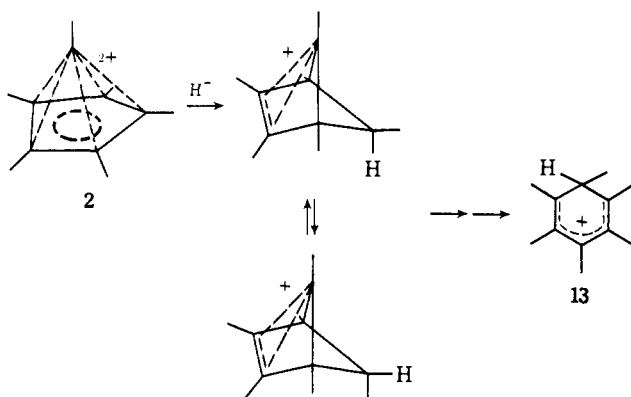
to hexamethylbenzenium ion **13**. In the sequence FHSO_3 , $\text{FHSO}_3\text{-SbF}_5$ (5:1 molar ratio), $\text{FHSO}_3\text{-SbF}_5$ (1:1 molar ratio), the pseudo-first-order rate constant of the reaction of **2** with hydride donors decreases (see Table II), presumably due to a lower concentration of

Table II. Pseudo-First-Order Rate Constants for the Hydride Transfer toward **2**

| Solvent | Hydride donor added ^a | Temp, °C | $10^5 k_1$, sec ⁻¹ |
|---|----------------------------------|-----------------|--------------------------------|
| FHSO_3 | | 21 ^b | 20 |
| $\text{FHSO}_3\text{-SbF}_5$ (5:1 molar ratio) | | 21 | 3.6 |
| | | 53 | 300 |
| $\text{FHSO}_3\text{-SbF}_5$ (1:1 molar ratio) | | 53 | 90 |
| FHSO_3 | Water ^c | 21 | 200 |
| $\text{FHSO}_3\text{-SbF}_5$ | Isopentane ^d | 21 | 1200 |

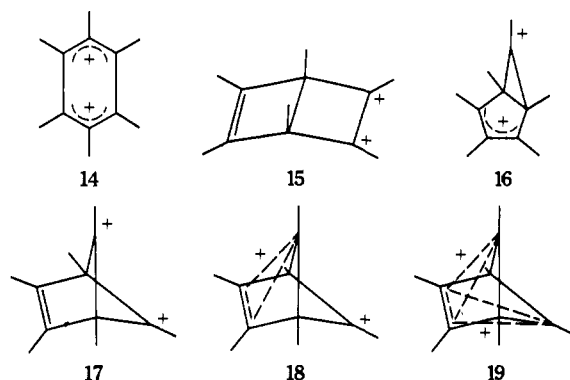
^a In all experiments at least 1 equiv of water is present (as H_3O^+) due to the precursor **7**. ^b At higher temperatures a straight first-order plot was not obtained. ^c Three per cent by weight. ^d The acid layer was saturated with isopentane, 0.09 mol/l. The second-order rate constant is calculated to be 0.13 l./(mol sec).

hydride donor in the stronger acidic¹⁵ medium. Upon addition of reagents able to donate hydride ions, such as water or isopentane, the rate increases sharply. In the latter case the rate enhancement is so large that the value of the pseudo-first-order rate constant of the hydride transfer step exceeds that of the first-order rate constant of the subsequent isomerization step¹⁶ and the intermediate monocations **1a** and **1b** (in a 3:1 equilibrium ratio)^{16,17} are observed in the pmr spectrum of the reaction mixture. These data, when added to previous reports^{16,18} on the conversion **1a**, **1b** → **13**, complete the scheme for the overall reaction **2** → **13**.



Possible Structures. The pmr chemical shifts, being far downfield from those of cations **1**,⁴ already suggest **2** to be a dication. This is confirmed by the fact that **2** is formed from precursors containing different functional groups. Because the number of skeleton carbon atoms of the quenching products is the same as that of the precursors, the possibility of a change in the number of skeleton carbon atoms in the formation of the dication can be excluded. For analogous reasons methyl shifts in the formation of the dication have not

to be envisaged: the methyl distribution in precursors and quenching products is the same. The important phenomena to be discussed here are the possible rearrangements of the carbon skeleton and the changes in the electronic structure. When structures with a localized twofold positive charge on one carbon atom are excluded for stability reasons, structures **14**–**19**, **5**, and **2** remain for further discussion.



