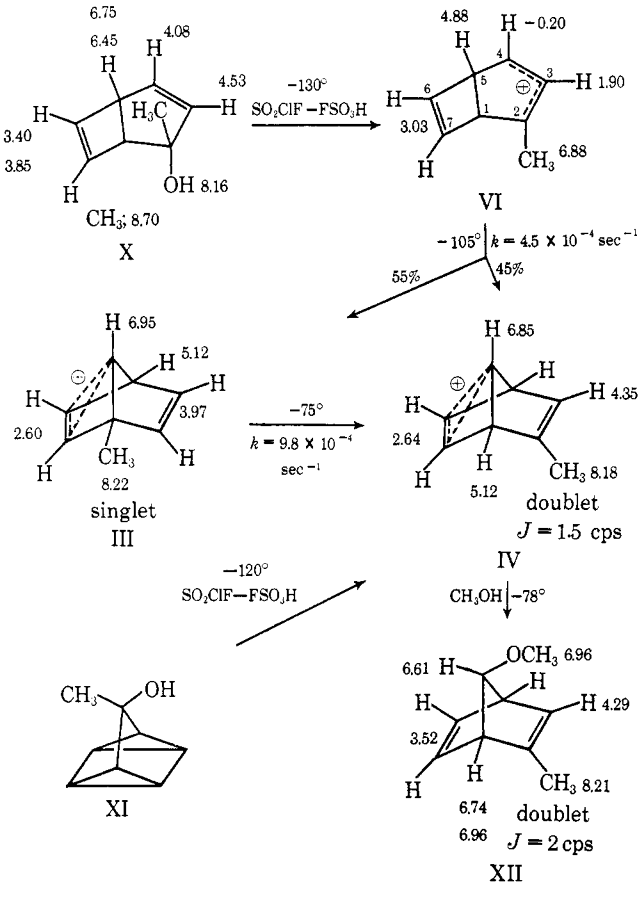
III, and VI, with IV, according to the present results, decomposing rapidly at −17°. Energetically, this is quite plausible.[13]

The present data make available rate constants for interconversion of the 1-methylnorbornadienyl ion III and the 2-methylbicyclo[3.2.0]heptadienyl cation VI, as well as an estimate of the equilibrium constant for VI $\rightleftharpoons$ III. The rate constant for the III → VI ring contraction is considerably larger ($\Delta F^{\ddagger}$ = 13.8 kcal/mol) than for the ring contraction of the parent norbornadienyl ion IX ($\Delta F^{\ddagger}$ = 16.6 kcal/mol), while the rate constant for the VI → III ring expansion is considerably smaller than for the VIII → IX ring expansion of the parent [3.2.0] ion. The latter process was too rapid to permit recording of the nmr spectrum of ion VIII at −78° before it isomerized to IX.[2b] We have now made the same observation at −120°, so that $\Delta F^{\ddagger}$ for the VIII → IX ring expansion must be less than 10.2 kcal/mol. These effects of the methyl group in III and VI are obviously associated with the much greater stabilizing effect of the methyl group in the terminal allylic position of VI than in the bridgehead position of III. At −100° the equilibrium constant for VI $\rightleftharpoons$ III is *ca.* 60, while it is $>1.2 \times 10^8$ in the parent case VIII $\rightleftharpoons$ IX.



The 1-methylnorbornadienyl ion III can be visualized to ring contract to the 1-methylbicyclo[3.2.0] ion V, but this process is apparently not competitive with the III → VI ring contraction.[14] If V were formed, it would be expected to give I at least as rapidly as III; however, I is not observed. Since the methyl group remains on the bridgehead in the III → V ring contraction, the rate of the latter would be expected to resemble that of the parent IX → VIII process ($\Delta F^{\ddagger}$ = 16.6). Thus, it is energetically consistent that III → V, with eventual formation of I, does not compete with III → VI ($\Delta F^{\ddagger}$ = 13.8).

Regarding relative stability of the different methyl-substituted norbornadienyl cations, the equilibrium between the 7-methyl ion I and its 2-methyl isomer II favors II by a factor of at least 50, and that between the 1-methyl ion III and its 5-methyl isomer IV favors IV[15] by a factor of at least 20. Because of the positions of the methyl substituent, II would be expected to be the most stable and III the least stable of the four [2.2.1] ions. However, there remains the interesting, still unanswered, question regarding the relative stability of I with a 7-methyl group and IV with a methyl substituent on the "unbound" olefinic group.

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(13) $\Delta F^{\ddagger}$ for ring contraction in the parent system[2b] IX is 16.6 kcal/mol. If this value is increased by the 7-methyl group in I to *ca.* 19 kcal/mol, ring contraction of I would become only competitive with rearrangement to II ($\Delta F^{\ddagger}$ = 18.9kcal/mol). The value of $\Delta F^{\ddagger}$ for I → IV depends, of course, on the partitioning of V, *i.e.*, on the ratio k_2/k_{-1}. This ratio is not expected to be prohibitively small.

