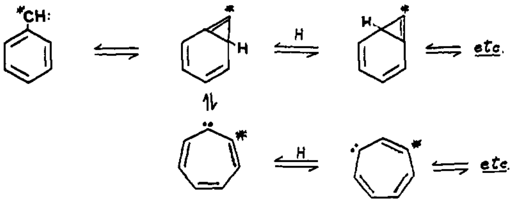
quaternary carbon atoms, C_5 and C_6, have the same degree of enrichment. Continual sweep scanning (1200 scans) without ^1H decoupling[20] and CAT output gave the following integration for the peak areas a:c–g:h = 1:5:1. This result demonstrates the *uniform* distribution of the ^{13}C label over *every* carbon atom of fulvenallene.[21] The enrichment of carbon atom C_6 of fulvenallene (which is formally derived from C_1 of phenylcarbene) is possible only *via* a hydrogen-shift mechanism *prior* to the formation of the prefulvene type intermediate[22] **6**.

The most likely mechanism which accounts for our labeling results involves the degenerate rearrangement of phenylcarbene *via* the bicyclic intermediate **8a** and the ring-expanded cycloheptatrienylidene (Scheme I) with concomitant hydrogen shifts (Scheme II). The occurrence of hydrogen shifts prior to ring contraction[23] of phenylcarbene has been observed for the closely related ring contraction of phenylnitrene to cyanocyclopentadiene.[24]

Scheme II



Our results are clearly consistent with the postulate that, prior to ring contraction, there is established a "preequilibrium" in which phenylcarbene rapidly interconverts with the bicyclic intermediate **8a** and with cycloheptatrienylidene.[25] We conclude that the formation of a pool of rapidly interconverting intermediates *via* the ring expansion route is a *basic* property of gas-phase generated arylcarbenes (and nitrenes[24]). Dimerization,[1,2] intramolecular trapping,[7] and ring contraction[1–3] are the major pathways leading from this pool. The absence of fulvenallene as a product from the direct generation of cyclophetatrienylidene[1,2,26] is surprising. However, we make the point that cycloheptatrienylidene may have been generated in a different electronic state[28] from that formed *via* phenylcarbene. Until data concerning the electronic states of these reacting species are available, we advocate caution in correlating results obtained for different generators.

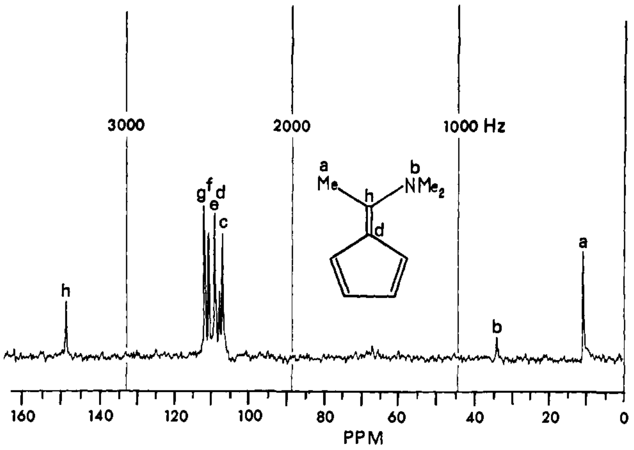


Figure 1. 22.63-MHz pulsed Fourier transform ^{13}C nmr spectrum (^1H broad-band decoupling) of 6-dimethylamino-6-methylfulvene (**7**) in deuteriochloroform.

Acknowledgments. This work is part of a project supported by the Australian Research Grants Committee, whose financial support is gratefully acknowledged. We thank H. B. Selby Pty. Ltd., Melbourne, for the use of their Bruker nmr spectrometer and Mr. Hans Hollenweger for determining the ^{13}C nmr spectra.

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and "off-resonance" partial decoupling: a, quartet; c, e, f, and g, doublets; d and h, singlets.

(19) E. Breitmaier, C. Jung, and W. Voelter, *Angew. Chem.*, **83**, 659 (1971); *Angew. Chem., Int. Ed. Engl.*, **10**, 673 (1971).

(20) Thereby eliminating nuclear Overhauser effects.