Hexamethylbenzene dication is antiaromatic but perhaps some stabilization is gained on behaving like a pair of rather localized allyl cations as in **14**. This structure, however, is incompatible with the pmr and cmr spectra of the dication and moreover the structure of the quenching products cannot easily be explained starting from a dication of this structure, so that **14** can be rejected as a possibility. For the same reasons the stabilized pericyclic¹⁹ structure **15** is ruled out. Structure **16**, although a stabilized pericyclic, is highly unstable due to the presence of a cyclopropyl cation group. This structure also is not in agreement with the structures of the quenching products. Expanding the discussion of Goldstein and Hoffmann¹⁹ on longicyclic stabilization to dipositive ions, **17** and its delocalized descriptions **18** and **19** must be regarded as stabilized because of their modal description (002). Using the descriptions **18** and **19**, the structure of the quenching products is explained readily; the pmr and cmr 5:1 peak ratios, however, are incompatible with these descriptions as well as with **17**.

In the structure **5** stabilization occurs on delocalization of the positive charge into the three-membered ring.²⁰ Description **5** can also be regarded as stabilized by viewing it as the collapsed (002) ion **17**.¹⁹ With **5** the formation of tricyclic quenching products is easily understood; **5** as static description, however, cannot account for the 5:1 peak ratios in the pmr and cmr spectra. In carbonium ion chemistry rapidly equilibrating structures are frequently encountered and the degenerate rearranging system of Figure 1 is strongly related to the "cyclopropane merry-go-round" observed in polymethylbicyclo[3.1.0]hexenyl cations.²¹ If this fivefold degenerate rearrangement is sufficiently rapid to make five carbon atoms (with the attached methyls) equivalent on the nmr time scale, the 5:1 ratio is accounted for. It should be noted that this only holds

(15) R. J. Gillespie and T. E. Peel, *J. Amer. Chem. Soc.*, **95**, 5173 (1973).

(16) H. Hogeveen and H. C. Volger, *Recl. Trav. Chim. Pays-Bas*, **87**, 385, 1042 (1968); **88**, 353 (1969).

(17) L. A. Paquette, G. R. Krow, J. M. Bollinger, and G. A. Olah, *J. Amer. Chem. Soc.*, **90**, 7147 (1968).

(18) H. Hogeveen and P. W. Kwant, *Tetrahedron Lett.*, 3197 (1972).

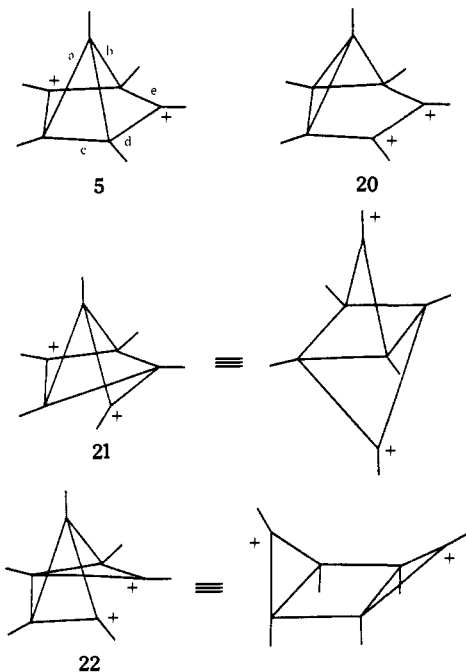
(19) M. J. Goldstein and R. Hoffmann, *J. Amer. Chem. Soc.*, **93**, 6193 (1971).

(20) G. A. Olah, D. P. Kelly, C. L. Jeuell, and R. D. Porter, *J. Amer. Chem. Soc.*, **92**, 2544 (1970).

(21) (a) R. F. Childs, M. Sakai, and S. Winstein, *J. Amer. Chem. Soc.*, **90**, 7144 (1968); (b) R. F. Childs and S. Winstein, *ibid.*, **90**, 7146 (1968).

for a rapid Wagner–Meerwein shift of bonds a, in the way indicated in Figure 1.

