Conclusion

Many purported examples of "spontaneous" radical formation from nitroso compounds which have (explicitly or implicitly) been identified as MAH processes are actually due to inadvertent photolysis. We suggest that the role of ordinary laboratory light on other "spontaneous" radical-forming processes should be investigated.

Note Added in Proof: After submission of this manuscript a paper appeared describing the hydroxylamines formed in the ene reactions of CF_3NO with a variety of olefins and the nitroxides formed by oxidation of these hydroxylamines.[60] It was pointed out[60] that the previously postulated[6] involvement of ion radicals in these reactions was based upon doubtful EPR evidence and a misidentification of the products from allyl compounds. It was also pointed out[60] that the evidence for the postulated rate-determining formation of a diradical in the reactions of 2,4,6-trichloronitrosobenzene with olefins[18] was doubtful.

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(60) Barlow, M. G.; Haszeldine, R. N.; Murray, K. W. *J. Chem. Soc., Perkin Trans. 1* **1980**, 1960.

Dication Ether Salts, R^+-O-$R^+\cdot 2CF_3SO_3^-$, from the Reaction of Trifluoromethanesulfonic Anhydride with Activated Ketones

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Contribution from the Departments of Chemistry, Medicinal Chemistry, and Biochemistry, The University of Utah, Salt Lake City, Utah 84112. *Received November 21, 1980*

Abstract: Reaction of activated ketones with triflic anhydride (Tf_2O) in either CH_2Cl_2 or CCl_4 results in the formation of novel dication ether salts, R^+-O-$R^+\cdot 2^-OTf$. Stabilized dications of the Hückel aromatic, 6π-heterocyclic, and substituted urea systems can all be prepared. The majority of these compounds are stable hygroscopic crystalline salts. They may be fully characterized by spectroscopic and chemical means. Hydrolysis results in the corresponding hydroxy salts and reaction with amines in the corresponding amino salts. These results are discussed in detail.

Carbocations are among the most ubiquitous reactive intermediates in chemistry. These electron-deficient species encompass a wide spectrum of structural features and possess a rich variety of chemical properties. Despite the ubiquitous nature and great variety of carbocations, bis(carbenium ions) linked by a single atom, **1a**, are to our knowledge unknown. Since coulombic

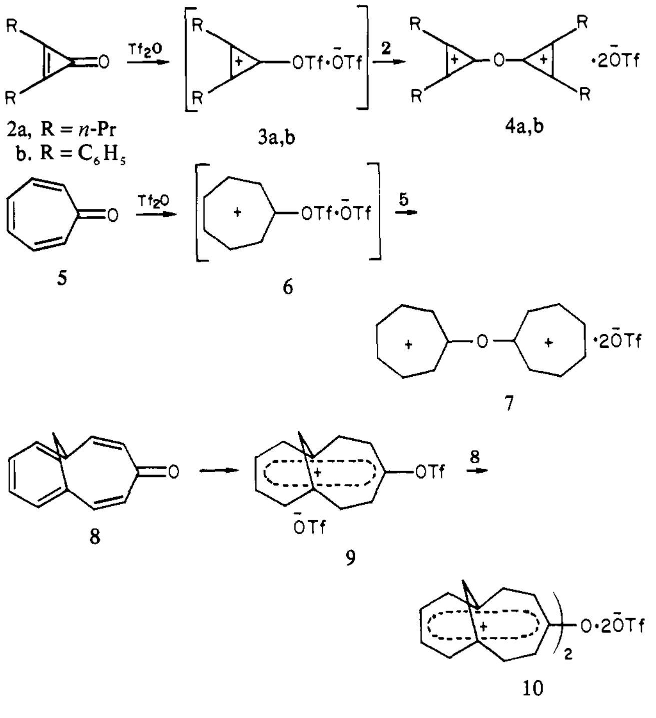
$$\underset{\mathbf{1a}}{R^+\text{-}A\text{-}R^+\cdot 2X^-} \qquad \underset{\mathbf{1b}}{R^+\text{-}O\text{-}R^+\cdot 2CF_3SO_3^-}$$

repulsion of two nearby concentrated like charges would result in considerable destabilization, species with highly delocalized carbenium ions linked by a heteroatom with lone-pair electrons would have the best chance of being observed. In this paper we report[1] the preparation, characterization, and some chemistry of remarkably stable, novel dication ether salts (**1b**), the first members of a class of new bis(carbenium ions) (**1a**).

Results and Discussion

A. Synthesis of Aromatic Cations of the Hückel Type. Addition of half an equivalent of triflic anhydride, $(CF_3SO_2)_2O$, Tf_2O, to a solution of the substituted cyclopropenones (**2**) or to tropone (**5**) in anhydrous CH_2Cl_2 or CCl_4 results in the rapid formation of the corresponding dication ether salts **4** and **7** as shown in Scheme I. Reaction most likely proceeds by initial sulfonation of these activated carbonyls to form monocations **3** and **6**. In the case of the cyclopropenones or tropone, the respective monocations could not be be isolated or observed even with inverse addition of the carbonyl to a large excess of Tf_2O. In contrast, reaction of Tf_2O with [11]annulenone **8** at room temperature yields only the monocation **9**. Cation **9** may be readily transformed into dication **10** by reaction with an equivalent amount of annulenone **8** at elevated temperature.

Scheme I



6π-Heteroaromatic Ions. Dimethylpyrone (**11**) xanthone (**13**), and *N*-methylpyridone (**15**) also react with triflic anhydride to give the respective dication ether salts **12**, **14**, and **17**, as shown in Scheme II. Once again reaction undoubtedly occurs via monotriflation and the intermediacy of monocations, but only in the case of *N*-methylpyridone (**15**) was the monocation isolable. Further reaction of monocation **16** at elevated temperatures results in dication **17**. In contrast to the above systems, reaction of

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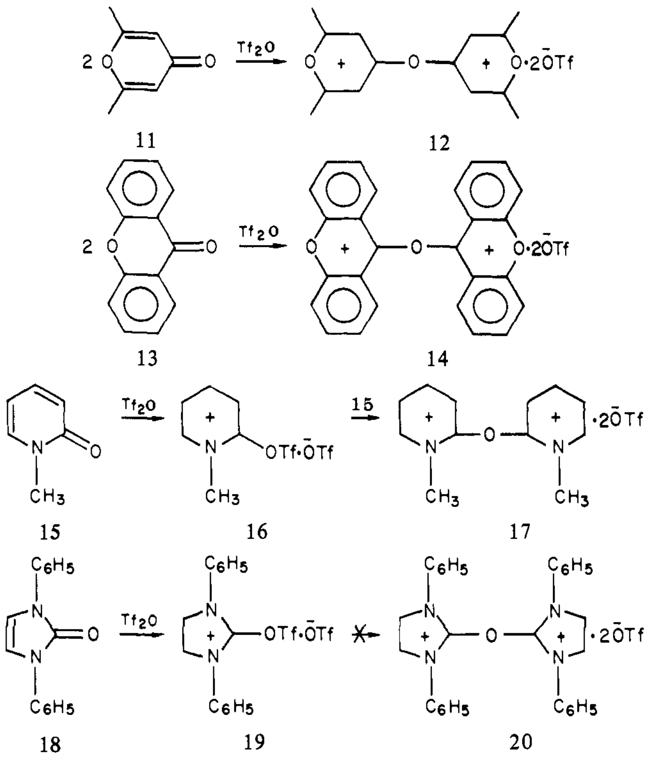
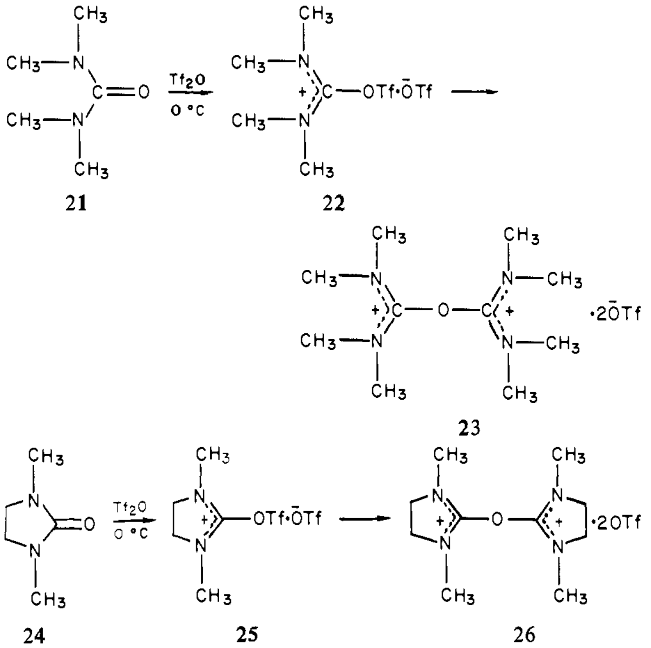
(1) For a preliminary communication, see: Stang, P. J.; Maas, G.; Fisk, T. E. *J. Am. Chem. Soc.* **1980**, *102*, 6361-6362.

0002-7863/81/1503-4837$01.25/0

Scheme II



Scheme III



imidazolone **18** gave only monocation **19**, which could only be characterized in solution. Monocation **19** could not be converted to the corresponding dication even at elevated temperatures. Prolonged heating of **19** with an additional mole of starting ketone **18** results in a dark-red solution, yielding two triflate-free unknown compounds whose mass spectra indicate dimers of **18**.

