Methoxymercuration of Allenes. Evidence for a σ-Bridged Mercurinium Ion[1a]

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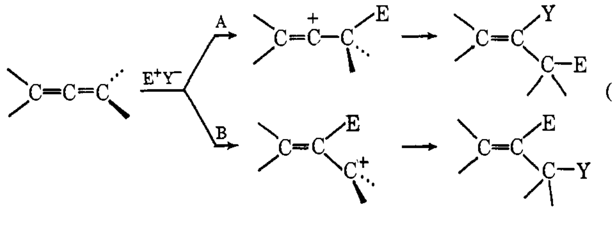
Abstract: The reactions of allene and its five methyl-substituted derivatives with mercuric acetate in methanol are described. All six allenes react rapidly at 25° to produce one or more adducts, which are characterized by their proton nmr spectra. Electrophilic attack of this reagent at methyl- and dimethyl-substituted allenic π bonds leads exclusively to monoadducts in which the acetoxymercuri group is bonded to the central carbon atom, whereas attack at unsubstituted π bonds occurs only at the terminal carbon to produce an allylmercury intermediate which undergoes further, rapid addition to a 1,3-bis(acetoxymercuriketal). Hydrolysis of this ketal function is exceptionally facile, and the resulting α,α′-dimercury-substituted ketones show remarkable stability. The order of reactivity of dimethyl-, monomethyl-, and unsubstituted allenic π bonds is approximately 16:4:1. Methoxymercuration of tetramethylallene occurs at least 10^4 times faster than that of tetramethylethylene. The results are interpreted in terms of a stable, σ-bond-bridged mercurinium ion intermediate.

The chemistry of allenes is unique in many respects due to the presence in these compounds of two orthogonal π bonds with a common terminus. Electrophilic addition to an allenic system is of particular interest because the vinyl cation and twisted, nonresonating allyl cation intermediates resulting from paths A and B, respectively (eq 1), could yield information on some long-standing theoretical questions, and are difficult to generate by other means.



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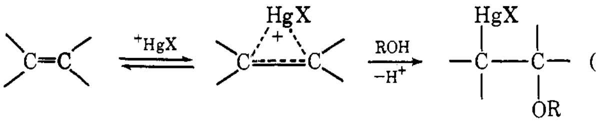
Though there are scattered reports in the earlier literature on the ionic addition of hydrogen halides to various allenes, systematic studies of this reaction have been carried out only rather recently by Jacobs and Johnson[2] and by Griesbaum, *et al.*[3] This work has established the orientation of addition (eq 1) for methyl-, 1,1-dimethyl-, and unsubstituted allene[2] and provided good evidence for a vinyl cation intermediate from allene,[3] but has also served to illustrate the exasperating over-all complexity of the reaction, which has virtually precluded firm mechanistic conclusions.[2]

Acid-catalyzed hydration of monosubstituted allenes in the presence of mercuric sulfate leads to methyl ketones,[4] furthering the similarity to the behavior of terminal acetylenes which had been noted for hydrogen halide addition.[3] The only reported attempt to assign structures to initial allene–mercuric salt adducts is that of Gardner and co-workers,[5] who have recently determined the orientation of addition of mercuric acetate to 1,2-cyclononadiene, 1,2,6-cyclononatriene, and 2,3-pentadiene in ethanol.

There are several discrete advantages in the choice of the oxymercuration reaction for a thorough investigation of the behavior of allenes toward electrophilic reagents. Although a number of mechanistic details remain uncertain, addition of a mercuric salt to an ordinary olefinic bond is generally believed to involve equilibrium formation of a bridged or π-complexed mercurinium ion followed by product-determining *trans* attack by solvent (or mercury ligand, in solvents of low nucleophilicity) (eq 2).[6–8] The orientation of addition follows Markovnikov's rule quite cleanly, and the reaction displays other characteristics[6] which are typical of electrophilic addition. However, there are some notable differences. The most characteristic feature of oxymercuration might be considered to be its relative unresponsiveness to gross structural changes in the olefinic substrate. For example, no 1,4 addition occurs with 1,3-butadiene.[9] Addition to norbornene is unaccompanied by the usual skeletal rearrangement,[8] and though a change from *trans* to *cis* addition occurs in this case, there is evidence[8b] that the mechanism remains substantially the same. Most importantly in the present context, oxymercuration of olefins which are particularly sensitive to acid-catalyzed π-bond migration (such as 2,3-dimethyl-1-butene and *p*-methallyl-



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[1] (a) Presented at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 29, 1966, Abstract K44. This work was supported in part by an institutional grant from the National Science Foundation. (b) National Defense Education Act Predoctoral Fellow, 1965–1966.

[2] T. L. Jacobs and R. N. Johnson, *J. Am. Chem. Soc.*, **82**, 6397 (1960).

[3] K. Griesbaum, W. Naegele, and G. G. Wanless, *ibid.*, **87**, 3151 (1965), and preceding papers in this series.

[4] M. M. Bouis, *Compt. Rend.*, **182**, 790 (1926); *Ann. Chim.*, **9**, 402 (1928).

[5] R. K. Sharma, B. A. Shoulders, and P. D. Gardner, *J. Org. Chem.*, **32**, 241 (1967). The results obtained by these workers are entirely consistent with those reported herein and previously.[1a]

[6] (a) J. Chatt, *Chem. Rev.*, **48**, 7 (1951); (b) N. S. Zefirov, *Russ. Chem. Rev.*, **34**, 527 (1965).

[7] (a) M. M. Kreevoy, G. Stokker, R. A. Kretcher, and A. K. Ahmed, *J. Org. Chem.*, **28**, 3184 (1963), and preceding papers in the series; (b) K. Ichikawa, K. Nishimura, and S. Takayama, *ibid.*, **30**, 1593 (1965).

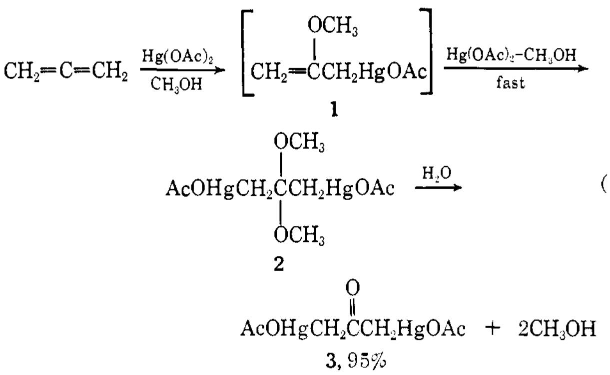
[8] (a) T. G. Traylor and A. W. Baker, *J. Am. Chem. Soc.*, **85**, 2746 (1963), and references cited therein; (b) T. G. Traylor, *ibid.*, **86**, 244 (1964); (c) H. C. Brown, J. H. Kawakami, and S. Ikegami, *ibid.*, **89**, 1525 (1967).

