Table XVII. Intensity Distributions of $[M - C_jH_{2j}]^+$ and $[M - H_2O - C_jH_{2j}]^+$ Peaks in Spectrum of Tristearin

j[a]	$[M - C_jH_{2j}]^+$	$[M - H_2O - C_jH_{2j}]^+$
	Rel intensity	
3		3
4	5	6
5	14	9
6	9	10
7	10	12
8	14	15
9	19	14
10	15	14
11	9	9
12	5	7
j'[b]	9	8, 9, 10
n'[c]	11	10, 11, 12

[a,b,c] See footnotes *b*, *c*, *d*, respectively, in Table XII. n' refers here to position in the stearate moiety; that is, the count includes the carboxyl carbon.

of triglycerides.[28,38] Table XVII shows the intensity distributions of the two series in our spectrum of tristearin, with the derived values of j' and n'. Almost certainly the underlying chemical events also resemble closely those in the TMA esters. The spectra of long-chain *n*-alkynes contain a series of peaks corresponding to $[M - C_jH_{2j}]^+$ ions,[39] and these may comprise a third family of compounds in this category.

Conclusion

The trimellitate anhydrides, trimellitimidates, 1,2-dimethyl trimellitates, and triglycerides have in common bulky groupings containing several oxygen atoms, and in the imides one nitrogen as well. Such groupings seem well equipped to accommodate the charge and radical site before abstraction and also to use the abstracted atom, presumably *via* hydrogen bonding, to attain a new resonance-stabilized configuration. The homologous series of ions produced by loss of olefin molecules from M^+, $[M - H_2O]^+$, and $[M - CH_3OH]^+$ and by loss of H_2O or CH_3OH from $[M - C_jH_{2j}]^+$ in the various compounds reflect a delicate balance in which the vibrational energy available following abstraction is sufficient to cleave the β carbon–carbon bond with but little interference from processes that so often intervene in other molecules.[40] These observations complement the earlier noted temperature and voltage effects on the competition of triple- *vs.* double-hydrogen migration in 4-*n*-alkyl TMA esters. Both lines of evidence would seem to support the view that alkyl hydrogen migration to the formally distant functional group occurs in a coiled—internally solvated—molecule rather than *via* flailing, an alternative suggested by a referee of an earlier paper.[4]

Several recent papers describe attempts to locate olefinic bonds in long chains by specific deuterogenation, nonselective carbon–carbon bond breaking either thermally[41] or by electron impact,[17b,38a,42] and isotopic analysis of the resulting fragments. The high specificity of the olefin-loss processes reported here suggests that they may be particularly useful for studies of this type.

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(38) (a) W. M. Lauer, A. J. Aasen, G. Graff, and R. T. Holman, *Lipids*, **5**, 861 (1970); (b) A. J. Aasen, W. M. Lauer, and R. T. Holman, *ibid.*, **5**, 869 (1970); (c) R. A. Hites, *Anal. Chem.*, **42**, 1736 (1970). The last cited of these papers is focused on quantitative analysis of triglyceride mixtures, and is concerned only incidentally with mechanistic considerations.

(39) H. Luftmann and G. Spiteller, *Org. Mass Spectrom.*, **5**, 1073 (1971).

(40) *Cf.*, *e.g.*, S. Meyerson, *J. Chem. Phys.*, **42**, 2181 (1965).

(41) K. K. Sun, H. W. Hayes, and R. T. Holman, *Org. Mass Spectrom.*, **3**, 1035 (1970).

(42) D. G. Earnshaw, F. G. Doolittle, and A. W. Decora, *ibid.*, **5**, 801 (1971).

Organometallic Chemistry. IV.[1a] Stable Mercurinium Ions

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Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. *Received April 5, 1972*

Abstract: The direct observation of stable mercurinium ions is reported, and evidence for their structure is discussed. Mercurinium ions can be prepared by both σ and π routes in superacid media of low nucleophilicity. The ethylenemercurinium, *cis-* and *trans*-dimethylethylenemercurinium, propylenemethylmercurinium, cyclohexenemercurinium, cyclohexenemethylmercurinium, norbornylenemercurinium, and norbornylenemethylmercurinium ions were obtained and studied by ^{1}H and ^{13}C nmr and by quenching experiments. Rapidly equilibrating β-mercurycarbenium ions as an alternate possibility to bridged mercurinium were ruled out on the basis of the observed ^{199}Hg–H couplings and cmr data.

Solvomercuration reactions were originally discovered at the turn of the century by Hoffmann and Sand.[2] Since then, solvomercuration reactions have been developed[3] into valuable synthetic reactions of great versatility and stereospecificity.

As might be expected, the mechanism of solvomercuration reactions has received a great deal of atten-

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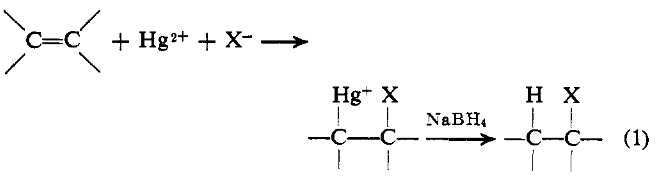
(1) Part III: G. A. Olah and Y. K. Mo, *J. Amer. Chem. Soc.*, **93**, 4942 (1971); (b) NIH Postdoctoral Fellow, 1969–1970; (c) preliminary communications appeared: G. A. Olah and P. R. Clifford, *J. Amer. Chem. Soc.*, **93**, 1261, 2320 (1971).