Substituted Urea Systems. The dication ether salts reported in Schemes I and II are unique in that the positive charge is extensively delocalized and stabilized via aromatic moieties. In order to examine if nonaromatic systems formed similar dication ethers, we investigated the reaction of substituted ureas with triflic anhydride. Indeed, both tetramethylurea **21** and cyclic urea **24** give, at 0 °C with 1 equiv of anhydride, the very hygroscopic monocations **22** and **25**, respectively, which react with excess urea at higher temperatures to give the respective dications **23** and **26** as shown in Scheme III.

Conversion of monocation **22** into **23** occurs more readily than the analogous reaction of monocation **25** with a second molecule of **24**. Furthermore, monocation **19** cannot be converted into its dication by reaction with another molecule of **18** that may also be considered a cyclic urea. This reactivity sequence corresponds to the anticipated decrease in electron density on the carbonyl oxygen from **21** to **24** to **18** and the consequent reduction of the nucleophilic potential of the respective carbonyl groups.

It should be mentioned that reaction of triflic anhydride with ureas differs from alkylation reactions of ureas with Meerwein (oxonium) salts[2] in two respects. First, alkylation of ureas occurs at both oxygen and nitrogen, whereas triflation occurs only at oxygen with no evidence for N-triflation. Secondly, both O-alkylated and N-alkylated ureas are very stable compounds resisting hydrolysis, whereas these dication ether salts, although thermally stable, are generally very hygroscopic.

B. Spectral Properties of Mono- and Dication Salts. Because of the extreme moisture sensitivity, the low solubility, and low volatility of many of these dication ether salts, it proved to be difficult in some cases to obtain complete spectral data on each and every one. The spectral data and their use in the characterization of the salts are best presented in two parts. Table I summarizes the mass spectra and IR, ^{1}H, and ^{19}F spectral data of the mono- and dication salts, and in Chart I we list the ^{13}C NMR data. Where unambiguous assigment of the ^{13}C was possible, they are given in Chart I; when it was not possible to make a complete assignment of all signals, they are given in summary form.

Reaction between starting ketone and triflic anhydride is indicated by the complete absence of the characteristic carbonyl absorption in the infrared spectra of all new products. The ionic nature of these new compounds is clearly indicated by both the physical (see the Experimental Section) and spectral (vide infra) properties of these substances. The major task is distinguishing between three different possible ionic species: monocations resulting from monotriflation, the proposed dication ether salts, and the product of their hydrolysis, the respective hydroxy cation salts.

The downfield shift of most signals in the proton and carbon-13 spectra of these new species, compared to the corresponding signals in the neutral precursors, is particularly characteristic of their cationic nature. This is well illustrated by the bridged annulenium ions **9** and **10**, where the low-field shift of all ring protons together with the upfield shift of the bridge hydrogens in the proton spectrum and the low-field shift of the ring carbons in the C-13 spectrum reveal the presence of a diamagnetic ring current in the ions absent in the precursor annulenone **8** that displays properties characteristic of a normal conjugated polyene.[3]

A clear distinction between triflated monocations and dication ether salts can be made based on the ^{19}F spectrum and to a lesser extent on the ^{13}C and IR spectrum. Monocations **9**, **16**, **19**, **22**, and **25** all give rise to two distinct fluorine signals for the covalently bound triflate at 93–94 ppm and for the anionic one at 85.4–87.6 ppm relative to C_6F_6. In contrast all dication ether salts as well as the hydroxy cation triflates, as expected, give only a single ^{19}F absorption in the appropriate anionic region. Similarly, the carbon atom in the covalent and anionic triflate group gives rise to two clearly separated signals in the ^{13}C spectrum. For example, the carbon in the covalent triflate group in monocation **16** appears at 119.2 ppm (q, J_{CF} = 321 Hz), whereas the carbon in the triflate anion shows up at 121.6 ppm (q, J_{CF} = 320 Hz). As required for the dication ether salts, ion **17**, for example, shows only a single ^{13}C absorption at 121.7 ppm (q, J_{CF} = 321 Hz) in the expected anionic region of the CF_3SO_3 group as does the hydroxypyridinium triflate **36** at 121.3 ppm (q, J_{CF} = 315 Hz). However, because

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(2) Meerwein, H.; Florian, W.; Schon, N.; Stopp, G. *Justus Liebigs Ann. Chem.* **1961**, *641*, 1–39.

(3) Grimme, W.; Reisdorff, J.; Jünemann, W.; Vogel, E. *J. Am. Chem. Soc.* **1970**, *92*, 6335–6337.

Table I. Spectral Properties of Dication Ether Salts and Monocation Salts

compd	FD mass spectra (int)[a]	^{1}H NMR[b]	^{19}F NMR[c]	IR, cm^{-1} [d]
4a		1.02 (*t*, *J* = 7.5 Hz), 1.94 (sext, *J* = 7.5 Hz), 3.13 (*t*, *J* = 7.5 Hz)	87.1	*e*
4b		7.64–8.80 (6 H), 8.20–8.48 (4 H)	87.4	1595 (m), 1500 (w), 1400 (br, m). 1250/1224/1173, 1030 (s)
7		8.98–9.58 (m)	87.1	1470 (s), 1300 (s), 1263 (s), 1227 (s) 1199 (s), 1160 (s), 1036 (s), 1030 (s)
9	(16 mA) 762 (6), 422 (10), 373 (9), 304 (17), 303 (100), 263 (10), 258 (15), 255 (6), 239 (6), 235 (9), 234 (6), 202 (7), 192 (7), 191 (17), 190 (14), 189 (45), 171 (15), 170 (37), 154 (8), 151 (24)	1.68 (dt, *J* = 11 and 2 Hz), −0.4 (d, *J* = 11 Hz), 8.56–8.9 (m) 8.85 and 9.50 (AA′BB′)	87.0 93.5	1433 (s). 1260 (vs, sh at 1248), 1224, 1166, 1134, 1043 (all s)
10	(13 mA) 623 (1.5), 511 (2), 509 (4), 491 (3), 474 (7.5), 473 (24), 393 (6), 339 (3), 325 (4), 324 (1.8), 323 (3), 227 (3). 191 (37), 190 (16), 189 (95), 171 (65), 162.5 (55), 162 (100)	−0.84 (dt, *J* = 11.5 and 1.5 Hz), −0.09 (d, *J* = 11.5 Hz), 8.64–9.00 (m, 6 H), 9.55 (part of AA′BB′, *J* = 11.5 Hz)	87.4	1555 (m), 1504 (m), 1257, 1151, 1127, 1030 (all s)
12		2.97 (s, CH$_3$), 8.03 (olef)	87.4	1615, 1450/1443, 1322, 1275, 1255, 1220, 1173, 1145, 1029 (all s)
14		7.47–7.74 (m. 8 H), 7.90–8.10 (m, 4 H), 8.38 (dd, *J* = 8.1 and 1.5 Hz, 4 H)	87.3	1599, 1522. 1497, 1300, 1272, 1153, 1135, 1038, 1022 (all s)
16		4.26 (s, CH$_3$), 7.96–8.16 (m, 2 H), 8.62–8.88 (m, 2 H)	87.3 93.8	1635 (s), 1580 (m), 1441 (s), 1462 (sh), 1285-1260 (s, br). 1229, 1173, 1133, 1042, 1033 (all s)
17		4.32 (s, CH$_3$), 7.80–8.03 (m, 4 H), 8.51–8.83 (m. 4 H)	87.1	1640 (m), 1579 (m), 1508 (s), 1468 (m), 1305 (m), 1280–1250 (s, br), 1228, 1183, 1160, 1038, 1030 (all s)
19		7.76–8.13 (m)	86.2 93.8	*e*
22		3.47 (s)	85.4 93.1	1648 (s), 1407 (m), 1278/1253/1229 (s, br), 1033 (s)
23	(14 mA) 879 (6), 552 (4), 536 (6). 367 (5), 366 (16), 365 (100), 349 (4), 202 (3), 169 (5.5), 119 (4), 115 (3), 108.5 (9), 108 (73), 101 (84)	3.22 (s)	87.6	1702/1680 (s), 1263, 1226. 1158, 1036 (all s)
25[f]		3.17 (CH$_3$), 4.18 (CH$_2$)	85.4 93.3	*e*
26	(17 mA) 871 (6), 548 (3), 532 (3), 362 (7), 361 (39), 247 (3), 211 (7), 209 (7), 114 (6), 106.5 (2.2) 106 (18), 99 (100), 97 (73)	3.12 (s, CH$_3$), 4.05 (s, CH$_2$)	87.1	1695, 1680, 1672 (all m), 1569 (m), 1275, 1267, 1228, 1155, 1038 (all s)

[a] Field desorption mass spectra at given anode voltage. [b] CD$_3$CN; internal standard, Me$_4$Si. except 4a, 19, 22, 25 in CDCl$_3$, internal standard, Me$_4$Si. [c] CD$_3$CN except 4a, 19, 22, 25 in CDCl$_3$ relative to C$_6$F$_6$. [d] Nujol mull except 9, 10, 23, 26 (KBr pellets), 22 (neat film). [e] Sample hydrolyses. [f] Contaminated by small amounts of hydroxy salt.

of the high relaxation time of the CF$_3$ carbon, its signal can only be observed in highly concentrated solution (difficult to achieve because of low solubility) or by applying a long pulse delay (10–15 s) and multiple aquisitions and hence is of limited diagnostic value. Triflated monocations may also be recognized by a medium strong absorption in the 1407–1447-cm^{-1} region due to the covalently bound CF$_3$SO$_3$ group that is absent in the anionic triflate of the dication ether salts. However, other absorptions at or near this region limits the usefulness of this observation. Because of the very low volatility of salts, characterization of these compounds by electron-impact or chemical-ionization mass spectrometry based on conventional thermal ionization is not feasible. Therefore field-desorption (FD) mass spectrometry, which can be used to generate ions from organic salts,[4,5] was explored as a means of producing useful structural information.[6] Successful results were realized for the monocation **9** and the dication salts **10**, **25**, and **26**. As is often the case with FD mass spectrometry, the reason for failure to produce ions in sufficient abundance for measurement from the remaining compounds is not clear. The extreme reactivity of these compounds to traces of moisture may be a factor and in some instances probably led to ions associated with small amounts of hydrolysis products. Pyrolysis or ion/molecule reaction at the surface of the FD emitter can also be responsible for production of unassigned ions. This feature is most pronounced for high-mass ions and has been noted by Wood and co-workers[5] in the case of bis(phosphonium) halides, Ph$_3$P$^+$(CH$_2$)$_x$P$^+$Ph$_3$·2X$^-$.