[9] K. H. McNeely and G. F. Wright, *ibid.*, 77, 2553 (1955).

anisole) takes place without incident.[10] Extension of this reaction to allenes might thus be expected to circumvent the problems brought about by kinetically competitive elimination and isomerization of these compounds to acetylenes and/or conjugated dienes which arise under more acidic reaction conditions.[2] It might be argued that the relative lack of carbonium character which is implied by the above observations makes oxymercuration a poor model for general electrophilic addition; however, this distinction is clearly one of degree rather than kind[8b] and does not affect the validity of conclusions to be drawn from product orientations.

Results

Allene. The reaction of allene (1,2-propadiene) with methanolic mercuric acetate produced only one product, 1,3-bis(acetoxymercuri)-2,2-dimethoxypropane (**2**), which hydrolyzed immediately under the usual reaction conditions to give an insoluble solid ketone, 1,3-bis(acetoxymercuri)-2-propanone (**3**, eq 3).



$$\mathrm{CH_2{=}C{=}CH_2} \xrightarrow[\mathrm{CH_3OH}]{\mathrm{Hg(OAc)_2}} \underset{\mathbf{1}}{\left[\mathrm{CH_2{=}\overset{\displaystyle OCH_3}{\overset{|}{C}}CH_2HgOAc}\right]} \xrightarrow[\text{fast}]{\mathrm{Hg(OAc)_2\text{-}CH_3OH}}$$

$$\underset{\mathbf{2}}{\mathrm{AcOHgCH_2\underset{\underset{\displaystyle OCH_3}{|}}{\overset{\overset{\displaystyle OCH_3}{|}}{C}}CH_2HgOAc}} \xrightarrow{\mathrm{H_2O}} \quad (3)$$

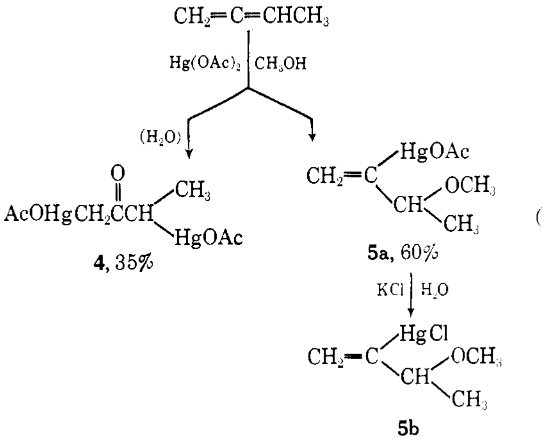
$$\underset{\mathbf{3},\ 95\%}{\mathrm{AcOHgCH_2\overset{\overset{\displaystyle O}{\|}}{C}CH_2HgOAc}} + \mathrm{2CH_3OH}$$

Careful attempts to prepare a monoadduct (*i.e.*, **1**) by slow addition of dilute mercuric acetate solution to a large excess of allene at −78° did not change this result: bisadduct **3** was still obtained in nearly quantitative yield based on mercury, and the remaining allene was recovered unchanged. The over-all reaction was very rapid even at low temperatures; inclusion of 1 equiv of water (less than 0.5% by volume) in the methanol solution resulted in an immediate, dense precipitate of **3**. Efforts to isolate ketal intermediate **2** proved almost equally frustrating, though with some care it was possible to transfer the compound to a carbon tetrachloride solution for observation of its nmr spectrum. By leaving the nmr tube open to the atmosphere, the rapid hydrolysis of **2** to **3** could be readily followed by monitoring the two methoxyl lines due to the ketal and methanol (eq 3).

The structure of ketone **3** was assigned primarily from microanalysis (two mercury atoms per allene unit) and nmr data (singlets at τ 7.92 and 6.97 in D_2O, relative area 2.14:1, with Hg^{199} satellites symmetrically distributed about the latter at 20 and 338 Hz; see Discussion). Treatment with iodine[6] gave 1,3-diiodo-2-propanone, identified by comparison with an authentic sample. The infrared spectrum of **3** (KBr disk) showed strong carbonyl absorption at 1616 cm^{-1} (bromomercuriacetone ν_{max} C=O 1633 cm^{-1}) in addition to the bands at 1570 and 1410 cm^{-1} which are characteristic of mercuric acetate and which vanished after conversion of **3** to the bis(bromomercuri) derivative with aqueous potassium bromide.[6]

The physical properties of compound **3** and its bis(halomercuri) derivatives are in marked contrast to those of the monoadducts obtained from the various methyl-substituted allenes (see below). Whereas the latter are oils or low-melting solids with solubility properties typical of nonpolar organic compounds, **3** is soluble to an appreciable extent only in water, and its high melting (>250° dec) bis(halomercuri) derivatives have negligible solubilities in all common solvents except excess aqueous halogen acids. Unlike the monoadducts, which decompose gradually unless specifically protected from light, irradiation of **3** or 1,3-bis(iodomercuri)-2-propanone with a 275-w sun lamp for extended periods, either as the powdered solids or suspended in various solvents, produced no detectable change.

Methyl-Substituted Allenes. Methoxymercuration of methylallene (1,2-butadiene) produced two major products, along with traces of at least two others. One of the major products (35% from mercuric acetate), an insoluble solid, was easily identified by infrared and elemental analysis as 1,3-bis(acetoxymercuri)-2-butanone (**4**), a bis adduct homologous to **3**. The primary product (60%) was an oil (**5a**) which after treatment with aqueous potassium chloride[6] yielded a solid (mp 123°, soluble in nonpolar solvents), assigned the structure 2-chloromercuri-3-methoxy-1-butene (**5b**, eq 4).



(4)

The orientation of addition leading to monoadduct **5b** was established by its nmr spectrum in benzene solution, which showed the presence of two vinyl protons (τ 4.79 and 5.48), an aliphatic methyl group (τ 9.10, doublet), and an oxymethinyl proton (τ 6.60, quartet), in addition to the methoxy line at τ 7.11. Conclusive evidence for these assignments was obtained from mercury–proton spin–spin coupling constants (see Discussion).

1,3-Dimethylallene (2,3-pentadiene) also produced two addition compounds in a combined yield of 93%, but both were monoadducts (**6a** and **7a**, eq 5). Treatment of the crude, oily product with aqueous potassium chloride[6] provided a mixture of solid chloromercuri derivatives which could be partially separated by fractional crystallization from hexane. The products were identified as *cis*- and *trans*-3-chloromercuri-4-methoxy-2-pentene (**6b** and **7b**, respectively) from their nmr spectra in carbon tetrachloride, which showed methoxyl

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(10) (a) E. F. Kiefer and W. L. Waters, *J. Am. Chem. Soc.*, **87**, 4401 (1965); (b) H. C. Brown and P. Geoghehan, Jr., *ibid.*, **89**, 1522 (1967).