Some other rearrangements of bonds in the dication deserve discussion. The other possibility of rearrangement for bond a would give the more symmetrical ion **17**, whereas, if bond b were involved in the rearrangement either **16** or **20** would be intermediate. These two structures are energetically unfavorable, **16** because of the cyclopropyl cation group²² and **20** because of the

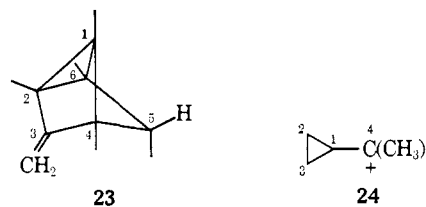


presence of positive charges on two neighboring carbon atoms. Involvement of bond c in a 1,2 shift would give rise to the highly symmetrical ion **21**. Rearrangement of bond d would either bring double positive charge on one carbon atom, which is most unlikely, or lead to **22** as an intermediate with two energetically unfavorable cyclopropyl cation groups.²² Rearrangement of bond e would involve double positive charge on one carbon atom or directly give another ion **5**. In the latter case, as well as when symmetrical intermediates **16**, **17**, **21**, or **22** are involved simultaneously with the rearrangement of Figure 1, complete scrambling of the six carbon atoms and the attached methyl groups would occur. In the pmr spectrum at 100°, however, such a scrambling is not indicated by line broadening so that free enthalpy of activation of one of these rearrangements of ion **5** is at least 21 kcal/mol.

Is the Dication Classical or Nonclassical? The experimental facts discussed so far are equally well explained by assuming a rapidly equilibrating system of classical ions **5** as by the static nonclassical structure **2**. From the fact that the pmr spectrum of the dication in $\text{FHSO}_3\text{-SbF}_5\text{-SO}_2\text{-SO}_2\text{F}_2$ at -140° displays no line broadening (except viscosity broadening) of the signals, it is calculated that the free enthalpy of activation for a rapid Wagner–Meerwein shift, causing the degenerate system of Figure 1, would be smaller than 5 kcal/mol. This would be a low barrier compared with those of degenerate rearrangements of analogous ions as hepta-

methylbicyclo[3.1.0]hexenyl cation (9 kcal/mol)^{21b} and *exo*-methylhexamethylbicyclo[3.1.0]hexenyl cation (12 kcal/mol).²³ It might, however, be argued that in the latter cases allylic stabilization in the ground state adds to the free enthalpy of activation so that the barrier of less than 5 kcal/mol for ion **5** is still compatible with such a classical structure.

Strong preference for the nonclassical alternative structure **2** is based on the following arguments. (1) The chemical shift of the ring carbon atoms was observed to be at 126.3 ppm. In the two alternative structures **2** and **5** this value means the chemical shift of C-1, -2, -3, -4, and -5 and the weighted average of the chemical shifts of these carbon atoms, respectively. Olah developed a method for testing whether an observed chemical shift is consistent with a system of rapidly equilibrating structures. The average chemical shift, which is calculated with the use of suitable model compounds and correction factors, was found to deviate less than 10 ppm from the observed average chemical shift of the carbon atoms involved in a degenerate rearrangement process.²⁴ In the case of structure **5** the model compounds are chosen to be compound **23**⁴ and dimethylcyclopropylcarbinyl cation



24.²⁰ The chemical shift of C-2 (45.0 ppm) and C-4 (47.7 ppm) of **23** are used as the chemical shifts of the quaternary carbon atoms adjacent to the sp^2 hybridized cation centers, the cation centers themselves are given the chemical shift of C-4 of **24** (281.4 ppm). The correction term for the presence of positive charge adjacent to the quaternary carbon atoms of the five-membered ring is taken to be two times the value of 13 ppm needed for correction of the calculated average of the carbon chemical shift of a five-membered ring for presence of one positive charge.²⁴ The average chemical shift is calculated to be now: $[2(281.4) + 2(45.0) + 47.7] / 5 + 2(13.0) = 166.1$ ppm. This value is about 40 ppm higher than the observed chemical shift, therefore the observed chemical shift cannot be explained with rapidly equilibrating structures **5**.

(2) The chemical shift of the single methyl cmr peak was found to be -2.0 ppm, a value that is upfield compared with the chemical shift of the C-1 methyl of **23** found at 4.7 ppm. As **23** has approximately the same geometry as **5**, one would expect a downfield shift, rather than an upfield shift on introduction of positive charges at C-3 and C-5, that is going from **23** to **5**. The observed upfield shift of 6.3 ppm, however, is readily explained with structure **2**, with the methyl at C-6 being in the shielding cone of the five-membered ring.