For the monocation **9** the molecular ion M$^+$, *m/z* 303, was observed as the base peak in the mass spectrum (Table I). The low-intensity peaks below mass 303 correspond principally to fragments associated with the cation moiety, such as *m/z* 154 (M − OTF)$^+$, the highly stabilized cation species. The mass 170 ion corresponds to the molecular ion of the ketone **8**, while *m/z* 189 corresponds to **8** plus a water molecule. While the latter may reasonably be attributed to hydrolysis of **9**, this appears unlikely because relatively volatile products such as **8** should desorb at substantially lower emitter currents. As in the case of minor higher mass ions that remain unassigned, these ions may be associated with dimers or trimers formed by ion/molecule reactions. This view is supported by the increased relative abundance of these ions at higher emitter temperatures. The *m/z* 151 due to protonated triflic acid is ubiquitous in the mass spectra of these salts.

In the mass spectrum of the corresponding dication ether salt **10**, the protonated molecular ion MH$^+$ appears at *m/z* 623 in low

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(4) Schulten, H.-R. *Int. J. Spectrom. Ion Phys.* **1979**, *32*, 99–283.

(5) Wood, G. W.; McIntosh, J. M.; Lau, P.-Y. *J. Org. Chem.* **1975**, *40*, 636–639.

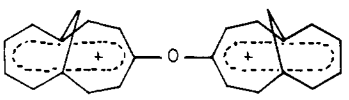
(6) An interesting approach to the problem of low volatility of ionic species is that of ion pairing.[7] EI and CI mass spectra of *n*-alkyl sodium sulfate and sulfonate salts were made possible by pairing with primary amines, although ions indicative of an intact ion pair were not observed.

Table II. Summary of Physical and Spectral Properties of Hydroxy Triflates 31-38

compd	% yield	mp, °C	^{1}H NMR^{a,b}	^{19}F NMR^c	IR,^{d} cm^{-1}	anal, calcd (found) C	anal, calcd (found) H
31a^e		oil	1.12 (t, *J* = 7.5 Hz, CH_3), 1.92 (sext, 2 H), 3.02 (t, *J* = 7.5 Hz, 2 H), 14.4 (s, 2 H)	86.4	1950-1600 (br, m, OH), 1522 (s), 1318 (s), 1230 (s), 1193 (s), 1015 (s)		
31b^f	80	144-146	7.86-8.2 (m, 6 H), 8.42-8.60 (m, 4 H), 13.82 (1 H)	85.9	1900-1730 (br, m, OH), 1597 (s), 1502 (s), 1447 (s), 1408 (s), 1293 (s), 1223 (s), 1187/1175/1120 (s), 1025 (s)	51.34 (50.9)	3.50 (3.47)
32	52	141-142.5	8.40-9.06 (m, 6 H), 12.80 (s, 1 H)	84.4 (g)	2800-2200 (br, m, OH), 1623 (m), 1510/1496/1475 (m), 1290/1250/1230/1216 (br, s), 1170 (s), 1032 (s)		
33	44	92-93	−0.33 (s, 2 H), 7.88 and 8.66 (AA'BB), 8.10 (m, 4 H), 10.30 (br, s, OH)	86.2	3100-2300 (br, m, OH), 1537 (m), 1248 (s), 1234 (s), 1200 (s), 1030 (s)		
34	95	80-84	2.72 (s, 6 H), 7.34 (s, 2 H), 13.04 (s, 1 H, OH)	85.6	3200-2200 (br, m, OH), 1638 (s), 1547 (s), 1490 (s), 1270/1242/1225 (s), 1165 (s), 1030 (s)	35.04 (55.1)	3.31 (3.29)
35 (h)	77	140-141	8.52-7.58 (m, 8 H), 13.4 (s, 1 H, OH)	87.6	2800-2150 (br, m, OH), 1615, 1602, 1587, 1523, 1498, 1305, 1181, 1167. 1153, 1022 (all s)	48.56 (48.3)	2.62 (2.65)
36	96	108-109	3.83 (s, 3 H), 6.99-7.33 (m, 2 H), 7.86-8.08 (m, 2 H), 12.2 (s, 1 H, OH)		2900-2200 (br, m, OH), 1644, 1603, 1523, 1483/1465, 1356, 1294, 1228, 1170 (br), 1031 (all s)	32.44 (32.2)	3.11 (3.07), N, 5.40 (5.3)
37		oil	3.03 (s, 6 H). 3.73 (s, 4 H), 13.1 (br, 1 H, OH)	85.3	3380, 3000-2100 (br, m, OH), 1650/1613, 1294/1230/1175 (br, s), 1035 (s)		

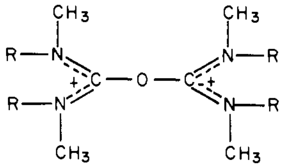
[a] 31a, 33, 34, 38 in $CDCl_3$; 31b, 32, 35, 36 in CD_3CN; internal standard, Me_4Si. [b] OH signal concentration dependent, values refer to ~10% sol (7% for 33, 35% for 36). [c] 31a, 33, 34, 38, in $CDCl_3$, 31b, 32, 35, 36, in CD_3CN; internal standard, C_6F_6. [d] 31a in $CHCl_3$ sol; 34 in KBr, 38 thin film, remainder in Nujol mull. [e] Incorporates 0.5 H_2O of crystallization. [f] Incorporates 1.0 H_2O of crystallization. [g] In CH_2Cl_2; internal standard, C_6F_6. [h] Pale yellow.

abundance, confirming the molecular weight. The most abundant ion is the doubly charged cation C_2^{2+}, *m/z* 162, verified by the half-mass isotope peak at *m/z* 162.5. The observed abundance of the *m/z* 162.5 ion (55%) is approximately double that required by presence of natural abundance ^{13}C (26.4%), showing the presence of a protonated species C_2H^{2+}. Loss of OTf from the molecular ion produces the ion *m/z* 473 having a net positive charge of 1, $C_2^{2+}OTf^-$. This ion species and the doubly charged ion *m/z* 162 are characteristic in all of the dication spectra (**10**, **23**, **26**), and correspond to similar observations noted for the bis(phosphonium) halides.[5] The minor ions at *m/z* 323-325 are associated with the odd-electron M − 2OTf$^+$ ion (324) by gain or loss of H. At 6-mA emitter current no molecular ion is observed, and the relative intensities of the major ions differ from those observed at 13 mA: *m/z* 473 becomes the base peak, while *m/z* 324 increases to 81%, and the doubly charged ion 162 is reduced to 3% relative intensity.

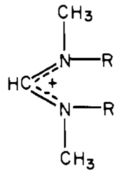


m/z 162

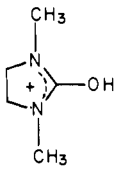
The FD mass spectra of diformamidinium ether salts **23** and **26** are similar, both showing peaks (*m/z* 108 and 106) for the doubly charged cation and for the characteristic $C_2^{2+}OTf^-$ ions, *m/z* 365 and 361, respectively. Cluster ions composed of two cations and three anions having low but significant intensities are observed at *m/z* 879 (**23**) and 871 (**26**). These species are analogous to *m/z* 365 (**23**) and 361 (**26**) and further point to the general occurrence[5] of ions of the type $C_x^+A_y^-$ where $x - y = 1$. Cleavage of the ether linkage in the dication leads to the formamidium ions *m/z* 101 and 99 (**27**) as well as the minor ions *m/z* 116 and 114, which appear to be closely related to ketones **21** and **24**, respectively. As indicated earlier the origins of these latter ions may involve pyrolysis or hydrolysis of the salt. It is interesting to note that although the most intense spectrum of **26** occurred at 17-mA emitter current, some desorption was observed at ~0 mA. Under the latter conditions, ions of *m/z* 115 (100), 229 (46), and 379 (21), **28**-**30**, are observed that do not occur at higher emitter temperatures. The low temperature and presence of added hydrogen in each case suggests that hydrolysis may precede ionization, from which spectra are produced prior to the onset of ionization of the ether salt.