(21) The complexity of the proton nmr spectrum in the olefinic region prevented an additional confirmation of the distribution of label obtained from the ^{13}C nmr spectrum. However, we were able to examine the ^{13}C satellites of the *C*-methyl group a. The percentage of label at this position was computed to be 16 ± 1%, a result consistent with complete scrambling of the label over all carbon atom sites.

(22) It is possible to envisage a process by which ^{13}C may "leak" into the 6 position of ethynylcyclopentadiene (**4a**) *via* scission of the C_5–C_6 bond, hydrogen migration in the acetylenic radical, and subsequent recombination of the radicals. Achievement of uniformly distributed label in the product by this mechanism would be very coincidental however.

(23) It is noteworthy that hydrogen shifts were not detected during the isomerization of *p*-tolylcarbene to *o*-tolylcarbene and methylphenylcarbene.[8] This observation suggests that the rate of hydrogen shifts may be much slower than the rate of carbene migration according to Scheme I, but that both processes are much faster than the rate of ring contraction.

(24) W. D. Crow and M. N. Paddon-Row, *Tetrahedron Lett.*, in press.

(25) We realize that our results do not demand the intermediacy of cycloheptatrienylidene as they may be accounted for in terms of a series of vinylcyclopropene rearrangements in the bicyclic intermediate **8a** with concomitant hydrogen shifts. This type of rearrangement has been discussed in ref 1b and 7. However, the evidence (although by no means unequivocal) for the phenylcarbene–cycloheptatrienylidene[2] and the diphenylcarbene–phenylcycloheptatrienylidene[1b] interconversions at lower temperatures argues for the intermediacy of cycloheptatrienylidene under our conditions of pyrolysis.

(26) A referee has pointed out the possibility that cycloheptatrienylidene actually may not have been exposed to the conditions assumed by the authors.[1a,2] This point becomes significant when it is realized that, unlike phenyldiazomethane, diazocycloheptatriene cannot be distilled from its tosylhydrazone sodium salt.[27]

(27) W. M. Jones, private communication.

(28) For example, calculations[29] have revealed that the difference in energy between the first two electronic states (singlet and triplet) of cycloheptatrienylidene may be small.

(29) R. Gleiter and R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 5457 (1968).

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The Oxymercuration of Bicyclo[2.2.2]octene. Evidence for a Solvated Mercurinium Ion

Sir:

Hydroxymercuration of bicyclo[2.2.2]octene (**1**), which is symmetrical about the double bond, produces both cis and trans hydroxymercurials.[1a] However, acetoxymercuration of **1** with mercuric acetate in acetic acid solvent has been reported to afford only the *cis*-2-acetoxymercurial **3**.[1a] A mechanism involving a single mercurinium ion intermediate leading to both cis and trans products was invoked by Traylor.[1a] The failure to observe any alteration in the trans oxymercuration products with the hydroxymercuration of **1**

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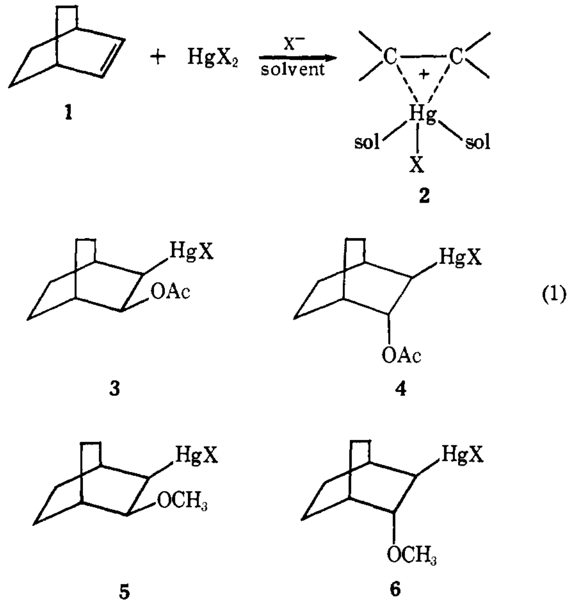
(1) (a) T. G. Traylor, *J. Amer. Chem. Soc.*, **86**, 244 (1964); (b) T. T. Tidwell and T. G. Traylor, *J. Org. Chem.*, **33**, 2614 (1968); (c) T. G. Traylor, *Accounts Chem. Res.*, **2**, 152 (1969).