(3) The dication can be viewed as the protonated monocation **10**. This monocation is expected to be stabilized due to its nature as an allylic cation with additional stabilization by delocalization of the positive

(23) V. A. Koptuyg, L. I. Kuzubova, I. S. Isaev, and V. I. Mamatyuk, *J. Org. Chem. USSR*, **6**, 2265 (1970).

(24) G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91**, 5801 (1969).

(22) (a) P. v. R. Schleyer, T. M. Su, M. Saunders, and J. C. Rosenfeld, *J. Amer. Chem. Soc.*, **91**, 5174 (1969); (b) W. F. Sliwinski, T. M. Su, and P. v. R. Schleyer, *ibid.*, **94**, 133 (1972).

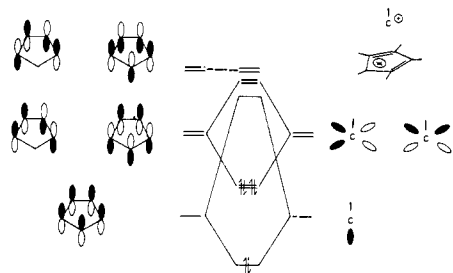


Figure 2. Interaction diagram of CCH_3^+ and pentamethylcyclopentadienyl cation.

charge into the adjacent cyclopropane ring.²⁵ To determine whether the dication occurs in equilibrium with **10**, attention was paid to the pmr spectra in $FHSO_3$; however, only peaks due to the dication were observed. When we compare this result with the literature data on allylic cations stabilized by a cyclopropane group—these cations are not protonated in $FHSO_3$ to give dications to a detectable extent²⁵—it is obvious that an unusual large stabilization of the dication is responsible for the equilibrium laying on the dication side in our case. In order to get information about the rate of deprotonation in the equilibrium $2 \rightleftharpoons 10 + H^+$, the rate of deuterium exchange was measured in deuterated acid. Such an experiment was carried out by generating the dication in $DFSO_3$ at low temperature and leaving the solution at room temperature during 1 day. This time exceeds 10 half-lives of the dication in the hydride (deuteride) transfer reaction in strongly acidic solution (see Table II), so that the dication was almost quantitatively converted to hexamethylbenzenium ion. The mass spectrum of the hexamethylbenzene obtained after quenching of this solution with water indicated 1% of deuterium to be present. The methyl hydrogens of the dication therefore have exchanged for deuteriums to an amount of only 1%. This implies the deprotonation $2 \rightarrow 10 + H^+$ to have a first-order reaction rate constant of about $5 \times 10^{-5} \text{ sec}^{-1}$. This low rate of deprotonation is in agreement with the view that the dication is unusually stabilized. The stabilization can readily be explained by nonclassical resonance stabilization as depicted by structure **2**.

(4) Carbonylation of the dication (0.14 mol/l.) was attempted using a solution of pivaloyl cation (0.57 mol/l.) in $FHSO_3-SbF_5$ (1:1 molar ratio) as the carbon monoxide donor.²⁶ After 24 hr at 21° (the dication was about half-decomposed due to the hydride transfer reaction) no products were detected that could be formed by carbonylation of the dication. The carbonylation rate of the dication at 21° was established in this way to be lower than $10^{-5} \text{ l.}/(\text{mol sec})$. The carbonylation rate of the dication is much lower than that of the dimethylcyclopropylcarbinyl cation **24**, being $3.6 \times 10^{-3} \text{ l.}/(\text{mol sec})$ at -68° .²⁷ As the rate of carbonylation decreases with increasing stability of the cation^{26,27} the dication has to be regarded in this way as much more stabilized than **24**. Structure **5** cannot account for such a high stabilization.

(25) T. S. Sorensen and K. Rajeswari, *J. Amer. Chem. Soc.*, **93**, 4222 (1971).

(26) (a) H. Hogeveen, F. Baardman, and C. F. Roobeek, *Recl. Trav. Chim. Pays-Bas*, **89**, 227 (1970); (b) H. Hogeveen, *Advan. Phys. Org. Chem.*, **10**, 29 (1973).

(27) H. Hogeveen and C. J. Gaasbeek, *Recl. Trav. Chim. Pays-Bas*, **89**, 359 (1970).