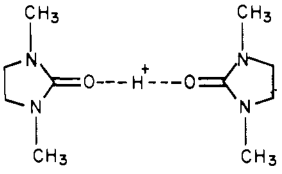
R = CH_3, *m/z* 108
R-R = CH_2-CH_2, *m/z* 106



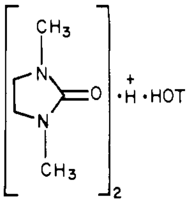
27a, R = CH_3, *m/z* 101
27b, R-R = CH_2-CH_2, *m/z* 99



28, *m/z* 115

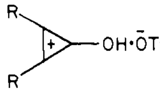


29, *m/z* 229

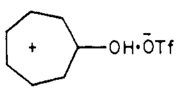


30, *m/z* 379

Chemistry of Dication Ether Salts. All monocations as well as dication ether salts are extremely moisture sensitive; hydrolysis leads in each case to the corresponding hydroxy salts **31**-**38**. The identity of these hydroxy salts (**31**-**38**) was readily confirmed by independent preparation via addition of triflic acid, CF_3SO_3H,



31a, R = n-C_3H_7
31b, R = C_6H_5



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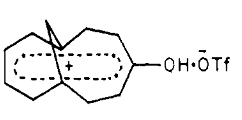

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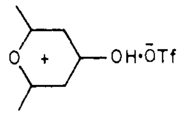

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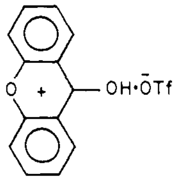

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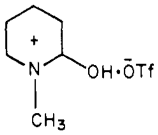

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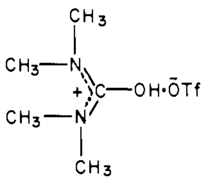

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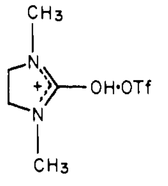
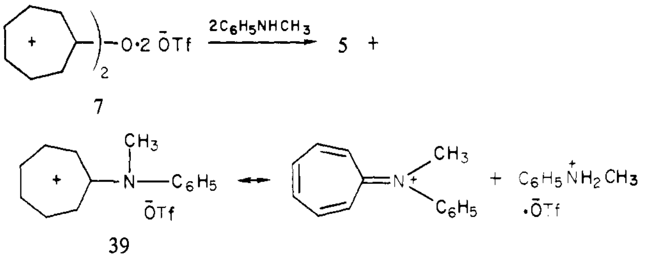


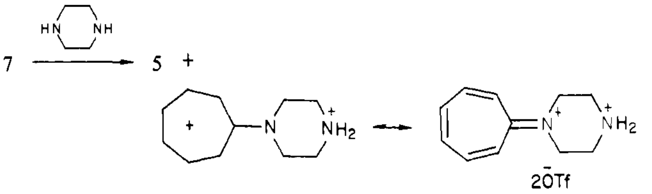
38

to the corresponding ketone. Their spectral properties are summarized in Table II. Crystalline hydroxycyclopropenylium,[8] hydroxytropenylium,[9] 4-hydroxybenzopyrilium,[10,11] 9-hydroxyxanthenylium,[12] and 2-hydroxypyridinium[13] salts have been previously reported and are known to be hygroscopic in some cases, forming stable crystalline hydrates. Hydroxyannulenium cation **33** has so far only been generated in solution by dissolving **8** in CF_3CO_2H.[3] With the exception of **31a**, **37**, and **38**, our hydroxy triflates are crystalline hygroscopic salts. Compound **31b** tends to incorporate 0.5–1.5 mol of water of crystallization, but the pure anhydrous salt may be obtained by vacuum drying. All hydroxy salts are characterized by low-field O–H signals in the proton NMR and a single fluorine signal at ~85 ppm, the appropriate region for ionic triflate, in the ^{19}F spectrum. In the IR the OH stretching shows up as a broad absorption between 2000–3000 cm^{-1} except for **31a** and **31b** where the OH absorption is shifted to 1600–1900 cm^{-1}. strongly indicating hydrate formation. A similar shift in the OH stretch has been observed upon going from anhydrous to hydrated hydroxytropenylium salts.[9]

Being strong acids, the hydroxy salts **31**–**38** are fully dissociated in aqueous solution and hence can be conveniently titrated with dilute NaOH. Since both the dication ether salts as well as the triflated monocations rapidly hydrolyze to the corresponding hydroxy salts, titration provides a convenient means of molecular-weight determination for all three types of salts. Unfortunately, titration is insufficiently accurate to distinguish between the molecular weights of the dication salts and the corresponding hydroxy salts as the latter can be looked upon as "hydrated" dication salts.

As expected, dication ether salts react with a variety of nucleophiles. Thus, either alcoholysis or alkaline hydrolysis both result in quantitative conversion to the starting ketone. Similarly, amines readily react with the dications. Reaction of 2 mol of N-methylaniline with **7** results in the formation of 1 mol of starting ketone **5**, and the aminotropylium salt **39** as well as 1 mol of anilinium triflate. We were unable to separate the mixture of the two salts in this reaction, but the presence of **39** is clearly shown by the ^{1}H NMR, which is in good agreement with the reported[14,15] values of the cation in **39**. Use of piperazine as the amine base results in the formation of **5** and the crystalline dication **40**, where the liberated acid has been picked up intramolecularly by the second nitrogen of the amine. Reaction of **7** with sec amines to give aminotropylium salts is of course analogous to the reaction of corresponding alkoxytropylium salts.[16] Likewise, reaction of dicyclopropenylium ether **4b** with diethylamine leads, besides the starting ketone and diethylammonium triflate, to the expected aminocyclopropenylium salt **41**, characterized by its IR spectrum (C=C at 1889, C=N at 1562 cm^{-1}). A similar reaction of the 1,2-diphenyl-3-ethoxycyclopropenyl cation with dimethylamine has been reported.[17] In contrast the analogous hydroxy cyclopropenylium triflate **31b** is only neutralized by diethylamine.





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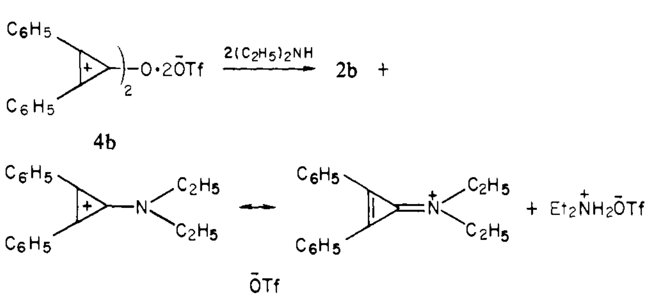
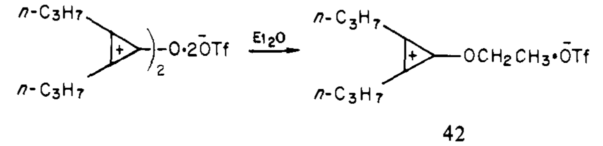


41

The most reactive salt seems to be the oily bis(2,3-di-n-propylcyclopropenylium) ether dication (**4a**). Its extreme moisture sensitivity and great reactivity prevented complete purification and full spectral characterization. In fact, **4a** reacts with solvents such as tetrahydrofuran and acetonitrile, to which the other cations are inert. Although no isolable products were obtained from the reaction of **4a** with THF or CH_3CN, reaction with ether gave the crystalline triflate **42**. The analogous fluoroborate has been made by alkylation of ketone **2a** with $Et_3O^+BF_4^-$.



42

Reaction of dication **26** with diethylamine gives the guanidinium salt **42** and starting urea **24** in equal amounts. In fact, this reaction, along with the reaction [19] of O-alkylated ureas and

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[7] Kirby, D. P.; Vouros, P.; Karger, B. L. *Science* **1980**, *209*, 495–497.

[8] Kursanov, D. N.; Volpin, M. E.; Koreshkov, Y. D. *Zh. Obshch. Khim., Engl. Ed.* **1960**, *30*, 2855–2860.

[9] Harmon, K. M.; Coburn, T. T. *J. Phys. Chem.* **1968**, *72*, 2850–2853.

[10] Schönberg, A.; Schutz, G. *Chem. Ber.* **1960**, *93*, 1466–1468.

[11] Föhlisch, B. *Chem. Ber.* **1971**, *104*, 348–349.

[12] Hori, M.; Kataoka, T.; Shimizu, H.; Onogi, K. *Yakugaku Zasshi* **1978**, *98*, 1341–1348; *Chem. Abstr.* **1979**, *90*, 72207p.

[13] Bell, C. L.; Shoffner, J.; Bauer, L. *Chem. Ind.* (*London*) **1963**, 1353–1354; Shoffner, J. P.; Bauer, L.; Bell, C. L. *J. Heterocycl. Chem.* **1970**, *7*, 479–485.

[14] Föhlisch, B.; Haug, E. *Chem. Ber.* **1971**, *104*, 2324–2337.

[15] Dauben, H. J., Jr.; Rhoades, D. F. *J. Am. Chem. Soc.* **1967**, *89*, 6764–6766.