Table I. Solvent Effects on the Oxymercuration of Bicyclo[2.2.2]octene

Mercuric salt[a]	Nucleophile, concn (*M*)	Solvent	**3**, %	**4**, %	**5**, %	**6**, %
$Hg(OAc)_2$		HOAc[b]	64	36		
$Hg(OAc)_2$	OAc^-, 0.33	HOAc[d]	60	40		
$Hg(OAc)_2$		CH_3OH[d]	7	3	13	77
$Hg(OAc)_2$	OAc^-, 0.33	CH_3OH[c]	37	40	1	22
$Hg(OAc)_2$	Cl^-, 0.33	CH_3OH[c]	46	34	3	17
$Hg(NO_3)_2$		CH_3OH[b]			19	81
$Hg(NO_3)_2$	CH_3OH, 0.66	CH_2Cl_2[c]			79	21
$Hg(NO_3)_2$	CH_3OH, 0.33	CH_2Cl_2[c]			>99[e]	
$Hg(NO_3)_2$	CH_3OH, 0.66	Dioxane[c]				>99[f]
$Hg(OAc)_2$	CH_3OH, 0.66	Dioxane[c]	66	26		8
$Hg(OAc)_2$		CH_2Cl_2[g]	98	2		
$Hg(OAc)_2$	CH_3OH, 0.33	CH_2Cl_2[c]	79	4	3	14
$Hg(OAc)_2$		Dioxane[g]	30	70		
$Hg(NO_3)_2$	HOAc, 0.66	Dioxane[c,h]	50	50		
$Hg(NO_3)_2$	HOAc, 0.33	CH_2Cl_2[c,h]	61	39		

[a] The concentrations of mercuric salt and **1** are both 0.33 *M* in the specified solvent. All reactions were carried out at room temperature. [b] Reaction time was 15 min. [c] Reaction time was 16 hr. [d] Reaction time was 1 hr. [e] The melting point of the *cis*-mercuri chloride was 109–110.5°. [f] The melting point of the *trans*-mercuri chloride was 88.5–90°. [g] Reaction time was 3 days and the isolated yield was 75%. [h] The reaction was carried out in the presence of 1 equiv of HgO.

in the presence of acetate ion prompted Tidwell and Traylor[1b] in a more recent study to exclude a mechanism for cis oxymercuration that required water and acetate ion to compete for a carbonium ion. Instead, they suggested that cis and trans oxymercurations involve different mechanisms. As a result of recently developed nmr techniques,[2] we now report that acetoxymercuration of **1** affords both *cis*- and *trans*-2-acetoxymercuri acetates, **3** and **4** (eq 1). This observation is inconsistent with a recently reported[1b,1c] mechanism and provides additional evidence for mercurinium ion intermediates[5] in the cis oxymercuration reaction.[4,6]



(1)

Acetoxymercuration of **1** in glacial acetic acid affords *both cis*- and *trans*-2-acetoxymercuri acetates, **3** and **4**, in a ratio of 64:36. Inclusion of 1 equiv of sodium acetate in the acetoxymercuration reaction did not significantly alter the product composition (Table I). Acetoxymercuration of **1** in aqueous acetone, in the presence of sodium acetate, affords the cis and trans hydroxymercurials as previously reported[1a] in addition to both *cis*- and *trans*-acetoxymercurials **3** and **4**, in a ratio of 46:54. Methoxymercuration of **1** with mercuric acetate in methanol solvent gave the *trans*-methoxymercurial **6** as the major product, but also afforded minor amounts of *cis*- and *trans*-2-acetoxymercurials. Addition of 1 equiv of sodium acetate *or* sodium chloride to the methoxymercuration reaction resulted in a marked increase in **3** and **4** and a concomitant decrease in **5** and **6**. This observation is consistent with our previous report[4] on the cis oxymercuration reaction where we observed that addition of anions *other than acetate ion* resulted in an increase in the ratio of 2-acetoxy- to 2-methoxymercurials. Most significant, however, is the marked increase in the *trans*-2-acetoxymercuri acetate **4**. The observation of cis and trans acetoxymercuration accommodates a mechanism where both **3** and **4** can be derived from collapse of an acetate ligand on mercury or by attack of free acetate ion in solution on the solvated mercurinium ion, **2**.