(2) K. A. Hoffmann and J. Sand, *Ber.*, **33**, 1340 (1900).

(3) (a) J. Chatt, *Chem. Rev.*, **48**, 1 (1951), and references therein; (b) W. Kitching, *Organometal. Chem. Rev.*, **3**, 61 (1968), and references therein; (c) S. Moon and B. H. Waxman, *Chem. Commun.*, 1283 (1967); (d) H. C. Brown and P. Geoghegan, Jr., *J. Amer. Chem. Soc.*, **89**, 1522 (1967); (e) H. C. Brown and M. H. Rei, *ibid.*, **91**, 5646 (1969); (f) H. C. Brown and J. T. Kurek, *ibid.*, **91**, 5647 (1969); (g) A. Lattes and J. J. Perie, *Tetrahedron Lett.*, 5165 (1967); (h) J. J. Perie and A. Lattes, *ibid.*, 2289 (1969); (i) C. H. Heathcock, *Angew. Chem.*, **81**, 148 (1969); (j) V. I. Sokolov and O. A. Reutov, *Zh. Org. Khim.*, **5**, 174 (1969); (k) D. H. Ballard, A. J. Bloodworth, and R. J. Bunce, *Chem. Commun.*, 815 (1969).

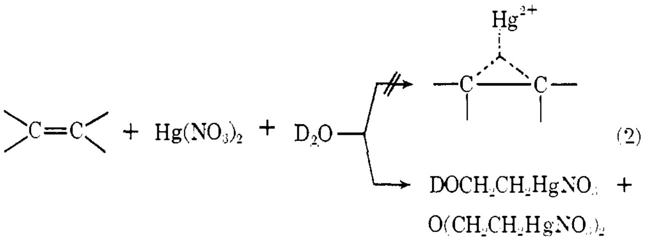


$$>C=C< + Hg^{2+} + X^- \longrightarrow -\overset{Hg^+}{C}-\overset{X}{C}- \xrightarrow{NaBH_4} -\overset{H}{C}-\overset{X}{C}- \quad (1)$$

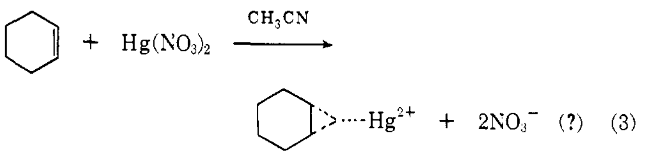
X = OH, OAc, OR, OOH, OOR, NR_2, NHCOR, N_3

tion. The principal debate concerning these reactions has been concerned with the possible intermediacy of mercurinium ions. An extensive number of studies have been conducted in which evidence was obtained for intermediate mercurinium ions.[4] However, an equally impressive number of studies indicated that mercurinium ions are either not present or play no important role in product formation in solvomercuration reactions.[5]

In view of this situation, it is not surprising that attempts have been made to observe stable mercurinium ions directly. For example, Saito and Matsuo[6] claimed to have observed the ethylenemercurinium ion[7] in D_2O. However, Kitching and coworkers demonstrated[9] that what was in fact observed under those conditions was the normal solvomercuration products. Reutov and coworkers[10] have also claimed to have observed a stable mercurinium ion, *i.e.*, the cyclohexenemercurinium ion in acetonitrile solution. This claim must be viewed with some skepticism because of the known reactivity of mercurinium ions toward acetonitrile.[11] In addition, the scanty spectral details reported seem much too tenuous a basis on which to claim direct observation of a stable mercurinium ion.



$$>C=C< + Hg(NO_3)_2 + D_2O \not\longrightarrow -\overset{Hg^{2+}}{C-C}- \qquad \longrightarrow DOCH_2CH_2HgNO_3 + O(CH_2CH_2HgNO_3)_2 \quad (2)$$



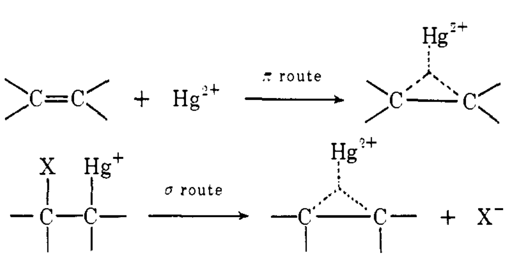
$$+\ Hg(NO_3)_2 \xrightarrow{CH_3CN} \cdots Hg^{2+} + 2NO_3^- \ (?) \quad (3)$$

1

Thus, at the inception of our work, there was no bona fide, incontrovertable report of the observation of mercurinium ions as stable, long-lived species. In two recent communications,[12,13] we presented evidence for the first direct observation of stable mercurinium ions. We would now like to present full details concerning our investigations.