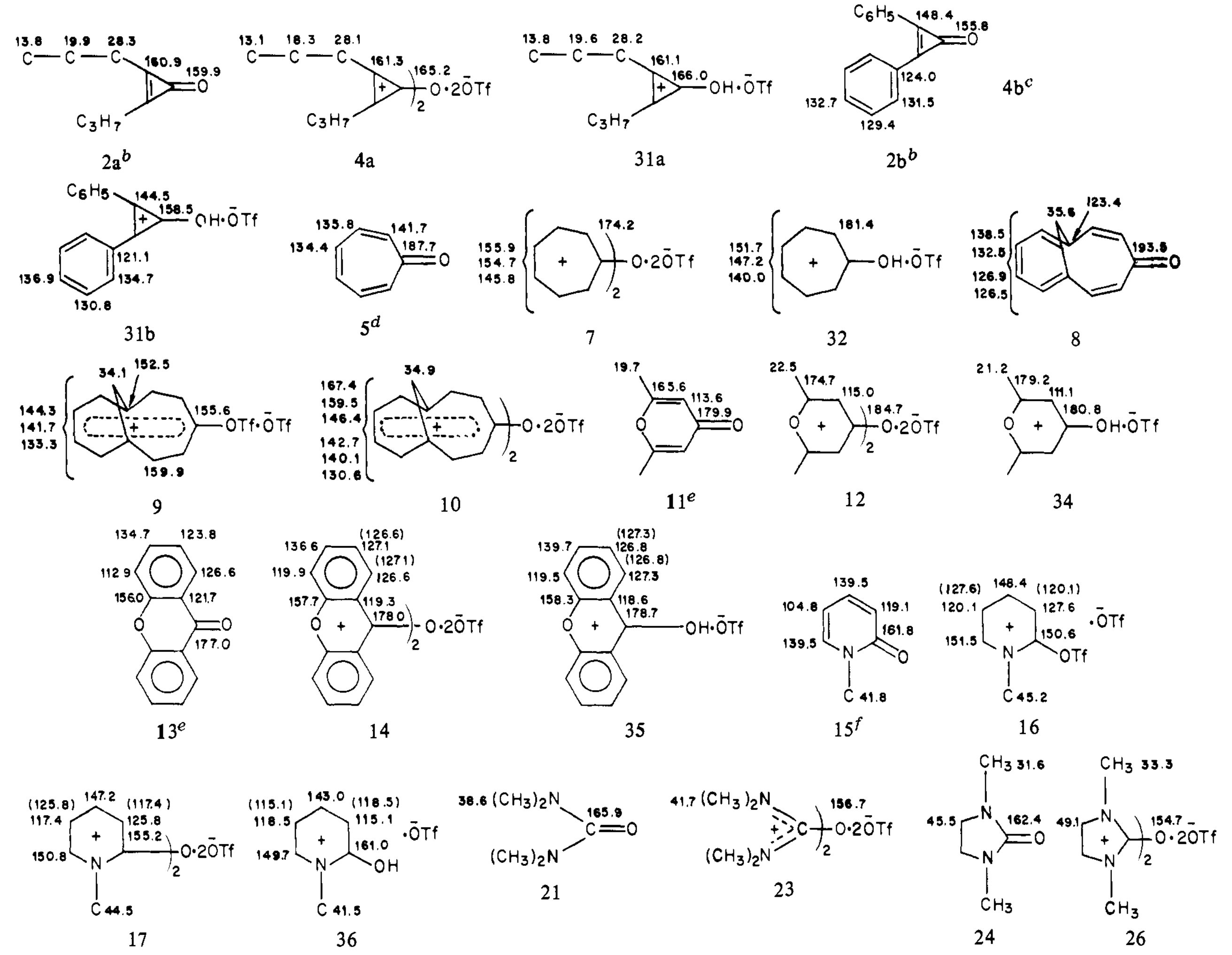
[16] Haug, E.; Fohlisch, B. *Chem. Ber.* **1971**, *104*, 2338–2340.

[17] Breslow, R.; Eicher, T.; Krebs, A.; Peterson, R. A.; Posner, J. *J. Am. Chem. Soc.* **1965**, *87*, 1320–1325.

[18] Dehmlow, E. V.; Zeisberg, R.; Dehmlow, S. S. *Org. Magn. Res.* **1975**, *7*, 418–421.

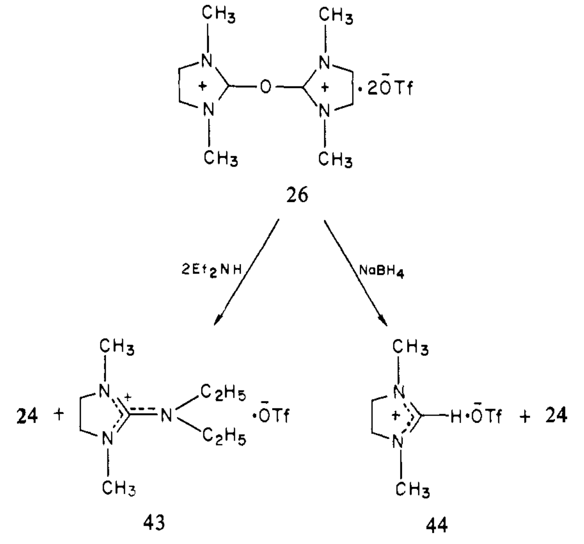
[19] Kanthlehner, W.; Kienitz, L.; Jaus, H.; Bredereck, H. *Justus Liebigs Ann. Chem.* **1979**, 2089–2095.

Chart I. ^{13}C Spectra of Starting Carbonyls, Dication Ether Salts, Hydroxy Triflates, and Monocations[a]

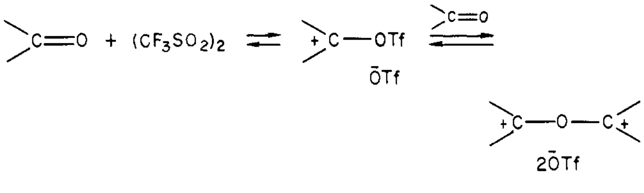


[a] 4a in $CDCl_3$, 31a in CD_2Cl_2, all others in CD_3CN. [b] Dehmlow, E. V.; Zeisberg, R.; Dehmlow, S. S. *Org. Magn. Res.* 1975, *7*, 418. [c] Impossible to obtain satisfactory spectrum because of low solubility and extreme moisture sensitivity. [d] Bagli, J. F.; St-Jacques, M. *Can. J. Chem.* 1978, *56*, 578. [e] Still, I. W. J.; Plavac, N.; McKinnon, D. M.; Chauban, M. S. *Can. J. Chem.* 1976, *54*, 280. [f] Vögeli, U.; Philipsborn, W. V. *Org. Magn. Res.* 1973, *5*, 551.

chloroformamidinium salts with sec amines, provides a simple entry into the guanidine system. Reaction of **26** with $NaBH_4$ yields equimolar amounts of **24** and imidazolium salt **44**, whose spectral data are in good agreement with similar salts.[20]



Thermodynamic and Structural Considerations. It is not immediately obvious why dication ether salts should preferentially form over simple triflated monocations. It is possible that formation of the dication is simply determined by solubility considerations and a rapid equilibrium between starting carbonyl, monocation, and dication, with the dication being least soluble and hence precipitating out of solution. The possible role of such an equilibrium is indicated by our inability to date to prepare a mixed dication ether salt. Reaction, for example, of monocation **16** with tropone results in the isolation of only the ditropyl species **7** with no mixed salt being observed. Further considerations include the superior leaving ability of the triflate anion[21] that allows its ready displacement by a second carbonyl as well as the nucleophilicity of the carbonyl. The latter factor is particularly significant as, for example, benzophenone and triflic anhydride do not react at all under these conditions and the starting material



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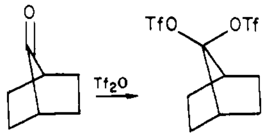
(20) Maas, G.; Stang, P. J. *J. Org. Chem.* **1981**, *46*, 1606-1610.

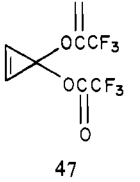
(21) Stang, P. J. *Acc. Chem. Res.* **1978**, *11*, 107-114; Stang, P. J.; Hanack, M.; Subramanian, L. R.; Hassdenteufel, J. R. *Synthesis*, in press.

is completely recovered. Even Michler's ketone must react incompletely as only a mixture of products was observed that proved to be impossible to separate and purify. Even less nucleophilic and nonenolizable, carbonyls such as 7-norbornanone (**45**) give upon reaction with triflic anhydride the stable *covalent* ditriflate **46**.[22] It is of course well-known[21] that enolizable carbonyls give vinyl triflates upon reaction with triflic anhydride.



45 46

On the other hand, even activated ketones, such as cyclopropenone, react with trifluoroacetic anhydride to give as the only product covalent diester **47**.[23]



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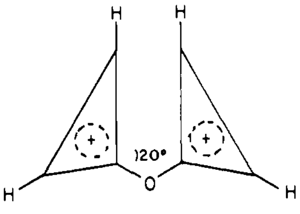
Finally, we briefly address the question of the structure of these novel dication ether salts. Several possibilities exist such as a perpendicular (pseudoallene) structure or a linear or bent free-rotating C–O–C arrangement. Unfortunately, due to poor solubility, moisture sensitivity, and reactivity with most nucleophilic solvents, it is extremely difficult to carry out low-temperature NMR studies. The room-temperature NMR as well as theoretical calculations[24] indicate a free rotor structure with a relatively low rotational barrier of only 2–5 kcal/mol for **48** and 8–10 kcal/mol for **49**. Moreover, calculations[24] indicate a bent planar structure with a C–O–C bond angle of nearly 120° for the parent di(cyclopropenylium) ether salt **48** but a perpendicular linear arrangement for the di(tropenylium) ether **49**. This unusual linearization of oxygen[25] is due to severe steric interaction between the *ortho* hydrogens of the two tropyl rings, especially in the planar conformation. Moreover, this linearization around oxygen results in a rehybridization of the remaining oxygen lone pairs from the usual $sp^2(O)$ and 2p(O) orbitals into *two* perpendicular 2p(O) orbitals that provide more efficient conjugation with *each* of the two rings via $2p\text{-}(O)\text{-}2p(C^+)$ overlap[24] and may account for the higher rotational barrier of **49** compared to **48**.