(5) The thermal stability of the dication is unusually high. Even the aromatic tetramethylcyclobutenium dication was reported to be more than 80% decomposed in a $FHSO_3-SbF_5-SO_2$ solution at -78° after 6 hr.²⁸ Dication **2**, however, can be handled in strongly acidic solution at room temperature and the hydride transfer described above is the only reaction that occurs. Also at elevated temperature (up to 100° in $FHSO_3-SbF_5$ 1:1 molar ratio) no other reaction was observed.

(6) The stability arguments are supported strongly by *ab initio* calculations of Jonkman and Nieuwpoort²⁹ on the parent $(CH)_6^{2+}$ dication. These authors calculated energies of many structures with C-6 at different positions above the plane of the five-membered ring. The energy was found to decrease sharply when C-6 approaches a point above the center of the ring—that is structure **2**. No evidence was found of other stable conformations, the lowest energies obtained were still about 25 kcal/mol higher than the calculated minimum energy of structure **2**. Although hexamethyl substitution is expected to stabilize all structures of $(CH)_6^{2+}$ the relative stabilities will be hardly affected^{7c} so that these results are applicable to $(CCH_3)_6^{2+}$.

It is our feeling that the arguments presented above are strong enough to prefer the nonclassical structure **2**. In cooperation with Dr. G. A. Sawatzky we will try to get additional evidence by measuring the esca spectrum of the dication.

Electronic Structure and Charge Distribution in Dication **2.** Stohrer and Hoffmann⁶ described the electronic structure of **3** with use of an interaction diagram between cyclobutadiene and CH^+ . Dication **2** can be treated in a similar way with an interaction diagram (Figure 2) showing how the orbitals of **2** are constructed from CCH_3^+ and pentamethylcyclopentadienyl cation. From the value of the carbon chemical shift of C-6, which can be interpreted to be a result of an upfield shift by rehybridization effects and a downfield shift due to positive charge,⁴ it can be concluded that there is by far no full positive charge at C-6. This conclusion on charge distribution is in agreement with the results of the *ab initio* calculations of Jonkman and Nieuwpoort²⁹ on $(CH)_6^+$, who conclude that the gross atomic orbital populations for the top CH group are $\sigma_{CH}^{2\pi 1.76} \sigma^{0.96}$. Starting from $\sigma_{CH}^{2\pi 2} \sigma^0$ one might say, according to these authors, that 0.96 electron has donated to the empty σ orbital of CH^+ accompanied by a π backdonation of 0.24 electron to the $(CH)_5^+$ ring. This would result in a positive charge of 0.28 unit at the top carbon atom and of 0.34 unit at each of the ring carbon atoms. The bond length of the five-membered ring bonds is calculated to be 1.45 Å and the top carbon atom is found at 1.21 Å above the center of the five-membered ring.

The Mechanism of Reactions of Dication **2 with Nucleophiles.** Attack on the carbon atoms of the five-membered ring of dication **2** is favored over attack at the top carbon atom by the somewhat higher positive charge and the statistical factor of 5. Due to the steric hindrance of C-6 at the top and the fact that a nucleophile prefers attack at the side with the lowest electron density, kinetically controlled attack will occur at the

(28) G. A. Olah, J. M. Bollinger, and A. M. White, *J. Amer. Chem. Soc.*, **91**, 3667 (1969).

(29) (a) H. T. Jonkman and W. C. Nieuwpoort, *Tetrahedron Lett.*, 1671 (1973); (b) personal communication.

bottom of the five-membered ring. On quenching dication **2** with sodium methoxide in methanol, potassium hydroxide in ethanol, or lithium aluminum hydride in ether, monocations are formed in the first step with the functional group in the endo position. The endo OCH_3 cation **1f** and the endo H ion **1b** react again in a kinetically controlled reaction at the most positive carbon atom at the side with the lowest electron density to yield **8** and **12**, respectively.⁴ This two-step mechanism is shown in Figure 3 for the formation of **12**. The endo OH ion formed according to this mechanism has first to isomerize to the exo OH ion **1e**, an assumption made previously,⁴ before undergoing nucleophilic attack to yield **11**.