We have also observed a striking solvent effect on the stereospecificity of the methoxymercuration of **1**. Thus, reaction of **1** with mercuric nitrate in methanol solvent

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(2) Our nmr technique for determining the ratio of **3** to **4** is an extension of the nmr method of Waters.[3] The resonances for the 2-acetoxy moieties in **3** and **4** are separated only by 0.5 Hz in CCl_4. However, we have found that use of pyridine as the solvent results in a chemical-shift difference of 3.6 Hz. The *cis*-mercurial **3** has a sharp singlet at 113.9 Hz while the resonance for the trans isomer is at 117.5 Hz. The cis:trans ratio of 2-acetoxymercurials was also determined by saponification of **3** and **4** (as the mercuri chlorides) and analysis of the *cis*- and *trans*-3-(chloromercuri)bicyclo[2.2.2]octan-2-ols by infrared spectroscopy according to the method of Traylor.[1a] Our nmr method was in good agreement with the infrared analysis. Saponification of **3** and **4**, as their mercuri acetates, resulted in hydroxide ion induced deoxymercuration[4] of **4** and an increase in the ratio of **3** to **4**. The chemical-shift differences for **5** and **6** are not only increased in pyridine, but the chemical shift relative to TMS for the two peaks is reversed. Thus, the anisotropy effects of pyridine solvent provide a unique method for assigning the stereochemistry of methoxy mercurials.

(3) W. L. Waters, *Tetrahedron Lett.*, 3769 (1969).

(4) R. D. Bach and R. F. Richter, *ibid.*, 3915 (1971).

(5) (a) H. J. Lucas, F. R. Hepner, and S. Winstein, *J. Amer. Chem. Soc.*, **61**, 3102 (1939); (b) G. A. Olah and P. R. Clifford, *ibid.*, **93**, 1261, 2320 (1971); (c) R. D. Bach and H. F. Henneike, *ibid.*, **92**, 5589 (1970); (d) R. D. Bach and P. A. Scherr, *ibid.*, **94**, 220 (1972).

(6) The cis oxymercuration reaction with norbornene was discovered by Traylor.[7] A cyclic π complex intermediate which was opened from the front side by ligand migration or ion pair collapse was suggested to account for the stereochemistry of addition. This mechanism is quite similar to that suggested in the present work. More recently, however, Traylor has suggested that methoxymercuration of norbornenes proceeds through a four-center transition state and acetoxymercuration through a six-center transition state.[1b]

(7) T. G. Traylor and A. W. Baker, *Tetrahedron Lett.*, 14 (1959); *J. Amer. Chem. Soc.*, **85**, 2746 (1963).

affords a mixture of the *cis-* and *trans*-methoxymercurials **5** and **6** in a ratio of 19:81. However, when methylene chloride is utilized as the solvent,[8] with 1 equiv of methanol as the attacking nucleophile, the *cis*-methoxymercurial **5** is formed to the exclusion of the trans adduct **6**. By contrast, utilization of dioxane as the solvent and methanol as the nucleophile resulted in a stereospecific synthesis of the *trans*-methoxymercurial **6**. These data strongly suggest that the mercurinium ion intermediate **2** involved in these reactions is solvated by methanol in methylene chloride solvent. Thus, when methanol is present in limiting quantity, collapse of the solvated mercurinium ion from the front side results in exclusive cis addition. However, with the donor solvent dioxane, methanol is displaced from the primary solvent shell surrounding the mercurinium ion and exclusive trans attack by free methanol in solution on **2** prevails.

The concentration of $^+$HgX, the rate of reaction, and the product composition are also influenced by the polarity of the solvent. Thus, in dioxane solvent, or when 2 equiv of methanol are present in dioxane, the oxymercuration of **1** with mercuric acetate affords the *cis*-2-acetoxymercuri acetate **3** as the major product in marked contrast to the results with mercuric nitrate. Similarly, in methylene chloride the addition of mercuric acetate to **1**, in the absence of methanol, results in essentially a stereospecific (98%) cis addition. Addition of 1 equiv of methanol to the methylene chloride solvent affords only 17% of **5** and **6**. With the more ionic mercuric nitrate as the electrophilic reagent and acetic acid as the added nucleophile, approximately equal amounts of **3** and **4** are produced in both dioxane and methylene chloride solvent.