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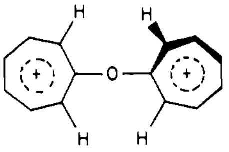

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Summary

We have discovered a simple direct means of preparing novel dictation ethers via interaction of nonenolizable activated carbonyl compounds with triflic anhydride. The method is applicable to the preparation of dications where the cationic moiety is a Hückel aromatic, a 6π-hetereoaromatic, or a substituted area. Most of these salts are stable, crystalline, but extremely hygroscopic. They readily hydrolyze to the corresponding hydroxy cation triflate salts and undergo reaction with a variety of other nucleophiles such as amines. Theoretical calculations[24] indicate a free rotor rather than the perpendicular pseudoallene structure for these ions, in accord with the room temperature NMR data.

Finally, these salts may have interesting implications as organic conductors via charge-transfer complexes. According to a recent classification[26] scheme of such complexes, dication ether salts would be closed-shell dication acceptors. This question as well as other aspects of these novel salts are under active investigation.

Experimental Section

Melting points are uncorrected and were obtained in sealed tubes on a Mel-Temp apparatus. Infrared spectra were obtained on a Beckman IR 5A and all Nujol mulls were prepared under an argon atmosphere. ^1H and ^{19}F NMR spectra were obtained on a Varian EM-390 spectrometer and ^{13}C spectra on a Varian FT-80 or SC-300 spectrometer. FD mass spectra were obtained on a Varian Mat 731 spectrometer operated at a resolving power of 1000. Samples were dissolved in anhydrous acetonitrile and were loaded on the emitter using the syringe technique.[27] Emitters were made by a standard Varian MAT apparatus and procedure. The emitter current was controlled by a device constructed in our laboratory.[28] Spectra were obtained by repetitive scanning, using a Varian SS-100 data system.

All commercially available reagents were redistilled or recrystallized immediately prior to use. Solvents were purified and vigorously dried and stored over molecular sieves. For elimination of all traces of acid, triflic anhydride[29] was redistilled twice from P_2O_5 under an Ar atmosphere. Elemental analyses were done on a Perkin-Elmer 240 Elemental Analyzer in Kaiserslautern, Germany; all moisture-sensitive compounds were handled in aluminum capsules in a drybox for the analytical process. Molecular weights were determined by dissolving a carefully weighed sample in 15 mL of ethanol and titrating to the phenolphthalein end point with 0.05 N NaOH. All crystalline hydroxy salts and dication ether salts may be stored in Ar-filled sealed capsules or in normal vials in a desiccator over P_2O_5. Because of the considerable moisture sensitivity of all these salts, great care must be taken in all handling and manipulation of these compounds. *All reactions, filtrations, etc. were carried out under an Ar atmosphere in carefully dried equipment.* All spectral data for the dication ethers and hydroxy salts are given in Table I and II, respectively.

Bis(2,3-di-*n*-propylcyclopropenylium) Ether Ditriflate (4a). General Procedure. In a three-necked round-bottomed flask equipped with an argon inlet and outlet, a magnetic stirring bar, and an addition funnel was placed 553 mg (4 mmol) of ketone **2a**[30] and 5 mL of CH_2Cl_2. After the solution was cooled to 0 °C, 0.34 mL (2 mmol) of Tf_2O was added dropwise. Upon addition the solution turns yellow, changing to brownish yellow after 20 min. After evaporation of the solvent at 0.5 torr, **4a** remains as a viscous brown oil. Molecular weight by titration was 552 (or 276), $C_{24}H_{28}F_6O_7S_2$ (calcd 558.6). Because of the extreme moisture sensitivity and reactivity of this compound, it proved to be impossible to crystallize and both the ^1H and ^{13}C spectra show impurities.

Bis(2,3-diphenylcyclopropenylium) Ether Ditriflate (4b). To 0.412 g (2 mmol) of ketone **2b**[31] in 10 mL of $CHCl_3$ was added dropwise 0.17 mL (1 mmol) of Tf_2O at room temperature. A white precipitate starts forming within a few seconds after the start of the addition. After addition is complete, the mixture is stirred for 30 min, and the white precipitate is filtered, washed with 2 mL of $CHCl_3$, and dried at 0.5 torr, yielding 0.51 g (82%) of white powdery **4b**, mp 134–136 °C.

Ditropenylium Ether Ditriflate (7). To 1.06 g (10 mmol) of tropone[32] (**5**) in 20 mL of CCl_4 at 0 °C was added 1.01 mL (6 mmol) of Tf_2O. The colorless crystalline precipitate was filtered and recrystallized from CH_3CN/ether, yielding 1.67 g (68%) of **7**: mp 154 °C (decomp); M_r found 491, calcd. 494.9.

1-Trifloxy-4,9-methano[11]annulenylium Triflate (9). To 340 mg (2 mmol) of ketone **8**[3] in 10 mL of CH_2Cl_2 at room temperature was added 0.34 mL (2 mmol) of Tf_2O. A yellow precipitate forms immediately; at the completion of Tf_2O addition, 15 mL of ether was added and the

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[22] Martinez, A. G.; Rios, I. E.; Vilar, E. T. *Synthesis* **1979**, 382–383.

[23] Breslow, R.; Oda, M.; Pecoraro, J. *Tetrahedron Lett.* **1972**, 4415–4419.

[24] Apeloig, Y.; Arad, D. *J. Am. Chem. Soc.*, submitted for publication.

[25] Linear H_2O. for example, is 26.3 kcal/mol less stable than H_2O in its optimal geometry. Furthermore, in H_2O the 2p(O) lone pair is 2.1 eV higher than the $sp^2(O)$; see Turner, D. W., "Molecular Photoelectron Spectroscopy"; Wiley: London, 1970.

[26] Sandman, D. J. *Chem. Eng. News* **1979**, *Nov. 12*, 28–29.

[27] Becky, H. D.; Heindricks, A.; Winkler, H. U. *Int. J. Mass. Spctrom.* **1970**, *3*, 9–14.

[28] Smith, D. L.; Mitchell, J. K.; McCloskey, J. A., unpublished results.

[29] Stang, P. J.; Dueber, T. E. *Org. Synth.* **1974**, *54*, 79–84.

[30] Breslow, R.; Altman, L. J.; Krebs, A.; Mohacsi, E.; Murata, T.; Peterson, R. A.; Posner, J. *J. Am. Chem. Soc.* **1965**, *87*, 1326–1331.

[31] Breslow, R.; Posner, J. "Organic Syntheses", Collect. Vol. 5; Wiley: New York, 1973; pp 514–516.

[32] Radlick, P. *J. Org. Chem.* **1964**, *29*, 960.

precipitate was filtered, yielding 790 mg (87%) of yellow crystalline **9**, mp 167 °C (decomp). Anal. Calcd for $C_{14}H_{10}F_6O_6S_2$ (452.3): C, 37.17, H, 2.23. Found; C, 37.1; H, 2.19.

Bis(4,9-methano[11]annulenylium) Ether Ditriflate (10). A solution of 226 mg (0.5 mmol) of **9** and 85 mg (0.5 mmol) of **8** in 30 mL of CH_2Cl_2 was refluxed for 10 h. After the mixture was cooled, it was filtered, yielding 175 mg (56%) of crude yellow crystalline **10**; recrystallization from CH_3CN/ether gave a yellow powder, mp 172–174 °C (decomp). Anal. Calcd for $C_{26}H_{20}F_6O_7S_2$ (622.6): C, 50.16; H, 3.24. Found: C, 48.7; H, 3.14.

Bis(2,6-dimethyl-4-pyrylium) Ether Ditriflate (12). To a solution of 1.24 g (10 mmol) of commercial **11** in 15 mL of CH_2Cl_2 cooled to -50 °C was added dropwise 0.84 mL (5 mmol) of Tf_2O. Addition results in the formation of a white precipitate; after completion of the addition the mixture is allowed to warm to room temperature and the precipitate is filtered. The precipitate is washed with 5 mL of CH_2Cl_2, yielding 2.25 g (85%) of nearly colorless crystalline **12**, mp 162–164 °C (crystallized from CH_3CN/ether). Upon storing **12** becomes faint pink and upon heating above 120 °C it becomes red. Anal. Calcd for $C_{16}H_{16}F_6O_9S_2$ (530.4): C, 36.23; H, 3.04. Found: C, 35.9; H, 3.08. The ^1H NMR indicates the presence of small amounts of the hydroxy salt **24**. If the reaction is carried out at room temperature, the solution turns dark red upon addition of the first drop of Tf_2O and only a dark polymer-like precipitate is formed that dissolves in water to give a dark-red solution.