In the hydride transfer reaction in strongly acidic solution it can also be assumed that the hydride is transferred to the bottom of the five-membered ring of dication **2**. The ion **1b** formed in this way rapidly isomerizes to give a 3:1 equilibrium mixture of **1a** and **1b**.¹⁶ The reaction of **2** with the base triethylamine can be understood equally well with use of a two-step mechanism (Figure 3). In the first step monocation **10** is formed by abstraction of a proton from a methyl group attached to one of the five ring carbon atoms bearing the highest positive charge³⁰ which is followed by a second proton abstraction to give diene **9**.

Experimental Section

Spectroscopic Measurements. Proton magnetic resonance spectra were recorded at 60 MHz using a Varian A-60 D or a Jeol C 60-HL spectrometer equipped with a variable-temperature probe. Chemical shifts were measured relative to internal methylene chloride (δ 5.30) and converted to values relative to internal TMS at δ 0. Natural abundance carbon-13 nuclear magnetic resonance spectra were obtained with a Varian XL-100 spectrometer operating at 25.2 MHz. Spectra were recorded with the use of Fourier transform and were proton-noise decoupled. The number of spectra accumulated varied between 500 and 5000, depending on sample concentration. Chemical shifts were calculated relative to external (capillary) TMS. The assignment of the cmr chemical shifts was made by use of off-resonance decoupled spectra to determine the extent of proton substitution. Mass spectra were determined with an AEI MS 9 mass spectrometer. The mass spectrum of hexamethylbenzene showed a parent peak at m/e 162 (100%) and an isotope peak at m/e 163 (14%). The mass spectrum of the partly deuterated hexamethylbenzene obtained in the deuterium exchange experiment showed a parent peak at m/e 162 (100%) and an isotope peak at m/e 163 (32%).

Preparations. *endo*-5-Chloro-1,2,3,4,5,6-hexamethylbicyclo[2.1.1]hexenyl Cation (**1c**). A solution of **1c** was prepared by dissolving hexamethyldewarbenzene in methylene chloride, followed by introduction of dry chlorine gas (1 equiv) at -70° .

endo-5-Bromo-1,2,3,4,5,6-hexamethylbicyclo[2.1.1]hexenyl Cation (**1d**). A solution of **1d** was obtained by mixing methylene chloride solutions of equimolar quantities of hexamethyldewarbenzene and bromine at -70° .

exo-5-Hydroxy-1,2,3,4,5,6-hexamethylbicyclo[2.1.1]hexenyl Cation (**1e**). A solution of **1e** was prepared by dissolving *anti*-5,6-dihydroxy-1,2,3,4,5,6-hexamethylbicyclo[2.1.1]hexene-2 (**6**) or hexamethyldewarbenzene epoxide (**7**) in methylene chloride at -70° and introducing dry hydrogen chloride gas until the ratio of dissolved HCl-methylene chloride was 1:2 v/v.

Dication 2. Solutions of monocations **1c**, **1d**, and **1e** were extracted with excess FHSO_3 or $\text{FHSO}_3\text{-SbF}_5$ (10:1 molar ratio) in an nmr tube at -70° . The pmr spectrum of the acid layer displayed at -70° peaks at δ 1.95 and 2.65.

Dication **2** was prepared as well in the following way: solutions of **6**, **7**, 3,5-dimethoxy-1,2,3,4,5,6-hexamethyltricyclo[2.2.0.0^{2,6}]-hexane (**8**), or 1,2,5,6-tetramethyl-3,4-dimethylenetricyclo[3.1.0.0^{2,6}]-hexane (**9**) in methylene chloride were cooled in liquid nitrogen and

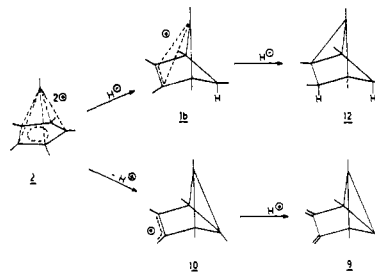


Figure 3. Two-step reactions of dication **2** with a nucleophile and a base.

subsequently FHSO_3 was introduced. The mixtures were allowed to warm up slowly in a bath of -90° and were stirred as soon as possible. The acid layer contained the dication according to the pmr spectrum.

Solutions of dication **2** in $\text{FHSO}_3\text{-SbF}_5$ (5:1 and 1:1 molar ratios) and in $\text{SbF}_5\text{-SO}_2$ were prepared by cooling the acid mixture in liquid nitrogen followed by introduction of crystalline **6**. The mixtures were allowed to warm up slowly and were stirred as soon as possible.