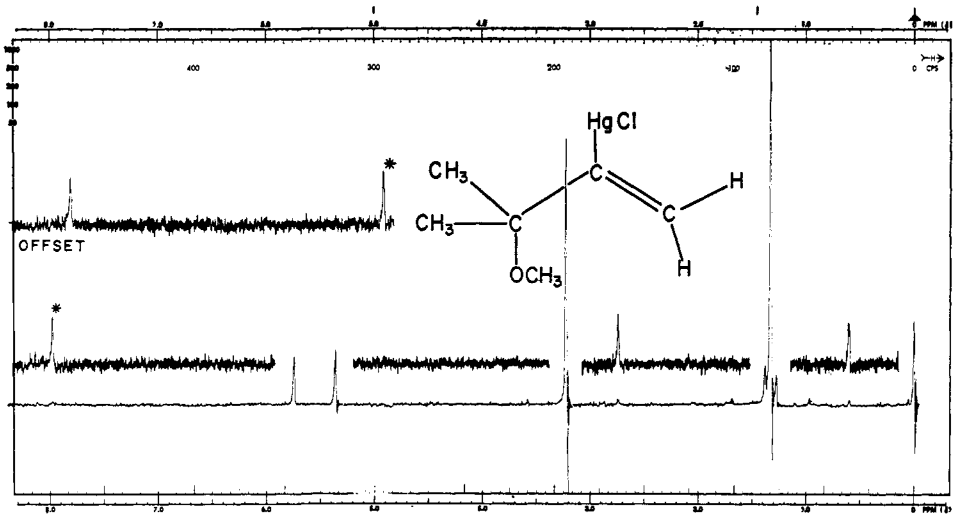
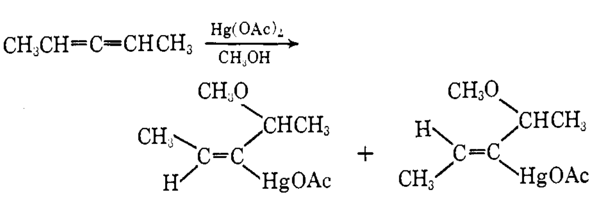


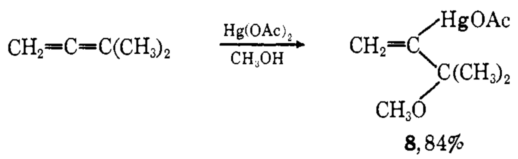
Figure 1. 2-Chloromercuri-3-methoxy-3-methyl-1-butene (**8b**), 60-MHz proton nmr spectrum, 20% in carbon tetrachlorode, 41°. Mercury-199 satellites of vinyl protons are shown at high gain (see Table II).

(τ 6.76 and 6.78, respectively), allylic methyl (τ 8.23, 8.09), aliphatic methyl (τ 8.82, 8.80), vinyl proton (τ 4.32, 3.71), and oxymethinyl proton resonances (τ 5.67, 6.12), each with the expected intensity and multiplicity. Assignment of the former lines to the *cis* isomer and the latter to the *trans* was consistent with the observed values of mercury-proton coupling constants (see Discussion). Only the major isomer **7b** was isolated pure; the nmr assignments for **6b** were made from the residual mixture enriched in **6b**. The ratio of **6a** to **7a** in the original mixture was approximately 1:4 (eq 5).



6a, 18% **7a**, 75% (5)

1,1-Dimethylallene (3-methyl-1,2-butadiene) produced only one product, an oil which was identified as 2-acetoxymercuri-3-methoxy-3-methyl-1-butene (**8**, 84%), corresponding to addition across the most highly substituted π bond (eq 6). Compound **8** was inert to excess mercuric acetate.



8, 84% (6)

The pure, crystalline chloromercuri derivative showed nmr lines characteristic of an aliphatic *gem*-dimethyl group (τ 8.68, singlet with $J_{\text{Hg}^{199}-\text{H}^1} = 6$ Hz), methoxyl group (τ 6.78, singlet), and two vinyl protons (τ 4.65 and 4.27, singlets with $J_{\text{Hg}^{199}-\text{H}^1} = 135$ and 620 Hz, respectively; see Figure 1 and Discussion). The nmr spectrum of the product obtained after iododemercuration of **8** with potassium iodide and iodine[6] displayed the same features except the Hg^{199} satellites had vanished and the vinyl protons were shifted downfield and weakly coupled ($J = 2$ Hz).

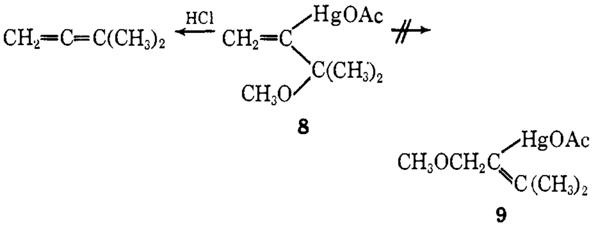
Oxymercuration of 1,1-dimethylallene with mercuric acetate in isopropyl alcohol and in *t*-butyl alcohol was carried out in an attempt to direct addition to the unsubstituted π bond. The decreased reactivity of these alcohols relative to the other nucleophilic species in solution (acetate ion and traces of water) is evident from the results (Table I), but none of the anticipated isomeric adduct was observed.

Table I. Effect of Solvent ROH on Oxymercuration of 1,1-Dimethylallene

$$CH_2{=}C{=}CMe_2 \xrightarrow{Hg(OAc)_2-ROH} CH_2{=}C(HgOAc)CMe_2X$$

R	X = OR, %	X = OH, %	X = OAc, %
CH_3	100	0	0
$(CH_3)_2CH$	58	28	14
$(CH_3)_3C$	10	60	30

Attempts to induce isomerization of **8** to the more stable primary ether **9** by heating in solution or treatment with mineral acid (eq 7) resulted only in deoxymercuration to the starting allene which under more vigorous conditions was converted to isoprene and polymeric products.



8 **9** (7)

Trimethylallene (2-methyl-2,3-pentadiene) reacted with mercuric acetate in methanol to produce a mixture of two monoadducts, *trans*-3-acetoxymercuri-4-methoxy-4-methyl-2-pentene (**10**) and 3-acetoxymercuri-4-methoxy-2-methyl-2-pentene (**11**) in a 4:1 ratio (eq 8).