Bis(9-xanthenylium) Ether Ditriflate (14). To 0.98 g (5 mmol) of commercial xanthone (**13**) in 20 mL of CH_2Cl_2 at room temperature was added 0.49 mL (2.5 mmol) of Tf_2O. The solution turns yellow and a yellow precipitate appears within 1 min of the addition. After addition, stirring is continued for 15 min, and then the precipitate is filtered and washed with 10 mL of CH_2Cl_2 and dried at 0.03 torr, yielding 1.32 g (78%) of yellow powder as **14**, mp 144 °C (decomp). Anal. Calcd for $C_{28}H_{16}F_6O_9S_2$ (674.5): C, 49.86; H, 2.39. Found: C, 49.0; H. 2.49.

2-Trifloxy-1-methylpyridinium Triflate (16). To 3.4 mL (20 mmol) of Tf_2O in 15 mL of CH_2Cl_2 at room temperature was added 2.18 g (20 mmol) of commercial **15** in 15 mL of CH_2Cl_2. After 2 h at room temperature, 20 mL of ether was added, and the precipitate was filtered off, yielding 6.1 g (77%) of crude **16**. Recrystallization from CH_2Cl_2/ether gave pure colorless **16**: mp 66–67 °C; M_r calcd 391.3, found 400.

Bis(1-methyl-2-pyridinium) Ether Ditriflate (17).[33] A solution of 0.98 g (2.5 mmol) of **16** and 0.275 g (2.5 mmol) of **15** was refluxed in 25 mL of CH_2Cl_2 for 2.5 h. After the solution was cooled and filtered, 0.93 g (74%) of colorless crystalline **17** was obtained: mp 185–186 °C; M_r calcd 500.4, found 506.

1,3-Diphenyl-2-trifloxyimidazolium Triflate (19). To a solution of 236 mg (1 mmol) of ketone **18**[34] in 5 mL of CH_2Cl_2 was added 0.17 mL (1 mmol) of Tf_2O. The colorless solution turned yellow brown and upon evaporation of the solvent at 0.5 torr a viscous oil remains. Because of extreme mositure sensitivity, no IR could be obtained and both the ^1H and ^{19}F spectrum indicate the presence of some of the corresponding hydroxy salt.

A solution of the above **19** and 236 mg (1 mmol) of **18** was refluxed in 10 mL of CH_2Cl_2 for 45 h. The dark-red solution was concentrated and the oily residue stirred with 5 mL of acetone/30 mL of ether for 15 min, resulting in a colored solution and a white precipitate. Filtration gave 87 mg of colorless crystals: mp 267 °C; IR (KBr) 1713 (s), 1690 (s), 1597 (m), 1499/1493 (s), 1427 (s), 1404 (s) cm^{-1}; mass spectrum, 540 (4), 472 (39), 352 (4), 329 (4), 262 (19), 261 (100), 236 (12). The filtrate was concentrated and placed on a silica column. Elution with 9:1 CH_2Cl_2/ethyl acetate gave two fractions: (a) a mixture of the above compound and the subsequent fraction; (b) 20 mg of white crystals; mp 229–232 °C; IR (KBr) 1692 (s, sh at 1710), 1592 (m), 1487 (s), 1420 (s) cm^{-1}: mass spectrum, 472 (100), 352 (7), 338 (2), 262 (10), 261 (45), 260 (17), 236 (18). Clearly, no dication ether salt was formed from **18**. The spectral data suggest a mixture of isomeric dimers of **18** for the two products.

***C*-Trifloxy-*N*,*N*,*N'*,*N'*-tetramethylformamidinium Triflate (22).** To a solution of 1.16 g (10 mmol) of commercial tetramethylurea in 10 mL of CH_2Cl_2 at 0 °C was added 1.68 mL (10 mmol) of Tf_2O in 5 mL of CH_2Cl_2. Evaporation of the solvent at 0.5 torr leaves a pale-yellow, oily **22**.

Bis(*N*,*N*,*N'*,*N'*-tetramethylformamidinium) Ether Ditriflate (23). A solution of 10 mmol of **22**, prepared as above, in 10 mL of CH_2Cl_2 was allowed to warm to room temperature and 1.16 g (10 mmol) of **21** in 5 mL of CH_2Cl_2 was added. The mixture was stirred for 2.5 h, during which time crystals appeared. At the end of this period, 20 mL of ether was added and the precipitate was filtered, yielding 950 mg (19%) of colorless crystalline **23**, mp 229–234 °C; Anal. Calcd for $C_{12}H_{24}F_6N_4O_7S_2$ (514.4): C, 28.02; H, 4.70; N, 10.89. Found: C, 27.7, H, 4.50, N, 11.0.

2-Trifloxy-1,3-dimethylimidazolinium Triflate (25). To a solution of 1.14 g (10 mmol) of **24** in 10 mL of CH_2Cl_2 at 0 °C was added 1.68 mL (10 mmol) of Tf_2O in 5 mL of CH_2Cl_2. Evaporation of the solvent gave extremely hygroscopic crystalline **25**.

Bis(1,3-dimethylimidazolinium-2-yl) Ether Ditriflate (26). To a solution of **25** in 15 mL of CH_2Cl_2, prepared as above, was added 1.14 g (10 mmol) of **24** in 5 mL of CH_2Cl_2, and the mixture was refluxed for 3 h, during which time crystals started forming. After the mixture was cooled, the precipitate was filtered and recrystallized from CH_3CN/ether, yielding 4.20 g (82%) of colorless **26**, mp 197 °C. Anal. Calcd for $C_{12}H_{20}F_6N_4O_7S_2$ (510.4): C, 28.23; H, 3.95; N, 10.98. Found: C, 28.0; H, 3.85; N, 10.9.

Hydroxy Triflates (31–38). These salts were prepared by the addition of an equimolar amount of neat CF_3SO_3H to a solution of the appropriate ketone (1–10 mmol) in CH_2Cl_2 at room temperature under an Ar atmosphere. Workup consisted of filtering the precipitated salt under an Ar atmosphere in a "closed" system or evacuation of the solvent under vacuum. The yields and physical and spectral properties of these compounds are reported in Table II. Most of these hydroxy salts were very hygroscopic and some crystallized with water of hydration.

Hydrolysis of 7. (a) To a suspension of 0.30 g (0.61 mmol) of **7** in 10 mL of CH_2Cl_2 was added 1 mL of H_2O, whereupon the crystals dissolve. This mixture was dried over 10 g of anhydrous Na_2SO_4: after filtration and evaporation of the solvent, 1.13 mmol (93%) of tropone was isolated.

(b) To a suspension of 0.255 g (0.5 mmol) of **7** in 5 mL of CH_2Cl_2 was added 0.25 mL of H_2O that resulted in a clear solution. The solvent was evacuated at reduced pressure, and the residue was dissolved in CH_2Cl_2 and precipitated with ether to give 0.13 g (100%) of hydroxytropenylium triflate (**32**), identical in all respects with authentic **32**.

Reaction of 7 with Amines and Formation of 39 and 40. (a) To a suspension of 444 mg (1 mmol) of **7** in 7 mL of CH_2Cl_2 at 0 °C is slowly added a solution of 214 mg (2 mmol) of *N*-methylaniline in 3 mL of CH_2Cl_2. During 30 min of stirring, the solution became homogeneous. Evaporation of solvent leaves an oil consisting of tropone (as seen by IR), *N*-methylanilinium triflate [NMR in $CDCl_3$, δ 3.2 (3 H, CH_3)], and *N*-methylanilinotropylium triflate (**39**) [δ 3.96 (3 H), 7.2–7.9 (6 H, +6 H of tropone)] in equimolar amounts.

(b) To a solution of 494 mg (1 mmol) of **7** in 5 mL of CH_3CN was slowly added 95 mg (1.1 mol) of piperazine in 10 mL of CH_3CN. After addition the solution was stirred for 20 min and then 50 mL of ether was added. The precipitate was filtered and twice recrystallized from ethanol to give 200 mg (42%) of yellow crystalline **40**: mp 284 °C, IR (KBr) 3380 (m, br, N^+H_2), 1630, 1546/1535, 1435 (all m), 1270, (br, s) 1227, 1160, 1038 cm^{-1}; NMR (CD_3CN) δ 3.61 (s, 4 H), 4.41 (s, 4 H), 6.46 (br, 2 H), 7.83–8.53 (m, 6 H). Anal. Calcd for $C_{13}H_{16}F_6N_2O_6S_2$ (474.4): C, 32.91; H, 3.40; N, 5.90. Found: C, 31.8; H, 3.41; N, 6.1.

Reaction of 4b with Et_2NH and Formation of 41. To a suspension of 567 mg (0.82 mmol) of **4b** in 5 mL of $CHCl_3$ was added a solution of 119 mg (1.63 mmol) of Et_2NH in 5 mL of $CHCl_3$, whereupon a homogeneous solution formed. Upon addition of 50 mL of ether, 276 mg of a mixture of the diethylammonium triflate and **41** were precipitated. The filtrate was concentrated and extracted with 20 mL of boiling cyclohexane, resulting in 167 mg (99%) of diphenylcyclopropenone. Treatment of filtered salt mixture with 15 mL of H_2O leaves **41** undissolved. Filtration and recrystallization from ethyl acetate gave 90 mg (27%) of crystalline **41**. mp 165–167 °C; IR (KBr) 1879 (C=C), 1588, 1557 (s, C=N), 1477, 1462, 1403, 1382, 1359 (all s), 1260 (vs), 1222 (s), 1145 (vs), 1031 (vs) cm^{-1}; NMR ($CDCl_3$) δ 1.50 (t, 6 H), 4.04 (q, 4 H), 7.6–7.8 (m, 6 H), 7.9–8.17 (m, 4 H). Anal. Calcd for $C_{20}H_{20}F_3NO_3S$: C, 58.39; H, 4.90; N, 3.40. Found: C, 57.7; H, 4.87; N, 3.4.