Quenching of 2 by Sodium Methoxide in Methanol and by Potassium Hydroxide in Ethanol. Quenches of dication **2** were performed by pouring solutions of **2**, prepared from 0.50 g of **6**, in sodium methoxide (5%) in methanol or potassium hydroxide (5%) in ethanol. A twofold excess of methoxide or hydroxide was used, calculated on the basis of the quantity of acid. The quenching reagents were cooled to -60° and with vigorous stirring the acid solution of **2**, kept at -60° , was poured in. Hereafter the reaction mixtures were allowed to warm to room temperature, water was added, and the mixtures were extracted with pentane. Washing with water, drying over anhydrous sodium sulfate, and evaporating the solvent gave crude products, which consisted of 95% of **8** and 80% of **11**, respectively (determined by pmr). Exposure to the air at room temperature during 1 day^{12b} afforded **6**,¹³ which was purified by crystallization from hexane, the yield was 0.43 g (85%) and 0.33 g (65%), respectively, calculated on the quantity of **6** used as the dication precursor.

Reaction of 2 with Triethylamine. A solution of dication **2** (prepared from 0.50 g of **7**) in FHSO_3 at -60° was added to a twofold excess (calculated on the basis of the quantity of acid) of triethylamine in a 25% solution in methylene chloride of the same temperature. After 2 hr at -60° the mixture was allowed to warm to room temperature. After dilution with 2 volumes of pentane the reaction mixture was washed with water until the smell of triethylamine disappeared. Drying the solution and evaporating the solvent yielded a crude product which consisted of 80% of **9**, determined by pmr and glc; preparative glc yielded 0.29 g (65%) of **9** as a colorless liquid.^{2b}

Reaction of 2 with Lithium Aluminum Hydride. A solution of **2**, prepared from 0.50 g of **7** as precursor, in FHSO_3 was cooled to -60° and added to a suspension of twofold excess lithium aluminum hydride (calculated on the basis of the acid used) in ether at -60° . After 2 hr at -60° an equal volume of pentane at room temperature was added and the mixture was allowed to warm to -5° . Water was added cautiously and after destruction of the excess lithium aluminum hydride the organic layer was washed with an aqueous sodium sulfate solution. Drying the solution and evaporating the solvent gave 0.44 g of crude product which consisted of 90% **12** (determined by pmr); preparative glc yielded 0.31 g (70%) of **12** as a colorless liquid.¹⁴

Kinetic Measurements. The solutions of **2** in $\text{FHSO}_3\text{-SbF}_5$ (5:1 and 1:1 molar ratios) and in FHSO_3 used in the hydride transfer rate measurements, the solution of **2** in FDSO_3 used in the deuterium exchange rate measurement, and the solution of **2** in $\text{FHSO}_3\text{-SbF}_5$ (1:1 molar ratio) used in the carbonylation rate measurement were all prepared from precursor **7**. The acid was cooled in liquid nitrogen and **7** was introduced at liquid nitrogen temperature. After warm up in a bath of -90° stirring was applied as soon as possible.

The rates of hydride transfer in strongly acidic media were determined by measuring the intensity of the pmr signals of **2** as a function of time. Starting concentrations of **2** varied between 0.5 and 1.0 mol/l. Straight pseudo-first-order plots were obtained

(30) H. Hogeveen and P. W. Kwant, *Tetrahedron Lett.*, 5357 (1972).

over a least 2 half-lives of dication 2. The hydride transfer rate measurement in $\text{FHSO}_3\text{-SbF}_5$ (5:1 molar ratio) with isopentane as hydride donor was performed by keeping the acid layer saturated with isopentane. This was effected by vigorous stirring between

the pmr measurements. From the integration of the pmr peaks of isopentane and of the acid the concentration of isopentane was calculated to be 0.09 mol/l. *tert*-Pentyl cation was observed as a reaction product.

Aromatic Substitution. XXXVI.¹ Aluminum Trichloride and Antimony Pentafluoride Catalyzed Friedel-Crafts Alkylation of Benzene and Toluene with Esters and Haloesters

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Abstract: The AlCl_3 or SbF_5 catalyzed alkylation of benzene and toluene with alkyl chlorosulfites, arenesulfonates, chloro- and fluorosulfates, arenesulfonates, triflates, pentafluorobenzenesulfonates, and trifluoroacetates as alkylating agents was investigated in nitromethane, methylene chloride, carbon disulfide, 1,1,2-trichlorotrifluoromethane, or excess aromatics solution. The inter- and intramolecular selectivities of the alkylations was studied based on competitive toluene/benzene rate ratio and isomer distributions. The mechanism of the alkylation reaction is discussed.