Although **10** and **11** were not isolated pure, conversion to a mixture of solid chloromercuri derivatives again facilitated partial separation by fractional crystallization so that the nmr lines due to the individual com-

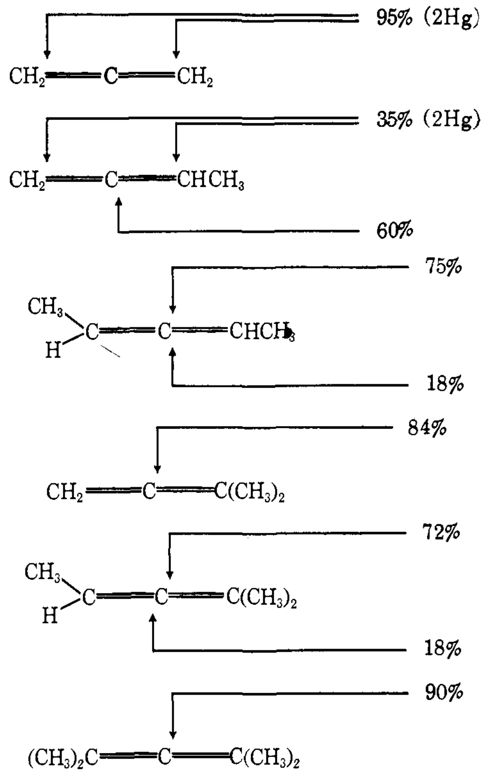
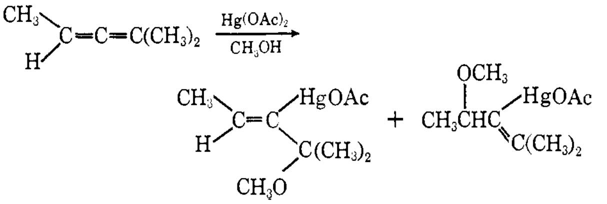


Figure 2. Orientation of addition of $Hg(OAc)_2$ to allenes. Arrows indicate the π bond to which addition occurs, and are biased toward the carbon to which the mercury atom is ultimately directed.

pounds could be readily identified. The assigned structures followed unequivocally from a comparison of chemical shifts and coupling constants with the other monoadducts (see above and below). Compound **10**

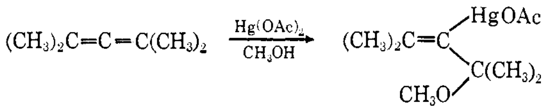


$$\mathrm{CH_3(H)C{=}C{=}C(CH_3)_2} \xrightarrow[\mathrm{CH_3OH}]{\mathrm{Hg(OAc)_2}} \mathrm{CH_3(H)C{=}C(HgOAc)C(CH_3)_2OCH_3} + \mathrm{CH_3CH(OCH_3)C(HgOAc){=}C(CH_3)_2} \quad (8)$$

10, 72% **11**, 18%

was assigned the *trans* configuration from the values of Hg^{199} coupling with the vinyl proton (566 Hz) and the allylic methyl protons (40 Hz; see Discussion). Because of the large number of lines in the spectra of the mixtures and the possibility of contamination with minor products (*e.g.*, *cis*-**10**), iododemercuration[6] was again employed to verify mercury-proton coupling assignments.

Tetramethylallene (2,4-dimethyl-2,3-pentadiene) gave the expected single monoadduct, 3-acetoxymercuri-4-methoxy-2,4-dimethyl-2-pentene (**12a**), in 90% yield (eq 9). In the nmr spectrum of the corresponding



$$\mathrm{(CH_3)_2C{=}C{=}C(CH_3)_2} \xrightarrow[\mathrm{CH_3OH}]{\mathrm{Hg(OAc)_2}} \mathrm{(CH_3)_2C{=}C(HgOAc)C(CH_3)_2OCH_3} \quad (9)$$

12a, 90%

chloromercuri derivative **12b**, the aliphatic methyl groups appeared as a singlet at τ 8.63 with 9-Hz coupling to Hg^{199}, and the allylic methyl groups at τ 8.10 ($J_{Hg^{199}-H^1}$ = 24 Hz) and τ 8.00 ($J_{Hg^{199}-H^1}$ = 38 Hz). The methoxyl singlet appeared at τ 6.78. The lines assigned to Hg^{199}–H^1 coupling again vanished after iododemercuration.

Since we have observed that tetramethylallene undergoes particularly facile acid-catalyzed isomerization to a conjugated diene (a trace of iodine, for example, initiates a violently exothermic reaction), this compound was chosen for an exploratory investigation of the reversibility of allene oxymercuration under acidic conditions. The usual deoxymercuration procedure[7a] did result in extensive isomerization, but it was found that this difficulty could be easily avoided by using a two-phase system. When a concentrated benzene solution of **12b** was treated with one drop of 6 *N* aqueous hydrochloric acid in a standard nmr tube, pure tetramethylallene (identified by reconversion to **12a**) was quantitatively regenerated within a few minutes.

It had also been observed in the course of this work that the reaction of all of the allenes with methanolic mercuric acetate was extremely fast. The fact that tetraalkyl substitution is known to decrease the rate of oxymercuration of ordinary olefins[6] therefore appeared to make tetramethylallene a promising candidate for a single experiment on the relative methoxymercuration rates of allenes *vs.* alkenes. This was carried out by mixing equal volumes of 0.050 *M* methanol solutions of mercuric acetate and tetramethylallene or tetramethylethylene in a standard nmr tube and following the disappearance of the single nmr line of each hydrocarbon. At a probe temperature of 43°, the half-life of tetramethylethylene was 40 min, while the allene reacted completely (*i.e.*, to at least five half-lives) in the shortest measurement time permitted by the technique (*ca.* 5 sec). If it is assumed that the tetramethylallene reaction was complete before the initial temperature of the solution (20°) could increase significantly, a calculated minimum rate difference in excess of 10^4 is obtained. The precipitation of mercuric acetate from methanol solution at lower temperatures precluded any attempt to obtain an actual rate ratio by this technique.

Discussion

The results of methoxymercuration of allene and its five methyl-substituted derivatives are summarized in Figure 2. The correct stereochemistry is shown for the 1,3-dimethylallene and major trimethylallene additions. Yields indicated are those actually obtained (unnormalized), based on $Hg(OAc)_2$.

A number of conclusions can be stated immediately upon inspection of Figure 2, not the least of which is that the title reaction is remarkably well behaved, considering the complications which have beset much related work.[2,3,6,8] Before arriving at an entirely self-consistent picture of the directive influence of methyl substituents, however, it is necessary to assume that bisoxymercuration of methylallene results exclusively from initial electrophilic attact at the *unsubstituted* π bond (*via* path A (eq 1), followed by rapid addition to the remaining π bond with the expected path A orientation[11]), whereas initial attack at the methyl-

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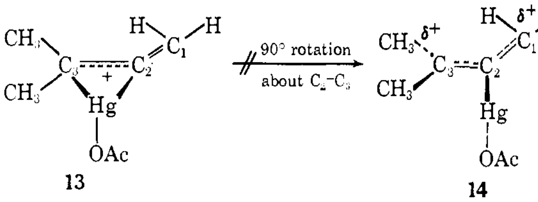
[11] In the present context, reference to eq 1 is not intended to imply a classical carbonium ion mechanism but is continued only to indicate the direction of π-bond polarization and to preserve the analogy with other electrophilic additions.

substituted π bond leads only to monoadduct **5** (*via* path B, eq 1). This assumption is supported strongly by the observation that oxymercuration of 1,3-dimethylallene proceeds only to monoadduct *via* path B,[12] and that of allene only to bis adduct *via* path A. The polarization of both mono- and dimethyl-substituted π bonds is then that shown in path B, with only unsubstituted π bonds reacting *via* path A.[11]

Examination of the results obtained with the unsymmetrical allenes reveals (after correction of the methylallene yields for stoichiometry) that each substitution of methyl for hydrogen activates an allenic π bond by a factor of about four. This behavior contrasts with that of simple 1,1-disubstituted olefins, for which oxymercuration rates generally decrease with further alkyl substitution.[7b,13] It seems probable that both steric and electronic factors contribute to this reversal (see below).