(14) The present results give no information regarding still another ring contraction–ring expansion, namely IV → VII. While such ring contraction would be disclosed by suitable labeling of IV, one would expect IV → VII to be considerably slower than IV → VI or III → VI.

(15) Judging by the τ 3.97 signal in the nmr spectrum of III, *ca.* 4% of the latter ion remains at equilibrium with IV at −75°. This has not yet been confirmed by quenching experiments. On the basis of 4% of III at equilibrium with IV, the rate constant for the IV → VI ring contraction is *ca.* 10^{-4} sec^{-1} at −75°.

(16) (a) National Institutes of Health Postdoctoral Fellow; (b) National Science Foundation Postdoctoral Fellow.

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Received October 14, 1968

syn-7-Bromobenzonorbornadiene. Synthesis and Solvolytic Reactivity

Sir:

The chemistry of benzonorbornadiene (**1**) and its derivatives has attracted considerable attention recently.[1] Whereas the solvolytic reactivity of several benzonorbornenyl and benzonorbornadienyl substrates has been reported,[2] that of the interesting *syn*-7-benzonorbornadienyl system has not.[3]

We wish to report the synthesis of the *syn*-7-bromide **6** and its solvolytic reactivity in 80% ethanol. Treatment of **1** in carbon tetrachloride with 1,2-dibromotetrachloroethane using a 275-W sunlamp quantitatively yielded a mixture of *trans*-2,3-dibromide (**2**, 89%), together with the *exo-cis* isomer (11%). The *trans* isomer was converted to *syn*-7-bromo-*exo*-2-acetoxybenzonorbornene (**3**, mp 101–102°) with silver acetate in acetic acid. Hydrolysis of **3** with methyl Grignard reagent to the bromohydrin **4** (mp 126–128°), followed by oxidation with chromium trioxide in pyridine, gave the *syn*-7-bromo ketone **5** (mp 135°). Irradiation of a rotating thin film of the lithium salt of the tosylhydrazone from **5** at 5 mm with a 275-W sunlamp

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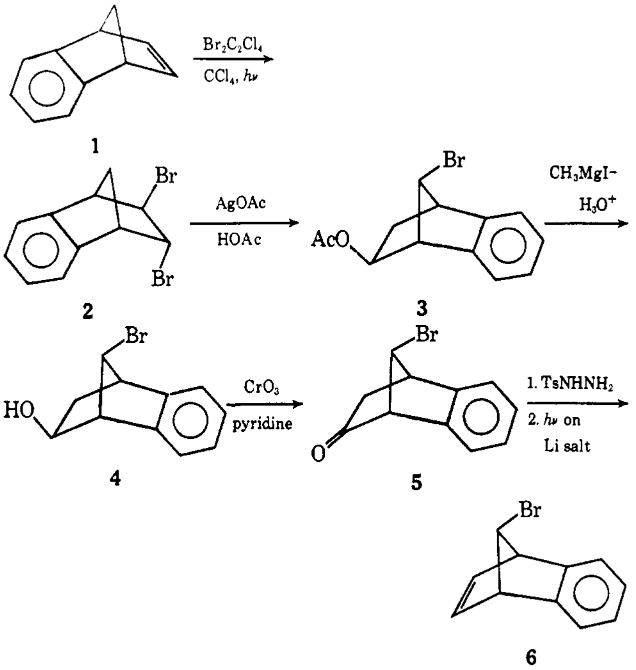
(1) For a recent paper with many additional references, *cf.* M. M. Martin and R. A. Koster, *J. Org. Chem.*, 33, 3428 (1968).

(2) H. Tanida, *Accounts Chem. Res.*, 1, 239 (1968), gives a well-documented summary.

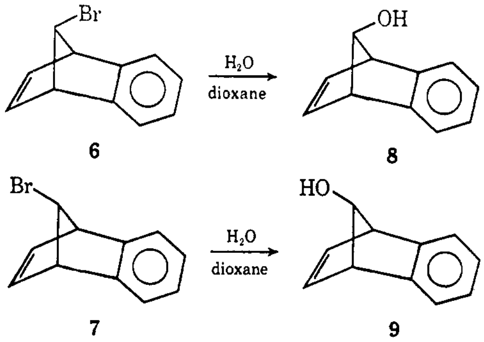
(3) S. J. Cristol and G. W. Nachtigall, *J. Org. Chem.*, 32, 3727, 3738 (1967), have mentioned briefly the *syn*-7 chloride and its nmr and mass spectra, with further details promised.

produced bromide **6** [mp 61.1–61.7°, λ^{KBr} 14.5 μ (HC=CH); $\delta^{CCl_4-CDCl_3}$ 7.0–7.42 m (ArH, A_2B_2), 6.85 t (HC=CH), 4.64 t (-CHBr-), 3.99 q (bridgehead H's). *Anal.* Calcd for $C_{11}H_9Br$: C, 59.75; H, 4.10. Found: C, 59.87; H, 4.29].