Results

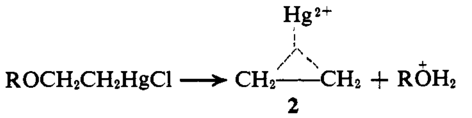
There are two possible approaches to the formation of mercurinium ions. In the first approach an olefin is treated directly with a mercuric salt. This is the π route of preparation. The alternative approach involves ionization of β-substituted organomercurials. This is termed the σ route. Whichever approach is used, the fundamental experimental condition needed for the observation of mercurinium ions is a low nucleophilicity medium.



$$>C=C< + Hg^{2+} \xrightarrow{\pi\ \text{route}} >\overset{Hg^{2+}}{C-C}<$$

$$-\overset{X}{C}-\overset{Hg^+}{C}- \xrightarrow{\sigma\ \text{route}} -\overset{Hg^{2+}}{C-C}- + X^-$$

The ethylenemercurinium ion **2** is best generated by the σ route from 2-methoxyethylmercuric chloride or 2-ethoxyethylmercuric chloride. The ionizing media which may be used include $FSO_3H\text{-}SbF_5\text{-}SO_2$, $SbF_5\text{-}SO_2$, $FSO_3H\text{-}SbF_5\text{-}SO_2ClF$, and $SbF_5\text{-}SO_2ClF$ solutions. The proton magnetic resonance (pmr) spectrum of the ethylenemercurinium ion at $-30°$ is a singlet at δ 7.68. Proton-mercury coupling is readily visible, $J_{^{199}Hg-^1H}$ = 190 Hz (Figure 1). The spectra, of course, also show the cleaved protonated alcohols. The ^{13}C nmr (cmr) spectrum of ion **2** (obtained by both the indor and fast Fourier transform (FFT) methods) shows the methylene carbons at $\delta_{^{13}C}$ 58.



$$ROCH_2CH_2HgCl \longrightarrow \overset{Hg^{2+}}{CH_2-CH_2} + R\overset{+}{O}H_2$$

2

Methylmercuric fluorosulfate[13] is prepared from dimethylmercury and fluorosulfonic acid or methylmercuric acetate and fluorosulfonic acid. When propylene in sulfur dioxide is added to methylmer-

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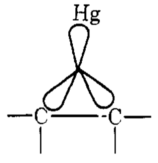
[4] (a) H. J. Lucas, F. R. Hepner, and S. Winstein, *J. Amer. Chem. Soc.*, **61**, 3102 (1939); (b) W. L. Waters and E. F. Keiter, *ibid.*, **89**, 6261 (1967); (c) W. L. Waters, W. S. Linn, and M. C. Caserio, *ibid.*, **90**, 6741 (1968); (d) R. D. Bach, *ibid.*, **91**, 1771 (1969); (e) D. J. Pasto and J. A. Gontarz, *ibid.*, **92**, 7480 (1970); (f) *ibid.*, **93**, 6902 (1971).

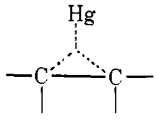
[5] (a) J. Halpern and H. B. Tinker, *ibid.*, **89**, 6427 (1967); (b) H. C. Brown, M. H. Rei, and K. T. Liu, *ibid.*, **92**, 1760 (1970); (c) H. C. Brown and K. T. Liu, *ibid.*, **92**, 3502 (1970); (d) S. Bentham, P. Chamberlain, and G. H. Whitham, *Chem. Commun.*, 1528 (1970); (e) R. C. Bahey, *Top. Stereochem.*, **3**, 318 (1968).

[6] Y. Saito and M. Matsuo, *Chem. Commun.*, 761 (1967).

[7] Many representations have been used for mercurinium ions. Whichever representation is used it is agreed that the primary interaction in mercurinium ions involves overlap of a mercury 6s orbital with the π cloud of an olefin. The interaction of olefin antibonding orbitals with mercury d orbitals has been calculated to be small.[8] Consequently, a good pictorial representation of mercurinium ions is structure I. Throughout this paper representation II, a shorthand designation



I



II

of I, will be used for mercurinium ions.

[8] R. D. Bach and H. F. Henneike, *J. Amer. Chem. Soc.*, **92**, 5589 (1970).

[9] W. Kitching, A. J. Smith, and P. R. Wells, *Aust. J. Chem.*, **21**, 2395 (1968).

[10] V. I. Sokolov, Yu. A. Ustynyuk, and O. A. Reutov, *Dokl. Akad. Nauk SSSR*, **173**, 1103 (1967).

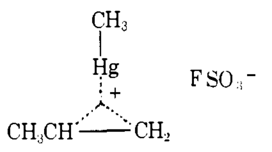
[11] In fact, when acetonitrile was added to solutions of stable mercurinium ions prepared in the manner described later in this paper, the mercurinium ions were immediately destroyed even at $-70°$. Unfortunately, we have not yet been able to elucidate the structure of the species produced in this reaction.

[12] G. A. Olah and P. R. Clifford, *J. Amer. Chem. Soc.*, **93**, 1261 (1971).

[13] G. A. Olah and P. R. Clifford, *ibid.*, **93**, 2320 (1971).

curic fluorosulfate the unsymmetrical propylenemethylmercurinium ion **3** is formed. The pmr spec-

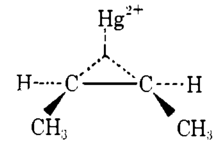
$$CH_3CH{=}CH_2 + CH_3HgOSO_2F \xrightarrow[\pi\ \mathrm{route}]{SO_2}$$



3

trum at −85° of **3** consists of complex signals at δ 7.23 and 5.76 due to the methine and methylene protons, respectively, as well as a doublet at δ 2.22 due to the methyl group coupled to the methine proton and a singlet at δ 1.40 due to the methyl on mercury.