The mutual independence of the orthogonal allenic π bonds throughout oxymercuration, implied in the above discussion, finds its most striking illustration in the behavior of 1,1-dimethylallene. From all that is known about the relative stabilities of oxymercurials[6] and of allylic isomers in general,[14] it can be assumed that compound **8** is the less stable of the two possible path B monoadducts **8** and **9** (eq 7). However, not only is **8** found to be the sole product of oxymercuration in methanol, but the orientation remains the same when the solvent is changed to the highly hindered *t*-butyl alcohol (Table I), and no equilibration of **8** and **9** could be induced on exposure to conditions under which methoxymercuration is readily reversible. We regard this result as the most direct evidence yet reported for the existence of the proposed[6-8,15] bridged mercurinium ion as a stable intermediate in oxymercuration. Bonding between the mercury atom and the terminal carbon in this intermediate (**13**) must be sufficiently strong to overcome the considerable allylic resonance energy to be gained by 90° C–C bond rotation (eq 10). In case any doubts remain (based on possible kinetic arguments[2]), the clean reversibility of this reaction to give back the allene clearly requires that **13** have lower energy than **14**.



(10)

Although the nature of the bonding in the mercurinium ion (*e.g.*, **13**) cannot be stated with certainty, there is good evidence that considerable rehybridization of C_2 and C_3 has occurred, so that the mercury bridge is more correctly represented as a three-membered ring rather than as a simple polarized π complex. It is difficult to explain the preferential formation of *trans*-oxymercuration products **7** and **10** (in which the mercury atom has entered *cis* to the bulkier methyl group on the remaining π bond) without accepting the following conclusions: (a) the mercurinium ion is formed reversibly, prior to the rate-limiting step,[7] and is not subject to important steric control; (b) opening of the mercurinium ion by solvent is both rate and product determining and is stereospecifically *trans*;[6-8] (c) the rate of the latter step is remarkably sensitive to steric influence of substituents on the opposite end of the allenic system, implying that the central carbon atom has acquired a good deal of trigonal character. The steric relationships shown in Figure 3 illustrate this point. It can be seen that the substituent R_4 is in an excellent position to exert the observed stereochemical control in intermediate **15**, but seems highly unlikely to have such a pronounced effect in the linear π complex **16**. The formation of an appreciable amount of *cis* isomer from 1,3-dimethylallene and none from trimethylallene can be interpreted as evidence that alkyl substituents R_1 and R_2 also contribute significantly to steric shielding of the back side of **15**; this conclusion is much more obvious when appropriate molecular models are examined. The failure of bulkier solvents to bring about a reversal of π-bond reactivity in 1,1-dimethylallene (Table I) is not surprising when it is suggested that the R_4 substituent exerts an equal or greater steric effect on the product-determining step than do the R_1, R_2 substituents, since R_4 = H in this case.

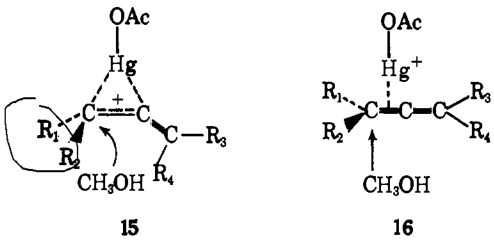


Figure 3. Relative steric hindrance to back-side solvent approach in σ-bonded (**15**) *vs.* π-bonded (**16**) mercurinium ions. When $R_1 = R_2 = CH_3$, the *trans*-olefinic product **10** ($R_3 = CH_3$; R_4 = H) is formed exclusively; when $R_1 = CH_3$ and R_2 = H (and *vice versa*), *trans* product **7** ($R_3 = CH_3$; R_4 = H) predominates over *cis* product **6** (R_3 = H; $R_4 = CH_3$) by 4:1.

Conclusions a and b above, which are prerequisite to c, are consistent with the generally accepted[5,7b] mechanism of oxymercuration[6,8a] and deoxymercuration[7a] proposed for monoalkenes, and are further supported by the results of more recent work with optically active 1,3-dimethylallene of known absolute configuration.[16]

If there is anything to be gained by comparison of our oxymercuration results with those of Jacobs and Johnson[2] and Griesbaum, *et al.*,[3] for hydrohalogenation of allenes, it can be summarized in the statement that mercury and hydrogen occupy opposite ends of what might be called the neighboring group scale. The high yields, orderly substituent effects on stoichiometry, rate, and orientation, and clean reversibility observed in mercuric acetate addition all point to a highly stabilized intermediate which is able to choose consistently the lowest energy path to kinetically controlled products. In contrast, proton addition to allenes displays the classic behavior expected for rate-limiting formation of a highly energetic intermediate, a vinyl or nonplanar allylic carbonium ion (eq 1), which then undergoes

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(12) *Cf.* also ref 5.

(13) W. L. Waters and E. F. Kiefer, unpublished observations.

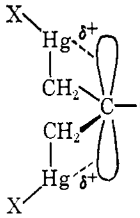
(14) R. H. DeWolfe and W. G. Young, *Chem. Rev.*, **56**, 753 (1956).

(15) H. J. Lucas, F. R. Hepner, and S. Winstein, *J. Am. Chem. Soc.*, **61**, 3102 (1939).

(16) M. C. Caserio and W. L. Waters, results to be published.

rapid solvolysis,[2,3] elimination,[2] and/or alkylation[3] with relatively little discrimination.

It is worth noting that the physical properties of compound **3** and its halo derivatives suggest a considerable degree of mercurinium ion character (*e.g.*, **17**) for



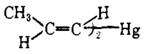
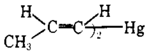
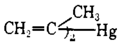
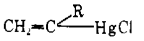
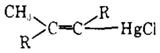
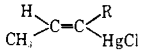
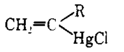
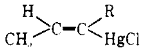
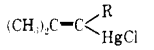
17

this species even in the ground state. The solubility behavior (see above section) is reminiscent of that of zwitterions and, more significantly, the infrared carbonyl stretching frequency indicates a degree of single-bond character which cannot be accounted for by an inductive effect alone. 1,3-Bis(iodomercuri)acetone, for example, absorbs at 1600 cm^{-1} (KBr) whereas the sodium salt of tropolone, which can have a maximum C=O bond order of 1.5, displays carbonyl absorption at 1606 cm^{-1} (KBr).[17] The former value is to our knowledge the lowest ever reported for a nonconjugated carbonyl compound.