Mercurinium ions derived from strained olefins should be relatively short lived if relief of strain cannot be attained on forming an olefin π complex.[5c] Therefore, cis oxymercurials may arise by attack of the displaced ligand X$^-$ on **2** before solvent separation of the intimate ion pair can occur. We therefore suggest that in the present study both cis and trans oxymercurials are derived from a common intermediate, the solvated mercurinium ion **2**, and that the product composition is a function of a ligand effect on the mercury.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, to the Research Corporation, and to Merck and Co. for support of this work.

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[8] Dissolution of $Hg(NO_3)_2$ in CH_2Cl_2 is not effected until the olefin is added, suggesting the formation of an olefin-solvated mercuric ion intermediate. An additional ∼16 hr was required for complete reaction.

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Mono-, Di-, and Tricatlons of Hexamethoxytriphenylene. A Novel Anodic Trimerization

Sir:

We report a new synthesis of triphenylene cations from the anodic oxidation of ethers of pyrocatechol in media containing trifluoroacetic acid (TFA). The cation radical **1** is remarkably stable in TFA or dichloromethane while dication **2** shows limited stability in TFA or TFA–$HFSO_3$ and the trication **3** is only observable at temperatures lower than about −50° in TFA–$HFSO_3$. The dication is particularly interesting since it is a ground-state triplet as predicted from theoretical considerations.

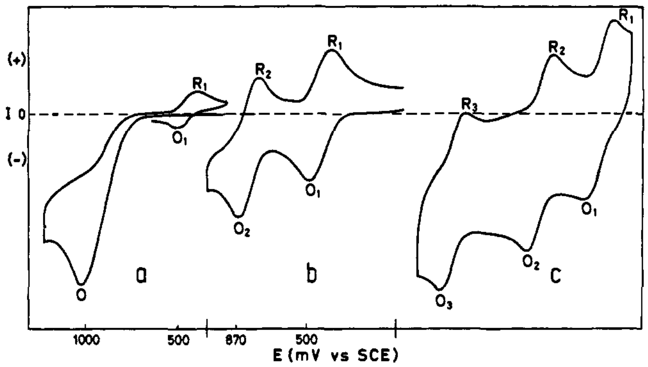
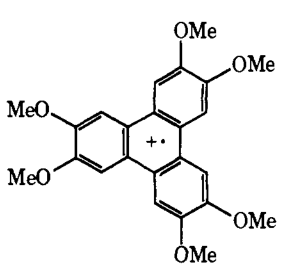
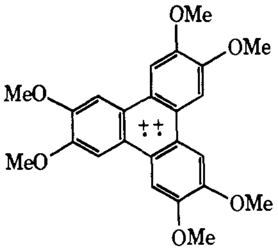


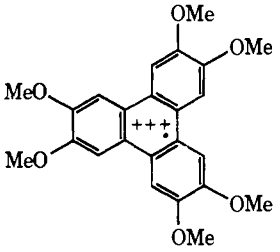
Figure 1. Cyclic voltammograms of (a) veratrole in CH_2Cl_2–TFA (9:1), (b) HMT in TFA, and (c) HMT cation radical in TFA–$HFSO_3$ (1:1). Supporting electrolyte was Bu_4BF_4 and the voltage sweep rate was 150 mV/sec. No reference electrode was used in c.



1



2



3

The reaction resulting in the formation of **1** is illustrated by the cyclic voltammogram of veratrole in dichloromethane–TFA (9:1) containing tetra-*n*-butylammonium fluoroborate (Figure 1a). The initial oxidation peak (O) corresponds to a $^7/_3$ electron oxidation of veratrole to **1** which is reduced at R_1 to the uncharged hexamethoxytriphenylene (HMT) which is oxidized to **1** at O_1. The use of TFA and dichloromethane–TFA for the anodic generation of cation radicals has recently been described.[1,2]

Figure 1b is the cyclic voltammogram of HMT in TFA. In addition to the R_1–O_1 couple in Figure 1a, the reversible oxidation of **1** to **2** can now be seen by the couple, O_2–R_2. No evidence for a further oxidation of **2** could be obtained in this medium. However, when

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[1] O. Hammerich, N. S. Moe, and V. D. Parker, *J. Chem. Soc., Chem. Commun.*, 156 (1972).

[2] U. Svanholm and V. D. Parker, *Tetrahedron Lett.*, 471 (1972).