The *cis*-**4** and *trans*-1,2 dimethylethylenemercurinium



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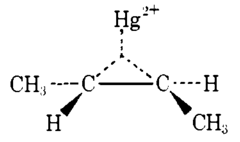
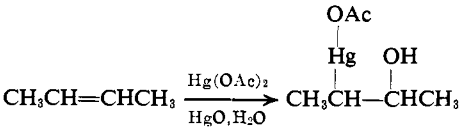


5

ions **5** are produced by the π route from *cis*- and *trans*-2-butene, respectively. Ion **4** shows two broad singlets at δ 7.89 and 2.83 (J_{CH_3-H} too small to be observed) in the pmr spectrum. Ion **5** exhibits a quartet at δ 8.23 and a doublet at δ 2.87 (J_{CH_3-H} = 4 Hz). The cmr spectra of ions **4** and **5** show the olefinic carbons at $\delta_{^{13}C}$ 45.3 and 46.7, respectively.

The precursors for the σ-route formation of ions **4** and **5** were prepared by oxymercuration of *cis*- and *trans*-2-butene. Assuming the usual stereochemistry of



$$CH_3CH{=}CHCH_3 \xrightarrow[HgO,H_2O]{Hg(OAc)_2} CH_3\overset{\overset{OAc}{|}\atop Hg}{\overset{|}{C}}H{-}\overset{OH}{\overset{|}{C}}HCH_3$$

addition,[3b] *threo*-3-acetoxymercuributan-2-ol is formed from *cis*-2-butene while *erythro*-3-acetoxymercuributan-2-ol is formed from *trans*-2-butene. What is particularly interesting is the apparent stereochemistry of mercurinium ion formation from these precursors. When *erythro*-3-acetoxymercuributan-2-ol is ionized in $FSO_3H-SbF_5-SO_2$, ion **4**, the product of a cis elimination reaction, is formed. Similarly, *threo*-3-acetoxymercuributan-2-ol gives ion **5** when treated with $FSO_3H-SbF_5-SO_2$.

The structures of the ions produced by the σ route were proven by adding solutions of ions **4** and **5** produced by the π route to solutions of ions produced by the σ route. Only one ion was observed by nmr when a solution containing ion **4** produced by direct mercuration (π route) was mixed with a solution containing the ion from *erythro*-3-acetoxymercuributan-2-ol (σ route). Similarly, only one ion was observed by nmr when a solution containing ion **5** produced by direct mercuration was mixed with a solution containing the corresponding ion from the threo precursor. However, when a solution of ion **4** produced by the π route was mixed with a solution of the ion from the threo precursor, or when a solution of ion **5** produced by the π route was mixed with a solution of the corresponding ion from the erythro precursor, two separate ions were observed.

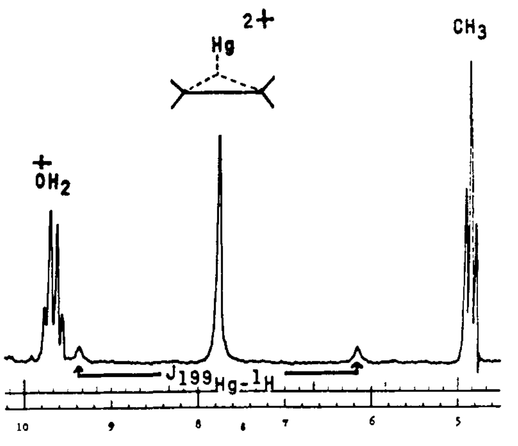
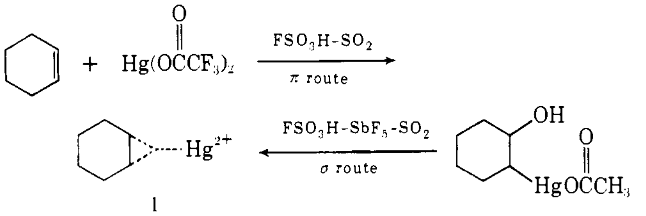


Figure 1. Pmr spectrum of ethylenemercurinium ion **2** (in $FSO_3H-SbF_5-SO_2$ at −30°, 60 MHz).



The cyclohexenemercurinium ion **1** can also be prepared by both the σ and π routes. The most convenient π-route preparation involves the addition of cyclohexene in sulfur dioxide to a solution of mercuric trifluoroacetate in fluorosulfonic acid and sulfur dioxide. Under these conditions, the pmr spectrum shows three slightly broadened singlets at δ 7.85, 2.58, and 1.60. Coupling of the mercury atom to the vinylic protons, $J_{^{199}Hg-^{1}H}$ = 182 Hz, is readily apparent. Ion **1** is prepared by the σ route from 2-acetoxymercuricyclohexan-1-ol by treatment with $FSO_3H-SbF_5-SO_2$. The cmr spectrum of ion **1** shows the olefinic carbons at $\delta_{^{13}C}$ 35.