Nmr Spectra. The nmr spectra of organomercurials are characterized by the presence of satellites resulting from a sizeable coupling of nearby protons with mercury-199, which has spin $I = {}^1/_2$ and a natural abundance of 16.92%. The dependence of this heteronuclear splitting on molecular structure has been investigated by several groups;[10,18a] particularly useful in the present work are well-established mercury-proton spin-spin coupling assignments for divinylmercury,[19] vinylmercuric acetate,[20] and the isomeric dipropenylmercuries.[21] These data are included in Table II together with the values assigned to *cis*- and *trans*-HgC=CH and -HgC=CCH$_3$ coupling in compounds **5-8**, **10**, and **12**. (Compound **9** was not formed, and **11** was analyzed only as the minor constituent of a mixture; positive identification of the weak Hg^{199} satellites could not be made.)

The data of Table II show a reassuring degree of consistence when the literature values for the dipropenylmercuries[21] are normalized using the proposed[20] linear relationship $J_{\text{RHgX}} = 2.2J_{\text{R}_2\text{Hg}}$. A very similar ligand effect has been noted for vinylthallium and vinyltin compounds.[19] The relationship $|J_{trans}| > |J_{cis}|$ for nuclei directly attached to a π bond has also been noted to hold for coupling of protons with thallium and tin[19] and with fluorine,[18b] as well as with other protons.[18c] The relationship $|J_{cis}| > |J_{trans}|$ observed here for coupling of the type HgC=CCH$_3$ has analogy in homonuclear allylic H-H and F-F coupling, though the reverse is true for H-F coupling.[18b,c]

Table II. Heteronuclear Coupling Constants in Alkenylmercury Compounds

Compound	J(HgC=CH) *cis*	J(HgC=CH) *trans*	J(HgC=CCH$_3$) *cis*	J(HgC=CCH$_3$) *trans*
(CH$_2$=CH)$_2$Hg	159.6	295.5	...	...
CH$_2$=CHHgOAc	291	658	...	...
	140 (308)[a]	...	...	5 (11)[a]
	...	244 (537)[a]	12 (26)[a]	...
	127.8 (281)[a]	256.5 (564)[a]	...	...
 **5**	290[b]	565[b]	...	...
 **6**	318[b]	...	...	25
 **7**	...	523[b]	38	...
 **8**	315[b]	620[b]	...	...
 **10**	...	566[b]	40	...
 **12**	...	...	38	24

[a] Calculated value for RHgX from J(RHgX) = 2.2J(R$_2$Hg).[20]
[b] Measured from the recorded spectra calibrated with external standards; probably accurate to better than ±2 Hz.

Weak long-range coupling of mercury-199 with aliphatic β-methyl protons was observed in compounds **8**, **10**, and **12** ($J_{\text{Hg-C-C(CH}_3)_2} = 5\text{-}9$ Hz) but not in compounds **5-7** ($J_{\text{Hg-C-CH-CH}_3} \sim 0$). This finding agrees with those reported earlier[10,22] for oxymercuration products of monoalkenes, *e.g.*, isobutylene ($J_{\text{Hg-C-C(CH}_3)_2} = 22$ Hz) and propylene ($J_{\text{Hg-C-CH-CH}_3} \sim 0$). Long-range Hg^{199}-H^1 coupling also occurs through the carbonyl group in **3** ($J_{\text{Hg-C-CO-CH}_2} = 20$ Hz). Each methylene group in this compound is thus coupled to two mercury atoms ($J_{\text{Hg-CH}_2} = 338$ Hz), reducing the center band intensity to $(1 - 0.17)^2 = 69\%$ of that expected relative to the unsplit acetoxy-mercuri line. The expected integrated area ratio is then (0.69)(2):3 = 1.38:3 (found: 1.4:3).

Experimental Section

General. Microanalyses were performed by Berkeley Analytical Laboratory, Berkeley, Calif. Melting points were determined in sealed capillaries and are uncorrected. Nmr spectra were determined with a Varian Associates A-60 spectrometer at a probe temperature of 42 ± 1°, usually employing concentrations of approximately 25% in order to detect mercury-199 satellites. Chemical shifts are reported relative to internal tetramethylsilane, generally with approximately 2% benzene as internal standard. Nmr line positions were measured from the recorded spectra and calibrated with external standards where this appeared desirable, *e.g.*, for large mercury-proton coupling constants. Infrared spectra were determined for KBr disks, using a Beckman IR-5 spec-

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[17] Y. Ikegami, value quoted in Y. Yukawa, "Handbook of Organic Structural Analysis," W. A. Benjamin, Inc., New York, N. Y., 1965, p 340.

[18] *Cf.* J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press Inc., Oxford, England, 1966: (a) pp 687-690, 1097-1100, for leading references; (b) pp 909-913; (c) pp 710-740.

[19] D. W. Moore and J. A. Happe, *J. Phys. Chem.*, **65**, 224 (1961).

[20] P. R. Wells, W. Kitching, and R. F. Henzell, *Tetrahedron Letters*, 1029 (1964).

[21] D. Moy, M. Emerson, and J. D. Oliver, *Inorg. Chem.*, **2**, 1261 (1963).

[22] S. Brownstein, *Discussions Faraday Soc.*, **34**, 25 (1962).

trometer. Analytical and preparative vpc employed Wilkins Aerograph Models 90P-3 and 700 gas chromatographs, respectively. Spectroscopic data on new compounds prepared are included in the Results and Discussion sections.

Materials. Allene was obtained from Matheson Company, Inc., and was found to be >99% pure by vpc and nmr. Methylallene (practical grade) was obtained from Columbia Organic Chemicals, Inc., and found to contain 30% 2-butyne and 1,3-butadiene as specified by the suppliers. After separation by preparative vpc (20 ft × $^3/_8$ in. column of 25% dimethylsulfolane on 60–80 mesh Chromosorb P, 40°, 150 cc/min helium flow rate), it showed no detectable impurities. 1,3-Dimethylallene was prepared from *trans*-2-butene by the method of Doering, *et al.*[23] A product containing no detectable impurities was obtained by preparative vpc (20 ft × $^3/_8$ in. column of 20% silicone SE-30 on 60–80 mesh Firebrick) from a distillation fraction of bp 35–50°. 1,1-Dimethylallene was prepared from 3-methyl-1-butyn-3-ol by the procedure of Bailey and Pfeifer,[24] bp 39.0–40.5°, and contained approximately 6% of several impurities (mostly 2-methyl-2-butene) by vpc. Trimethylallene was prepared from 2-methyl-2-butene by the Doering–La Flamme–Hoffmann procedure[23] and contained small amounts of tetrahydrofuran (solvent) and isooctane (distillation chaser) as contaminants. Tetramethylallene was obtained from Aldrich Chemical Co. and showed no detectable impurities by vpc and nmr. Anhydrous methanol and mercuric acetate, reagent grade, were used without further purification.