Reaction of 4a with Diethyl Ether and Formation of 42. A solution of **4a** in 5 mL of CH_2Cl_2 was prepared as above. After addition of 90 mL of ether at room temperature crystallization starts. Filtration gives 400 mg (32%) of faint-yellow hygroscopic crystalline **42**; mp 91 °C; IR (Nujol) 1887 (m), 1505 (m), 1277–1255 (br, s), 1155 (s), 1035 (m); ^1H NMR ($CDCl_3$) δ 1.06 (t, J = 8.5 Hz, 4 H), 1.57 (t, 2 H), 1.94 (sext, J = 7.6 Hz, 4 H), 2.97 (t, J= 7.5 Hz, 6 H), 4.93 (q, 3 H); ^{13}C NMR ($CDCl_3$; internal standard, Me_4Si) 13.5, 14.5, 19.0, 27.9, 79.1, 159.5, 165.9; ^{19}F ($CDCl_3$; internal standard, C_6F_6) 85.7; M_r calcd 313, found 316 by titration.

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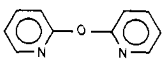
[33] An ion identical with **17** but with FSO_3^- as counterion, prepared by reaction of 2,2′-oxydipyridine



with excess CH_3OSO_2F, has been reported: Pirzada, N. H.; Summers, L. A. *Z. Naturforsch. B* **1976**, *31*, 122–123.

[34] Schönherr, H.-J.; Wanzlick, H. W. *Chem. Ber.* **1970**, *103*, 1037–1046.

Reaction of 26 with Et_2NH and Formation of 43. To a suspension of 2.55 g (5 mmol) of **26** in 20 mL of CH_2Cl_2 at 0 °C was added 730 mg (10 mmol) of diethylamine in 5 mL of CH_2Cl_2. A homogeneous pale-yellow solution formed and was stirred for 30 min. The ^1H NMR of this solution shows equimolar amounts of urea **24**, diethylammonium triflate, and **43**. The solution was extracted with 400 mg of KOH dissolved in 20 mL of H_2O, and the organic layer was dried over Na_2SO_4. After removal of solvent, a yellow oil remains that crystallized upon addition of 20 mL of ether. After filtration and recrystallization from $CHCl_3$/ether, 1.17 g (73%) of pale-yellow crystalline **43** was obtained: mp 59–61 °C; IR (KBr) 1607, 1560 (s, $C\overset{-}{\cdot\cdot}N$), 1310 (s), 1265 (vs), 1223 (s), 1148 (vs), 1033 (vs); NMR ($CDCl_3$; internal standard, Me_4Si) δ 1.23 (t, J = 7.5 Hz, 6 H), 3.00 (s, 6 H), 3.36 (q, J = 7.5 Hz, 4H), 3.81 (s, 4 H). Anal. Calcd. for $C_{10}H_{20}F_3N_3O_3S$(319.35): C, 37.61; H, 6.31; N, 13.16. Found: C, 37.5; H, 6.13; N, 13.3.

Reaction of 26 with $NaBH_4$ and Formation of 44. A mixture of 510 mg (1 mmol) of **26** and 38 mg (1 mmol) of $NaBH_4$ in 10 mL of CH_3CN is refluxed for 3 h with vigorous stirring. After removal of solvent, the residue is extracted with two 15-mL portions of boiling CH_2Cl_2. After removal of CH_2Cl_2, the residual oil is extracted twice with 20-mL portions of ether, yielding 113 mg (100%) of urea **24**. The residual oil, 124 mg (50%), corresponds to **44**: IR (film) 1665 (s, $C\overset{-}{\cdot\cdot}N$), 1275, 1250 (s, br), 1225, 1157, 1032 (all s); NMR (CH_3CN; internal standard, Me_4Si), δ 3.16 (s, 6 H), 3.94 (s. 4 H), 8.03 (br, s, 1 H). NMR of the original reaction mixture indicates an equimolar amount of **44** and **24**.

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Aluminum Chloride Catalyzed Skeletal Rearrangement of Permethylated Acyclic Polysilanes

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Abstract: Permethylated linear polysilanes, $Me(Me_2Si)_nMe$ with n = 4–10 and 12, underwent skeletal rearrangement to give branched isomers in almost quantitative yields when treated with a catalytic amount of aluminum chloride in refluxing benzene. From the linear polysilanes with n = 4, 5, and 6, $(Me_3Si)_3SiMe$, $(Me_3Si)_4Si$, and $(Me_3Si)_3SiSiMe_2SiMe_3$ were obtained, respectively, as single isomers. The polysilanes with n = 7, 8, and 9 were converted into an equilibrium mixture, each consisting of a pair of branched isomers: $(Me_3Si)_3SiSiMe_2SiMe_2SiMe_3$ (**15**) and $(Me_3Si)_3SiSiMe(SiMe_3)_2$ (**16**); $(Me_3Si)_3SiSiMe_2SiMe(SiMe_3)_2$ (**18**) and $[(Me_3Si)_3Si]_2$ (**19**); and $(Me_3Si)_3SiSiMe_2SiMe_2SiMe(SiMe_3)_2$ and $[(Me_3Si)_3Si]_2SiMe_2$ respectively. Under identical conditions, from **15** an equilibrium mixture of **15** and **16** was formed, while from **19** an equilibrium mixture of **18** and **19** was formed. Isomerization of the polysilane with n = 10 produced $[(Me_3Si)_3SiSiMe_2]_2$ as a single product, and the polysilane with n = 12 was converted to a single isomer $[(Me_3Si)_3SiSiMe_2SiMe_2]_2$. The ^{29}Si NMR chemical shifts for permethylated linear polysilanes with n = 4–12 and for isomerization products are recorded.

Isomerization of saturated hydrocarbons catalyzed by Lewis acids has been extensively studied; many papers dealing with the skeletal rearrangements of linear and cyclic hydrocarbons have been published.[2] However, no interest had been shown in the rearrangements of catenate compounds other than carbon-chain compounds until 1969, when we found a first example of the skeletal rearrangement of dodecamethylcyclohexasilane in the presence of a catalytic amount of anhydrous aluminum chloride.[3] Further work showed that the rearrangement is a general one for permethylated cyclic and acyclic polysilanes.

In this paper, we report the behavior of some permethylated linear and branched polysilanes toward a catalytic amount of aluminum chloride.

Results and Discussion

Isomerization of Lower Polysilanes. In a preliminary experiment[4] we found that the linear permethylated polysilanes, $Me(Me_2Si)_nMe$ with $n = 4 \sim 6$, underwent readily skeletal rearrangement, giving rise to the corresponding branched isomers when refluxed in benzene in the presence of a catalytic amount of anhydrous aluminum chloride. Thus decamethyltetrasilane[5-7] (**1**) was converted to tris(trimethylsilyl)methylsilane (**2**) as the sole product. Monitoring the progress of the reaction by VPC revealed

$$\underset{\textbf{1}}{Me(Me_2Si)_4Me} \xrightarrow{AlCl_3} \underset{\textbf{2}}{(Me_3Si)_3SiMe}$$

that a trace of compound whose retention time was identical with that of 1-chloro-2-(trimethylsilyl)hexamethyltrisilane always appeared in the early stage of the reaction and remained throughout.

In sharp contrast to acid-catalyzed isomerization of the saturated hydrocarbons which never yielded neopentyl derivatives, that of permethylated polysilanes afforded tetrakis(silyl)silane derivatives. Thus, the aluminum chloride catalyzed rearrangement of dodecamethylpentasilane[6] (**3**) gave tetrakis(trimethylsilyl)silane (**4**) in almost quantitative yield. In all respects, products **2** and

$$\underset{\textbf{3}}{Me(Me_2Si)_5Me} \xrightarrow{AlCl_3} \underset{\textbf{4}}{(Me_3Si)_4Si}$$

4 were identical with the respective authentic samples prepared by known methods.[8,9]

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(1) (a) Kyoto University. (b) Government Industrial Research Institute.

(2) Pines, H.; Hoffman, E. "Friedel-Crafts and Related Reactions", Vol. II, Part II; Interscience: New York, 1964; pp 1211–1252.

(3) Ishikawa, M.; Kumada, M. *Chem. Commun.* **1969**, 567.

(4) Ishikawa, M.; Kumada, M. *Chem. Commun.* **1970**, 157.

(5) Wilson, G. R.; Smith, A. G. *J. Org. Chem.* **1961**, *26*, 557.

(6) (a) Kumada, M.; Ishikawa, M. *J. Organomet. Chem.* **1963**, *1*, 153. (b) Urenovitch, J. V.; MacDiarmid, A. G. *J. Am. Chem. Soc.* **1963**, *85*, 3372.

(7) Gilman, H.; Inoue, S. *J. Org. Chem.* **1964**, *29*, 3418.

0002-7863/81/1503-4845$01.25/0