The cyclohexenemethylmercurinium ion **6** is readily prepared by adding cyclohexene in sulfur dioxide to either a slurry of methylmercuric fluorosulfate and sulfur dioxide, or a solution of methylmercuric acetate in FSO_3H-SO_2. Ion **6** shows pmr absorbances at δ 7.27 (singlet, 2 H, $J_{^{199}Hg-H}$ = 54 Hz), 2.65 (multiplet, 4 H), 1.86 (multiplet, 4 H), and 1.46 (singlet, 3 H). Also observable at −90° are singlets at δ 1.54 due to excess CH_3HgOSO_2F and δ 2.86 (due to protonated acetic acid) if methylmercuric acetate is used in ion preparation (Figure 2). The cmr spectrum of ion **6** shows the vinylic carbons at $\delta_{^{13}C}$ 46.6.

The spectrum of **6** is temperature dependent. On warming to −60° each of the absorbances due to the ring protons broadens slightly, the singlets at δ 1.54 and 1.46 merge, and the mercury-proton satellites disappear.

The norbornylenemercurinium ion **7** is observed when *exo*-*cis*-3-hydroxy-2-norbornylmercuric acetate is treated with $FSO_3H-SbF_5-SO_2$. The pmr spectrum (Figure 3) at −70° has the following absorbances: δ 8.13 (2 H, H_2H_3), 4.18 (2 H, H_1, H_4), 2.64 (2 H, H_5 exo, H_6 exo), 1.92 (1 H, H_7 syn), 1.49 (3 H, H_7 anti, H_5 endo, H_6 endo). ^{199}Hg-H coupling was not ob-

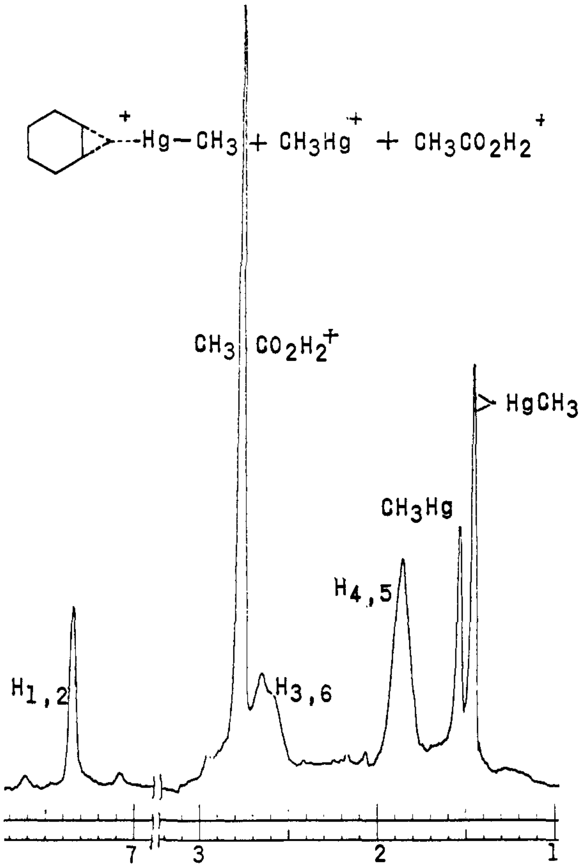
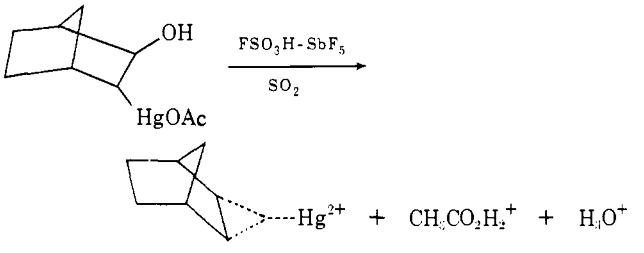


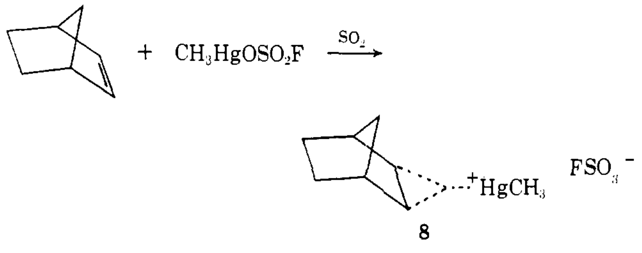
Figure 2. Pmr spectrum of cyclohexenemethylmercurinium ion 6 (in FSO_3H-SO_2 at −80°, 100 MHz).



7

served, probably because the satellites were obscured by other peaks in the spectrum. On warming to −30°, all the peaks from δ 4.18 to 1.49 merge into a single, broad absorption centered at ∼δ 2.7. Cooling back to −70° regenerates 7. The cmr absorption of the vinylic carbons is at $\delta_{^{13}C}$ 34.2.

Closely related to 7 is the norbornylenemethylmercurinium 8 which is prepared from norbornylene



8

and methylmercuric fluorosulfate in sulfur dioxide. The pmr spectrum of 8 does not show the same temperature dependance as that of 7.

The ^{13}C chemical shifts of the vinylic carbons were also obtained for each of the ions. The cmr shifts for all the ions were found within the range +45 ± 13 ppm (relative to CS_2).