Methoxymercuration of Allene. Preparation of 1,3-bis(acetoxymercuri)-2-propanone (**3**) was most conveniently carried out by passing gaseous allene slowly through a magnetically stirred solution of mercuric acetate (1.60 g, 0.005 mole) and water (eight drops) in 25 ml of methanol until a negative mercuric ion test was obtained. In this test, which was used routinely to check for completeness of oxymercuration, a drop of the reaction mixture is added to a few milligrams of powdered sodium carbonate on a watch glass; yellow mercuric oxide forms rapidly if any mercury is present as the free salt. Some oxymercurials are decomposed slowly to produce a faint yellow coloration after standing for several seconds.

Compound **3** separated as a dense white precipitate during addition; after filtration and thorough washing with methanol, a pure product was obtained, mp 176.6–177.5° dec. Evaporation of the filtrate produced an additional quantity of **3**; total yield 1.37 g (95.2%).

Anal. Calcd for $C_7H_{10}O_5Hg_2$: C, 14.61; H, 1.75. Found: C, 14.63, 14.63; H, 1.78, 1.90.

Compound **3**, like the majority of other oxymercuration products below, was converted to the chloromercuri-, bromomercuri-, and iodomercuri derivatives by treatment with an approximate threefold excess of dilute aqueous potassium halide. The heavy insoluble halomercuri derivatives were formed quantitatively. All three decomposed without melting well above 200°, and were characterized by their infrared spectra (see Discussion). Treatment of 0.1459 g (2.05 mmoles) of 1,3-bis(iodomercuri)-2-propanone with 0.1120 g (4.40 mg-atoms) of iodine in 25 ml of benzene for 2 hr yielded, after decantation from red HgI_2 and evaporation of the solvent, 0.0560 g (88%) of 1,3-diiodo-2-propanone, mp 65–66° after vacuum sublimation (lit.[25] 65–66°). The infrared spectrum was identical with that of authentic 1,3-diiodoacetone prepared by treatment of 1,3-dichloroacetone with aqueous potassium iodide, and a mixture melting point was not depressed.

The reaction of allene with methanolic mercuric acetate was carried out under a wide variety of conditions, with qualitatively similar results; two significant examples are described in the Results section.

Methoxymercuration of Methyl-Substituted Allenes. General Procedure. All reactions were carried out on a 0.1–1-g scale. The neat liquid allene was added to an equimolar (or slightly smaller) quantity of mercuric acetate dissolved in 25 ml of methanol at room temperature, with magnetic stirring. After 5 min, 1 equiv of powdered sodium carbonate was added to neutralize liberated acetic acid and assure completion of the equilibrium reaction, and the mixture was filtered if necessary. After evaporation of the methanol at reduced pressure and room temperature, the oily product was extracted from residual sodium acetate with a small amount of benzene. The benzene was then flash evaporated and the residual product analyzed by nmr. Purification was accomplished after treatment with aqueous potassium chloride as described above. The solid chloromercuri derivatives usually crystallized readily from 60–80% aqueous ethanol or from hexane. Where necessary, nmr assignments were confirmed by further conversion to a bromomercuri derivative which showed slightly larger Hg–H coupling constants, or to an iodomercuri derivative, in which the mercury satellites were too broad to be observed.[10] Iododemercuration of the latter as described above removed all heteronuclear coupling and provided a final spectral verification.

In all preliminary runs, excess mercuric acetate was present in order to explore the over-all reaction stoichiometry. Subsequently, mercuric acetate was made the limiting reagent to allow precise determination of monoadduct yields from the volatile allenes.

Methylallene (0.14 g, 2.5 mmoles) was added to 0.80 g (2.5 mmoles) of mercuric acetate in methanol. A white solid soon began to separate; the mixture was stirred for 24 hr to assure completion of precipitation. After filtration of the solid, the solution was worked up as described above to give 0.52 g (60%) of 2-acetoxymercuri-3-methoxy-1-butene (**5a**) which was identified by infrared and nmr spectroscopy after conversion to the chloromercuri derivative **5b** (mp 122–123°). The combined solid product above (more was deposited during the work-up) was washed with cold methanol and treated directly with aqueous potassium chloride. The resulting compound was insoluble in all common solvents and decomposed without melting above 200°, so its purity could not be readily determined. It was assigned the structure 1,3-bis(chloromercuri)-2-butanone (**4b**) on the basis of infrared (ν_{max} 1616 cm^{-1}; compound **3b** ν_{max} 1616 cm^{-1}) and microanalytical data which, though somewhat high on carbon, indicated the presence of two mercury atoms per allene unit.

Anal. Calcd for $C_4H_6OCl_2Hg_2$: C, 8.88; H, 1.12. Found: C, 9.34, 9.42; H, 1.11, 1.14.

Iododemercuration of **4b** with iodine in benzene produced a soluble compound, the nmr spectrum of which was entirely consistent with the structure 1,3-diiodo-2-butanone. The total yield of **4a** was 35%, based on mercuric acetate.

1,3-Dimethylallene was oxymercurated on the same scale as methylallene to produce 0.832 g (93%) of an oily mixture of two benzene-soluble monoadducts in a ratio of 4:1, as determined by nmr. Treatment with aqueous potassium chloride gave a solid which could be enriched in the major component by repeated recrystallization from hexane, allowing separate nmr assignments for both compounds to be made (see Table II). The major product was assigned the structure *trans*-3-chloromercuri-4-methoxy-2-pentene (**7b**, mp 88–90° after further recrystallization), and the minor component that of the *cis* isomer (**6b**, not isolated).

1,1-Dimethylallene (0.2085 g, 3.06 mmoles) was allowed to react with 0.7877 g (2.47 mmoles) of mercuric acetate in methanol to produce 0.748 g (84% yield) of 2-acetoxymercuri-3-methoxy-3-methyl-1-butene (**8**). Since no other benzene-soluble products were detected, the relatively low yield may be the result of mechanical losses, but it is also possible that a small amount of benzene-insoluble bisadduct analogous to **3** and **4** was formed which failed to precipitate from the original methanolic reaction medium. The structure of **8** was verified from nmr spectra of the chloromercuri derivative (Figure 1) and the iododemercuration product, and by microanalysis of the bromomercuri derivative, mp 90–92°.

Anal. Calcd for $C_6H_{11}OBrHg$: C, 18.98; H, 2.92. Found: C, 19.19, 19.33; H, 2.84, 3.00.

Oxymercuration of 1,1-dimethylallene in isopropyl alcohol and in *t*-butyl alcohol produced oily products, the nmr spectra of which indicated in both cases the presence of three different monoadducts with structures analogous to **8**. Iododemercuration of the mixtures as described above resulted in simplified spectra without significantly affecting product ratios, which were determined (Table I) by integration of the sharp singlets arising from the *gem*-dimethyl group in each compound. The alcoholysis products could be identified by integration of the alkoxide lines in each case; the hydroxy and acetoxy compounds were separately prepared and characterized by reaction of 1,1-dimethylallene with mercuric acetate in aqueous 2-propanol and in benzene, respectively.

