UV), Ms. Barbara Warren (mass spectra), and Mr. G. Robertson and Mr. R. Oeckinghaus (elemental analyses).

Volume Profile of the Degenerate Equilibration of a Nonclassical 7-Norbornadienyl Cation

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In an earlier paper,[2] we described the effect of pressure on the degenerate Wagner–Meerwein shift of the 1,2-dimethoxy-2-norbornyl cation (1). In this interconversion
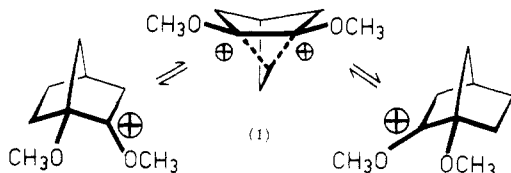
of ions known to be classical,[3] symmetry demands full charge delocalization in the transition state. Since the rate of this equilibration can conveniently be determined by means of the temperature dependence of the methoxy proton magnetic resonance line shapes, use was made of our recently developed apparatus for measuring NMR spectra of solutions under pressure.[4] The volume of activation for the reaction was found to be +8 cm³/mol, in good, if qualitative, agreement with the result expected on the grounds that charge dispersal leads to diminished solvent–ion interactions (Drude–Nernst or Born formalisms[5]) and hence to expansion. We concluded that this finding supports the validity of the use of activation volumes as a criterion for carbon participation in solvolysis,[6] at least in those cases in which the positive charge is equally distributed among at least two centers in the incipient cation.

Another interesting test of this proposal is made possible by the 7-methyl-7-norbornadienyl cation (2). In that instance, the degenerate rearrangement known as bridge flipping[7] interconverts known[8] nonclassical ions via a

classical transition state; in this respect, the reaction is the exact reverse of the equilibration described above. Charge concentration now takes place as the transition state is approached; as a result of this, increased solute–solvent interaction should occur, resulting in a contraction which should reveal itself in the form of a pressure-enhanced equilibration rate.
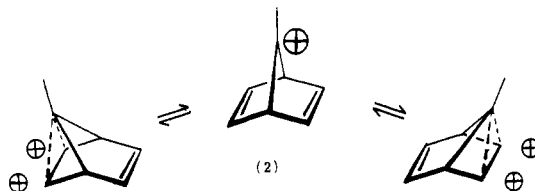
A complication arises when the probable magnitude of this effect is appraised. The symmetry-allowed sigmatropic[9] 1,2-shift in the 2-norbornyl ion occurs without bond cleavage: the two-center 1,6 bonding pair simply becomes a three-center pair in the transition state.[10] In contrast, the three-center bond in the nonclassical 7-norbornadienyl cation is broken in the transition state, and hence this should make a positive contribution to $\Delta V^{\ddagger}$. If the charge concentration effect is gauged at −8 cm³/mol (the opposite of the dispersal effect in the equilibration of 1) and the contribution of the breaking bond at +10 cm³/mol,[11] one is led to anticipate a small activation volume of uncertain sign and relative indifference of the rate to the application of pressure.

We have investigated the ¹H NMR spectra of 2 in fluorosulfonic acid as a function of both temperature and pressure. The temperature-dependent spectra, while showing higher resolution than those reported by Lustgarten et al.,[12] were completely consistent with their results. At −55.4 °C, we find a clearly resolved spectrum exhibiting the bound vinyl protons at δ 7.3, the unbound vinyl protons at δ 5.9, the bridgehead protons at δ 4.9, and the methyl protons at δ 1.6. As the temperature is raised, the two vinyl proton signals broaden and finally coalesce at −16 °C; at still higher temperatures, irreversible decomposition occurs. The pressure dependence was determined at roughly 30-MPa intervals over a range of 200 MPa (~2000 atm) and at a temperature of −23 °C where broadening is already clearly visible at atmospheric pressure. As can be seen in Figure 1, the application of pressure causes no change in the NMR spectrum of 2 other than that attributable to the thermal decomposition.

The insensitivity of the bridge-flipping process of 2 to pressure is in sharp contrast to the dramatic sharpening of the methoxy signals of 1 engendered by pressure. It was pointless to simulate the spectra of 2 under pressure because all of them were superimposable except for the decomposition; however, from the sensitivity of the spectra to temperature, the resolution (estimated to be 1 Hz), the known value of $\Delta G^{\ddagger}$ (52 kJ/mol = 12.4 kcal/mol), and the expression $\Delta V^{\ddagger} = (-RT\delta \ln k)/\delta p$, it is possible to appraise the precision of our result: $\Delta V^{\ddagger} = 0 \pm \leq 3$ cm³/mol. We conclude that, if one allows for the known effect of bond breaking, the pressure effects on the equilibration rates

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Method for Sulfide S-Benzylation or S-Allylation Using Trimethylsilyl Triflate Activated Benzyl or Allyl Ethers