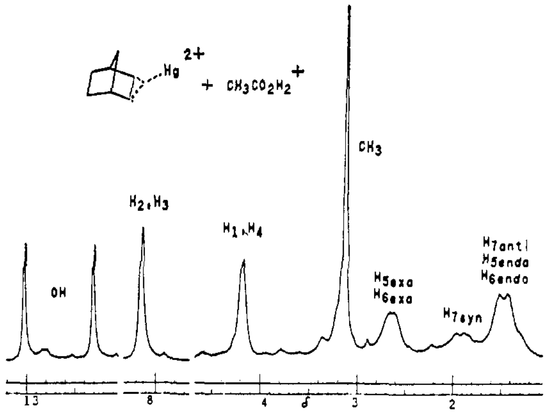
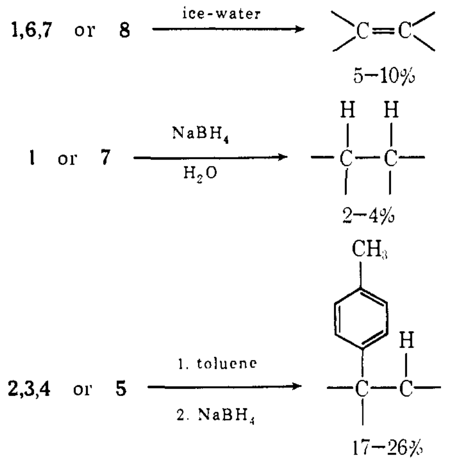


Figure 3. Pmr spectrum of norbornylenemercurinium ion 7 (in FSO_3H-SbF_5-SO_2 at −70°, 100 MHz).

Quenching experiments were also performed. Quenching of mercurinium ions in ice-water regenerates the corresponding olefins, while quenching with $NaBH_4$–H_2O produces the hydrocarbon corresponding to the hydrogenated olefins. Treatment of the mercurinium ions with toluene, followed by reduction with $NaBH_4$, produces alkyl toluenes (primarily para substituted).



Discussion

The evidence that mercurinium ions have, in fact, been observed may be summarized as follows.

1. **Pmr Evidence.** Each of the mercurinium ion spectra were compared with the spectra of silver–olefin complexes in sulfur dioxide solution. In each case the spectrum of the mercurinium ion was identical with the spectrum of the silver–olefin complex in all but two respects. First, all of the absorbances in the mercurinium ion spectra were deshielded relative to the corresponding absorbtions for the silver–olefin complexes. For the vinylic protons the difference in the shielding was between 1 and 2.5 ppm. Second, ^1H–^{199}Hg coupling could be observed for the mercurinium ions while no silver–proton coupling could be observed in the silver–olefin complexes.[14] Taken together the

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(14) To our best knowledge, silver-proton coupling has never been observed in silver–olefin complexes.[15] We have cooled SO_2 solutions of silver–olefin complexes to −115° and have not been able to observe such coupling.

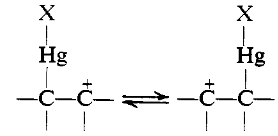
(15) For nmr studies of silver-olefin complexes, see H. W. Quinn and R. L. Van Gilder, *Can. J. Chem.*, **48**, 2435 (1970), and earlier papers in this series.

deshielding of the vinyl protons and the observation of proton–mercury coupling indicate that mercury is bonding to olefin and charge is leaking from the mercury atom onto the carbon skeleton.

2. Cmr Evidence. That charge has accumulated on the carbon skeleton is also apparent from the ^{13}C chemical shift data. The ^{13}C chemical shifts of several silver–olefin complexes have been obtained by Roberts.[16] The ^{13}C chemical shifts of the vinyl carbons of mercurinium ions are 20–35 ppm deshielded from the ^{13}C chemical shifts of the vinyl carbons in the corresponding silver–olefin complexes. Though it is tempting to ascribe the differences in ^{13}C chemical shifts to a lower degree of back donation from metal d orbitals to olefin antibonding orbitals in the mercurinium ion, such a suggestion is, at present, purely speculative.

3. Results of Quenching Experiments. In all cases the results of the quenching experiments are consistent with the formulated structures. All but one of the reactions are analogous to known reactions postulated to proceed by mercurinium ion pathways. As far as we have been able to ascertain, the formation of alkanes or cycloalkanes on treatment of mercurinium ions with $NaBH_4$-H_2O has no precedent in mercury chemistry.

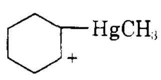
While no one of the above results taken by itself constitutes unambiguous proof of the existence of mercurinium ions, if all results are considered together there is no other satisfactory explanation of data. Alternatively, however, it could have been suggested that what is being observed are rapidly equilibrating systems of β-mercury-substituted carbenium ions. However, this assumption can be discarded for the following reasons.



9a **9b**

1. In order for ^{199}Hg–^{1}H coupling to occur, the lifetime of **9a** and **9b** must be long relative to the reciprocal of the coupling constant. For a coupling constant of 182 Hz (*cf.* ion **1**) the lifetime of the equilibrating species must be greater than 0.012 sec while for a coupling constant of 54 Hz (*cf.* ion **6**) the lifetime must be greater than 0.019 sec. Thus if equilibration were occurring at all it would have to be a slow equilibration and one which could be easily stopped by cooling. However, for none of the ions is it possible to see any indication of ions **9a** or **9b** even when the solutions are cooled 100° below temperatures at which coupling is observed.