The solvolysis of **6** in 80% ethanol was followed conductometrically: k_1 = (19.4°) 5.01 × 10^{-4} sec^{-1}; (25.4°) 1.09 × 10^{-3} sec^{-1}; (32.9°) 2.38 × 10^{-3} sec^{-1}; $\Delta H^{\ddagger}$ = 20.6 kcal mol^{-1}; $\Delta S^{\ddagger}$ = −3.3 eu. Bromide **6** is very reactive in solvolysis. Its rate at 25° is some 4.4 × 10^4 times faster than that of the *anti* epimer **7**[4] (k_1 = 2.4 × 10^{-8} sec^{-1} by Volhard titration) and nearly three times faster than that of *t*-butyl bromide (k_1 = 3.85 × 10^{-4} sec^{-1}).[5]

The solvolysis product from **6** in 70% dioxane containing 1.2 equiv of 2,6-lutidine was solely the *syn*-7-alcohol **8** (mp 92.5–94°). The alcohol and ether products in 80% ethanol were also only *syn*-7 derivatives.[6] Similarly, the *anti* epimer **7** afforded only the *anti*-7-alcohol **9**[7] in aqueous dioxane.



These results are of interest in the area of π participation and particularly in the contrast between aromatic and olefinic abilities to stabilize homoallylic cationic centers. It is curious that *both syn*- and *anti*-7-bromobenzonorbornadienes solvolyze with retention.

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Received October 14, 1968

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[4] J. W. Wilt, G. Gutman, W. J. Ranus, Jr., and A. R. Zigman, *J. Org. Chem.*, **32**, 893 (1967), report its synthesis. Its solvolysis was part of the present study.

[5] O. T. Benfey, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 2494 (1952). We found a rate constant at 25.9° of 4.2 × 10^{-4} sec^{-1} by conductometry.

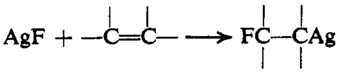
[6] All new compounds except **2** have been fully characterized by analysis and consonant spectra. Dibromide **2** had the proper spectra but was not as yet purified for analysis.

[7] P. D. Bartlett and W. P. Giddings, *J. Amer. Chem. Soc.*, **82**, 1240 (1960).

Perfluoroalkylsilver Compounds

Sir:

We wish to report the preparation of perfluoroalkylsilver compounds by the nucleophilic addition of silver fluoride to fluoro olefins.



$$AgF + \overset{|}{-C}=\overset{|}{C}- \longrightarrow F\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}Ag$$

The silver fluoride addition reaction has been investigated with perfluoropropene, 2-chloroperfluoropropene, and perfluoro-2-methyl-2-pentene. Unlike the previously known silver alkyls,[1] the perfluoro compounds are relatively stable materials which are soluble in organic solvents and can be isolated as solvates. They decompose thermally to yield perfluoroalkyl free-radical products and are useful as synthetic intermediates.

For example, 0.100 mol of AgF in 100 ml of CH_3CN absorbed 0.100 ± 0.005 mol of CF_2=$CFCF_3$, added as a gas during 2 hr at 25°, with solution of the AgF. Filtration of the brown reaction mixture under a nitrogen atmosphere yielded a clear light yellow solution of perfluoroisopropylsilver, $(CF_3)_2CFAg$, which slowly darkened on standing. The presence of the silver compound was shown by treating duplicates of the above filtered reaction product as follows. (1) The addition of HCl in CH_3CN at 0° yielded 0.095 mol of CF_3CHFCF_3 and AgCl. A reaction with water also yielded CF_3CHFCF_3. (2) The addition of bromine in CH_3CN at 0° gave 0.062 mol of $CF_3CBrFCF_3$ and AgBr. (3) Removal of CH_3CN to a final bath temperature of 60° (0.05 mm) left a residue corresponding in weight to $(CF_3)_2CFAg \cdot CH_3CN$. Heating the solvate at 100° during 1.5 hr gave as volatile products, in addition to CH_3CN, 0.007 mol of CF_3CHFCF_3, 0.002 mol of CF_3CF=CF_2, and 0.033 mol (66%) of $(CF_3)_2CFCF(CF_3)_2$. The residue contained 0.093 g-atom of Ag^0 and 0.002 g-atom of Ag^+. The reaction products CF_3CHFCF_3, CF_3CF=CF_2, and $CF_3CBrFCF_3$ were isolated by distillation and determined quantitatively by glpc with a 0.25 in. × 15 ft 20% dioctyl phthalate on Chromosorb P column at 25°. Their identities were confirmed by comparison of their infrared and mass spectra with those of authentic samples. The C_6F_{14} was separated by distillation. Its properties were bp 58.0° (745 mm); ir max (gas) 1290, 1272, 1248 (shoulder), 1151, 995, 982, 963, 894, 747, and 730 cm^{-1}; mass spectrum, molecular ion − 19, 319 ($C_6F_{13}^+$) (no molecular ion at 338); nmr (^{19}F) 56.6 and 144.3 ppm up-

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[1] Very few alkylsilver compounds are known. Methyl- and ethylsilver are sparingly soluble solids which decompose below room temperature: G. E. Coates and F. Glocking in "Organometallic Chemistry," H. Leiss, Ed., Reinhold Publishing Corp., New York, N. Y., 1960, p 447.