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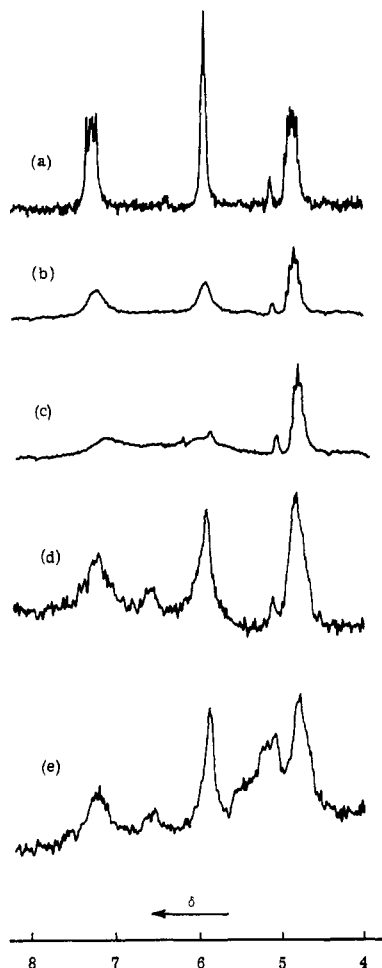
Figure 1. Temperature and pressure dependence of 7-methyl-7-nornornadienyl cation; the bound vinyl, unbound vinyl, and bridgehead ^{1}H NMR signals occur at δ 7.3, 5.9 and 4.9, respectively. (a) At -45.7 °C; (b) at -25.8 °C; (c) at -15.6 °C; a, b, and c were recorded at atmospheric pressure with a 5-mm spinning sample tube. (d) At atmospheric pressure and -23 °C; (e) at 195 MPa and -23 °C; d and e were recorded with the sample in the high-pressure vessel.

in 1 and 2 both are in excellent agreement with expectations based on the Drude–Nernst correlation between volume and charge distribution.

Experimental Section

The solution of 7-methyl-7-norbornadienyl cation was prepared from quadricyclanone in three steps. 7-Methylquadricyclanol was prepared in a reaction of methylmagnesium bromide with quadricyclanone. The isomerization to 7-methylnorbornadienol was carried out with a catalytic amount of bis(chlorodicarbonyl-rhodium) in CCl$_4$ solution under an argon atmosphere; this is a modification of the procedure described by Lustgarten et al.^{12} The reaction was complete in 30 h. The 7-methylnorbornadienol was dissolved in CD$_2$Cl$_2$, degassed with a freeze–thaw cycle, and dissolved in triply distilled FSO$_3$H under high vacuum at -80 °C. This solution was placed in the capillary cell, and spectra were obtained by means of a Brucker WP-60 at -23 °C as previously described.^{4}

Registry No. 2, 19005-48-2.

Attempts in our laboratory to prepare benzyl triflate from benzyl alcohol and trifluoromethanesulfonic anhydride–pyridine have been unsuccessful. Although small amounts of the triflate apparently do survive long enough in solution to be trapped by subsequent addition of sulfides (<10% salt formation), a practical synthetic procedure has so far proved elusive.

We now report that the combination of benzyl trimethylsilyl ether with trimethylsilyl triflate is synthetically useful as a substitute for benzyl triflate. When these reagents are combined in the presence of a sulfide, good yields of S-benzylsulfonium triflates can be isolated (Table I). A similar procedure allows preparation of S-allyl-sulfonium triflates from a variety of allyl ethers. Although yields of crystalline S-allyl salts are modest, the procedure may prove advantageous in situations where the high reactivity of allyl triflate^1 is an intimidating factor.

The exact identity of the reactive alkylating agent formed from benzyl or allyl ethers and (CH$_3$)$_3$SiOTf is not known. In methylene chloride, either the oxonium salt **1** or the derived triflate **2** may be involved. With acetonitrile as solvent, the nitrilium salt **3** must also be considered since allyl triflate attacks acetonitrile rapidly.^{1} In general, acetonitrile has proved to be the best solvent for alkylation of relatively unreactive sulfides which are inductively deactivated by carbonyl substituents. In one case (Table I, entry 4), the alkylation of a deactivated sulfide is sufficiently fast in methylene chloride.
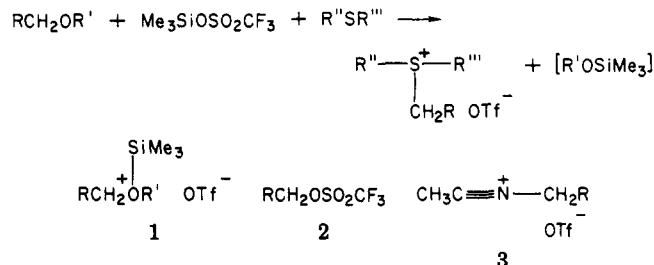
More reactive sulfides such as 1,3-dithiane can also be alkylated in less polar solvents (4:1 toluene–CH$_3$CN), using CH$_2$=CHCH$_2$OSi(CH$_3$)$_3$/(CH$_3$)$_3$SiOSO$_2$CF$_3$. The initial salt **4** has not been obtained in crystalline form, but the reaction is quite efficient as evidenced by conversion of **4** into **5** (2,3-shift) upon treatment with KOC(CH$_3$)$_3$ (68% yield over two steps).
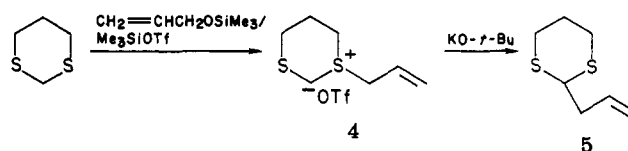
Similar treatment of *n*-propyl trimethylsilyl ether with (CH$_3$)$_3$SiOSO$_2$CF$_3$ in the presence of sulfides gives no isolable sulfonium salts at temperatures up to 80 °C. Evidently, the solvolytic reactivity of the benzyl or allyl

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