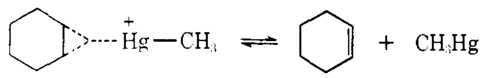
2. All the mercurinium ions studied have cmr absorptions for the vinylic carbons of δ 35 and 58. Ion **6** has a typical ^{13}C chemical shift of δ +46.6 for the vinyl carbons. The cmr shift of the sp^2 carbon in hypothetical ion **10** should be similar to that of the sp^2 carbon in the isopropyl cation,[17] *i.e.*, ~ -125 ppm.



10

The carbon bearing mercury in ion **10** should have a cmr shift inductively deshielded by about 15 ppm from that of a similar carbon atom in a neutral alkyl mercurial. Since dimethylmercury shows a cmr shift of +169 ppm,[18] the cmr shift of the carbon bearing mercury in **10** may be estimated at δ +155. On this basis the observed cmr shift for the carbons in question should be $[+155 + (-125)]/2 = 15$ ppm. This calculated shift is sufficiently different from the observed value for the equilibrating system to be ruled out.

3. The ^{199}Hg-CH_3 coupling in compounds of the type CH_3HgX is a function of X.[19] As the amount of s character on mercury increases with increasing electronegativity of X, so the value of $J_{^{199}\text{Hg}-\text{C}^1\text{H}_3}$ increases. In structures of the type RCH_2HgCH_2R (R = H or alkyl), $J_{^{199}\text{Hg}-\text{H}}$ is in the range 90–110 Hz. CH_3-$HgOSO_2F$ has $J_{^{199}\text{Hg}-\text{CH}_3} = 246$ Hz. In ion **10**, $J_{^{199}\text{Hg}-\text{CH}_3}$ should be closer to 90–110 Hz than to 246 Hz. Equilibration would not change this expected value. The value observed, $J_{^{199}\text{Hg}-^1\text{H}} = 240$ Hz for ion **6**, precludes the presence of equilibrating ions of structure **10**.[20]



6

Certain mercurinium ions do participate in other types of equilibria. For example, the spectral changes observed for ion **6** on warming from −90 to −60° can be explained in terms of equilibration between **6** and free olefin. The coupling between the vinyl protons and

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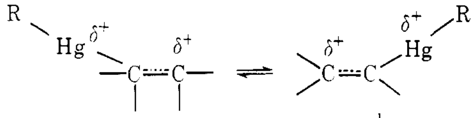
(16) R. G. Parker and J. D. Roberts, *J. Amer. Chem. Soc.*, **92**, 743 (1970).

(17) G. A. Olah and A. M. White, *ibid.*, **91**, 5801 (1969).

(18) F. J. Weigert, M. Winokur, and J. D. Roberts, *ibid.*, **90**, 1566 (1968).

(19) (a) J. V. Hatton, W. G. Schneider, and W. Seibrand, *J. Chem. Phys.*, **39**, 1330 (1963); (b) G. Singh, *J. Organometal. Chem.*, **5**, 577 (1966).

(20) One referee has suggested that the data presented may be also explained on the basis of rapidly equilibrating vertically stabilized ions of the type a ⇌ b as suggested by Traylor.[21] Hoffmann, *et al.*,[22] on theoretical ground and Olah and Liang[23] studying highly rigid carbocation systems experimentally pointed out that there is a continuum of charge delocalization in carbocations and no reason for suggested dichotomy between participation with and without bridging, since nuclear motion always must accompany electronic motion. The question only is, how much nuclear movement is involved in a specific system? Clearly, unsymmetrically substituted ions, *e.g.*, **3**, cannot be symmetrically bridged. Traylor's vertically stabilized ions represent, in our view, only one extreme of a continuum of ions, limited on the other extreme by symmetrically bridged ions. The ions studied in the present work clearly contain olefin-like carbon atoms and they are bound (complexed) with mercury. For the propylenemercurinium ion **3** which can neither be symmetrically bridged nor, from the data shown, rapidly equilibrating, the distinction between unsymmetrically bridged or "vertically stabilized" classification (if such distinction would exist) becomes a question of bond angles. The exact angle between the carbon–carbon bond and the carbon–mercury bond obviously cannot be determined from presently available data. We cannot, however, perceive the significance to stress this point further, as both unsymmetrical mercury bridging and "vertical stabilization" are expressions of the same concept of charge delocalization. Varying degree of nuclear movement accompanying electron delocalization, however, does not mean differences in principle, although the new term would seem to indicate such.



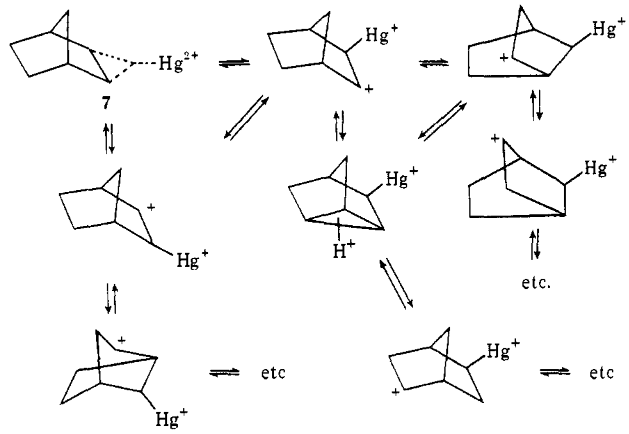
a b

(21) T. G. Traylor, *Accounts Chem. Res.*, **2**, 152 (1969); T. G. Traylor, W. Haustein, H. J. Berwin, N. A. Clinton, and R. S. Brown, *J. Amer. Chem. Soc.*, **93**, 5715 (1971), and references given therein.