Trimethylallene yielded with equimolar mercuric acetate (2.5 mmoles) in methanol a mixture of monoadducts (0.84 g, 90%) which could not be readily separated. Hexane was unsuitable for crystallization of the low-melting halomercuri derivatives, and recrystallization from aqueous ethanol resulted only in slight enrichment of the minor component. Advantage was taken of the latter observation, however, to allow individual nmr assignments for the two compounds which were thus identified as *trans*-3-acetoxymercuri-4-methoxy-4-methyl-2-pentene (**10**) and 3-acetoxy-

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[23] (a) W. von E. Doering and P. M. La Flamme, *Tetrahedron*, **2**, 75 (1958); (b) W. von E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.*, **76**, 6162 (1954).

[24] W. J. Bailey and C. R. Pfeifer, *J. Org. Chem.*, **20**, 95 (1955).

[25] O. Volker, *Ann.*, **192**, 95 (1878).

mercuri-4-methoxy-2-methyl-2-pentene (**11**), formed in a 4:1 ratio. No nmr lines which might be assignable to the *cis* isomer of **10** could be observed.

Tetramethylallene (3.3 mmoles) on reaction with 2.6 mmoles of mercuric acetate produced a single compound, readily identifiable by nmr as 3-acetoxymercuri-4-methoxy-2,4-dimethyl-2-pentene (**12a**, 90% yield). Microanalysis of the bromomercuri derivative, mp 94–95°, confirmed the monoadduct structure.

Anal. Calcd for $C_8H_{15}OBrHg$: C, 22.57; H, 3.71. Found: C, 23.55, 23.68; H, 3.58, 3.72.

The Reaction of Diazonium Salts with Nucleophiles. XII. Equilibria, Rates, and Mechanisms in the Acidification of *anti*-Diazotates[1]

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Abstract: The existence and basicity of *anti*-diazotates is confirmed by concordant pH and kinetic measurements. The ionization of the conjugate acids (the position of protonation is unknown) fits the Hammett equation, $pK_a = 7.3 - 1.45\sigma$, in adequate agreement with much earlier work, but in sharp diagreement with one recent paper. These conjugate acids (*anti*-$ArN_2O^- \cdot H^+$) are intermediates in the quantitative conversion of *anti*-diazotates to the diazonium salts. The rate is given by the expression $d(ArN_2^+)/dt = k_1(ArN_2O^- \cdot H^+) + k_2(ArN_2O^- \cdot H^+)(H^+)$. The rate constant k_2 fits the Hammett equation roughly with a large negative ρ, but k_1 shows a distinct minimum in the Hammett plot; this observation suggests a mechanistic complexity, and two mechanisms for the unimolecular term are proposed. Ultraviolet maxima and extinction coefficients of diazonium salts and diazotates are reported, which are useful in estimating purities.

One of the oldest continuing controversies of organic chemistry is concerned with the structures of the substances present when diazonium salt solutions are made alkaline. The existence of stereoisomeric diazotates and their conjugate acids has been a subject of dispute since this isomerism was first proposed by Hantzsch in 1894.[2] More recent publications (in chronological order) have confirmed the Hantzsch scheme,[3] and have questioned the existence of the ionized *anti*-diazotate in water solution,[4] and have questioned the existence of the *syn*-diazotate.[5] Furthermore the rate of reaction of diazonium ion with hydroxide ion has been reported to be fast and reversible[3,6–8] and also to be slow.[5] The further structural problems in the nature of intermediate stages of protonation or hydroxide ion addition leading to the terms "diazohydroxides,"[9] "diazoanhydrides,"[10] and "nitrosamines,"[11] have not been yet entirely resolved, largely because of the mobility of the proton in the first and last, as explained by Zollinger.[12]

It is our opinion that the questions regarding the existence of the two diazotates are not well founded, but there does seem a need to resolve the problems posed by the apparently conflicting experimental results. This paper represents a study of several *anti*-diazotates and the equilibria and rates involved in their acidification. We shall not touch upon the question of the existence of the *syn*-diazotates raised by Porai-Koshits[5] except to note the ultraviolet absorption characterization of *syn*-diazotates reported by Lewis and Suhr[7] and their report of rapid equilibration (in good agreement with that of Wittwer and Zollinger[6]) seems unequivocal evidence of the presence of this isomer in solution, even though the characterization of the solids is unconvincing. The recent low-temperature preparation of solid *syn*-diazotates by Müller and co-workers[13] remove some of the remaining elements of doubt.

Results and Discussion

Several years ago, we presented evidence based upon ultraviolet absorption for the existence of four separate species in solutions of diazonium salts at various pH's.[3] These were: I, the diazonium ion, the only stable species at low pH; II, the *syn*-diazotate, present transiently on adding diazonium salts to high pH solution; III, the *anti*-diazotate, the rearrangement product of the *syn*-diazotate, and the stable species at high pH; and IV, the conjugate acid of III, formed transiently by acidifying III and slowly (and in poor yield) by adding diazonium salt to solutions of intermediate pH. The position of the equilibrium III + $H^+ \rightleftarrows$ IV was sharply questioned by LeFevre, Roper, and Reece,[4] who suggested that IV (or an isomer) was not extensively ionized even in fairly concentrated alkali solutions. While the isolation of clearly metal-containing salts from aqueous solutions

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(1) From the Ph.D. Thesis of Milton P. Hanson, Rice University, 1964.

(2) A. Hantzsch, *Ber.*, **27**, 1702 (1894).

(3) E. S. Lewis and H. Suhr, *J. Am. Chem. Soc.*, **80**, 1367 (1958).

(4) R. J. W. LeFevre, R. Roper, and I. H. Reece, *J. Chem. Soc.*, 4104 (1959); R. J. W. LeFevre and R. Roper, *ibid.*, 1875 (1963).

(5) B. A. Porai-Koshits, *Tetrahedron*, **11**, 30 (1960); B. A. Porai-Koshits and K. T. Ching, *Tr. Leningr. Tekhnol. Inst. im. Lensoveta*, **60**, 92, 103, 111 (1960).

(6) C. Wittwer and H. Zollinger, *Helv. Chim. Acta*, **37**, 1954 (1954).

(7) E. S. Lewis and H. Suhr, *Chem. Ber.*, **91**, 2350 (1958).

(8) J. S. Littler, *Trans. Faraday Soc.*, **59**, 2296 (1963).

(9) A. Hantzsch, *Ber.*, **31**, 340 (1898), and many others.

(10) E. Bamberger, *ibid.*, **29**, 446 (1896); **53**, 2314 (1920).

(11) E. Bamberger, *ibid.*, **27**, 679 (1894), and many others since.

(12) H. Zollinger, "Azo and Diazo Chemistry," Interscience Publishers, Inc., New York, N. Y., 1961, p 58.

(13) E. Müller, W. Rundel, H. Haiss, and H. Hagenmaier, *Z. Naturforsch.*, **15b**, 751 (1960).