The alkylation of aromatics with esters was known since Friedel and Crafts in 1877 observed the ethylation of benzene by ethyl chloroformate.³ Esters since reported to effect the alkylation of aromatics include alkyl sulfates, sulfites, phosphates, orthosilicates, carbonates, borates, chloroformates, hypochlorites, halo-sulfates, chlorosulfites, arenesulfonates, and perchlorates.⁴ In contrast to the vast literature of solvolysis of esters their alkylation reactions received but scarce attention.

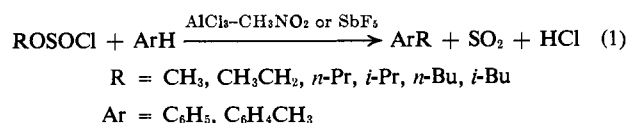
In continuation of our studies on aromatic substitution⁵ we therefore undertook a study of the Friedel-Crafts alkylation of benzene and toluene with alkyl chlorosulfites, arenesulfonates, tosylates, chloro- and fluorosulfates, trifluoromethanesulfonates (triflates), pentafluorobenzenesulfonates, and trifluoroacetates. The use of haloesters in aromatic alkylations has not yet been investigated and their comparison with arenesulfonates and tosylates also was of interest. Our studies were primarily directed toward an understanding of the mechanistic aspects of the reactions, particularly their selectivity and not to necessarily establish optimized preparative conditions. Consequently, our interest was directed to obtain relative reactivity data and isomer distributions reflecting the selectivity of the reactions.

In the alkylation of aromatic with esters, the acid formed as a by-product is generally nonvolatile and thus cannot escape from the reaction mixture, as do, for example, hydrogen halides formed in alkylation with alkyl halides. Since the continuously increasing

acid concentration, which results as the reaction proceeds, may cause secondary reactions (*i.e.*, isomerization and disproportionation), there are few quantitative studies of alkylation with esters allowing evaluation of the mechanism, including selectivities of the reactions.

Results

(i) **Alkyl Chlorosulfites.** The alkylation of aromatics with alkyl chlorosulfites was little studied in the past. Barkenbus, *et al.*,⁶ investigated butylation by *n*-butyl chlorosulfite, which took place without concurrent chlorination characteristic for related alkylations with alkyl chlorosulfates. We have now studied the alkylation of benzene and toluene with methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, and isobutyl chlorosulfites.



Except for the reaction with methyl chlorosulfite, ready alkylation of benzene and toluene took place when using aluminum chloride-nitromethane as catalyst. Methyl chlorosulfite did not give methylated products under similar conditions even at 70°. Antimony pentafluoride, a much stronger Lewis acid catalyst than aluminum chloride, however, effects methylation of benzene and toluene with methyl chlorosulfite at 20°.

The reactions with *n*-propyl, *n*-butyl, and isobutyl chlorosulfite gave isopropylation, *sec*-butylation, and *tert*-butylation, accompanied by *n*-propylation, *n*-butylation, and isobutylation, respectively. In all cases, formation of skeletal rearranged products exceeded that of nonrearranged alkylates corresponding to the original alkylating agents. The ratio of skeletal re-

(1) Part XXXV: G. A. Olah and H. C. Lin, *J. Amer. Chem. Soc.*, in press.

(2) Postdoctoral Research Associate, 1971-1973.

(3) C. Friedel and J. M. Crafts, *C. R. Acad. Sci.*, **34**, 1450 (1877); *Ann. Chim. Phys.*, (6), **1**, 527 (1884).

(4) (a) F. A. Drahowzal, "Friedel-Crafts and Related Reactions," Vol. II, G. A. Olah, Ed., Interscience, New York, N. Y., 1964, p 641, and references cited therein. (b) G. A. Olah, "Friedel-Crafts Chemistry," Wiley-Interscience, New York, N. Y., 1973.

(5) For review, see G. A. Olah, *Accounts Chem. Res.*, **4**, 240 (1971).

(6) C. Barkenbus, R. L. Hopkins, and J. F. Allen, *J. Amer. Chem. Soc.*, **61**, 2452 (1939).