(22) R. Hoffmann, L. Radom, J. A. Pople, P. v. R. Schleyer, W. J. Hehre, and L. Salem, *J. Amer. Chem. Soc.*, **94**, 6221 (1972).

(23) G. A. Olah and H. Liang, *J. Amer. Chem. Soc.*, **95**, 3792 (1973).

$^{199}Hg^+$ disappears at −60° because $CH_3{}^{199}Hg^+$ is exchanging with $CH_3{}^{200}Hg^+$ and $CH_3{}^{201}Hg^+$. Another equilibrium process may be used to explain the temperature-dependent spectrum of ion 7.



Finally, it is necessary to indicate the relationship of the observation of stable mercurinium ions to the solvomercuration systems discussed in the introduction. It has now been demonstrated that mercurinium ions are capable of existing as stable, long-lived species and that they may be generated by both direct mercuration of an olefin and ionization of β-substituted organomercurials under stable ion conditions. While these observations do lend credence to those reports in which mercurinium ions have been implicated as reaction intermediates, they do not prove that mercurinium ions are present under any other set of conditions. Each reaction must be examined independently to determine if mercurinium ions are, in fact, important reaction intermediates.

Experimental Section

The reagents not otherwise indicated were commercially available. Pmr spectra were recorded on either a Varian 56-60 or a Varian HA-100 nmr spectrometer. Cmr spectra were obtained both by Fourier transform cmr spectroscopy and by the indor method, as described previously.

Preparation of Methylmercuric Fluorosulfate. Method 1. Methylmercuric fluorosulfate was prepared *in situ* by adding methylmercuric acetate to a small excess of fluorosulfuric acid in sulfur dioxide at −70°. Vigorous stirring led to a solution which exhibited the pmr spectrum of protonated acetic acid. In addition, the pmr spectrum consisted of a singlet at δ 1.58, $J_{^{199}Hg-CH_3} = 246$ Hz, indicative of the presence of methylmercuric fluorosulfate.[1c]

Method 2. A solution of fluorosulfonic acid in sulfur dioxide was cooled in a flask to −70°. An equimolar amount of dimethylmercury (5 g) was introduced slowly into the fluorosulfuric acid solution. A white precipitate of methylmercuric fluorosulfate formed and was used without further purification, mp 59° (sealed tube, decomposition).

Preparation of *exo-cis*-3-Hydroxy-2-norbornylmercuric Acetate. *exo-cis*-3-Hydroxy-2-norbornylmercuric acetate was prepared from 9.4 g (0.1 mol) of norbornene, 10.8 g of mercuric oxide, and 15.9 g of mercuric acetate according to the method of Traylor and Baker.[24] The yield was 21.2 g (58%).

2-Acetoxymercuricyclohexan-1-ol and *threo-* and *erythro*-3-acetoxymercuributan-2-ol were also prepared from cyclohexene, *cis*-2-butene, and *trans*-2-butene, respectively, by the method of Traylor and Baker.[24]

Preparation of Mercurinium Ions. σ Route. To a FSO_3H–SbF_5–SO_2 (SO_2ClF) or SbF_5–SO_2ClF solution cooled to −78° was added the appropriate β-substituted organomercurial (Cl, OH, OAc). While stirring, the mixture was allowed to warm tc −20° for several minutes, resulting in a clear solution. After cooling the solutions back to −70° they were studied by nmr and quenching experiments.

π Route. Mercuric trifluoroacetate or methylmercuric acetate were dissolved in a slight excess of FSO_3H–SbF_5–SO_2 and the corresponding olefin in SO_2 was added to the stirred, cold solution, under conditions similar to those used for the π routes of preparation.

Nmr Study of Mercurinium Ions. Solutions of the mercurinium ions were prepared from the appropriate (see text) σ and π precursors in FSO_3H–SbF_5–SO_2, SbF_5–SO_2, FSO_3H–SbF_5–SO_2ClF, and SbF_5–SO_2ClF solutions as described previously in the preparation of stable carbocations.[25] Solutions were studied by ^1H and ^{13}C nmr spectroscopy. Pmr spectra were recorded on either a Varian 56-60 or a Varian HA-100 nmr spectrometer. Cmr spectra were obtained both by Fourier transform cmr spectroscopy and by the indor method. Chemical shifts are given from capillary TMS (^1H) and CS_2 (^{13}C), respectively. Quenching experiments of the solutions were carried out in a manner similar to that described in the case of superacid solutions of stable carbocations.[25]

Acknowledgment. Support of our work by grants of the National Science Foundation and the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

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(24) T. G. Traylor and A. W. Baker, *J. Amer. Chem. Soc.*, 85, 2746 (1963).

(25) For experimental details, see series on Stable Carbocations by G. A. Olah, *et al.*, in *J. Amer. Chem. Soc.*