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THE METHOXYMERCURATION OF SOME STYRENE DERIVATIVES

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Summary

Product analyses have been carried out and reaction rates and activation parameters determined for the methoxymercuration of some styrene derivatives and related compounds in methanol. The behaviour of α- and β-alkyl substituted styrenes generally parallels that of the similarly substituted vinylferrocenes. The anomalous reactivity of β,β-dimethylstyrene is suggested to arise from the structural features of this compound. The reaction of the stilbenes was found to be stereospecific. The results are consistent with an unsymmetrically bridged structure for the cationic intermediate possibly involving varying degrees of bridging depending on substrate.

Introduction

The methoxymercuration of alkenes has been studied extensively, but the mechanism is still not well understood, especially not in connection with the nature of the cationic intermediate. The subject has been recently reviewed by Ambidge et al. [1]. Evidence has been presented in support of a free carbonium ion [2,3] as well as of symmetrically [4,5] or unsymmetrically bridged [6] mercurinium ion for the structure of the intermediate.

Recently we reported results on the methoxymercuration of some vinylferrocenes [7] which are consistent with the hypothesis of a bridged species as an intermediate. However, some problems remained unsolved, especially with respect to the competition between the addition to the double bond and substitution in the aromatic ring. One of these was to ascertain the role of the ferrocenyl group in the observed effects of alkyl group substitution. For this reason we now report on the product analysis and the reaction kinetics for a number of styrenes as the phenyl analogues of the previously investigated vinylferrocenes, and for such related structures as allylbenzene and the stilbenes.

Results and discussion

The reaction of the substrates with mercuric acetate was carried out in methanol at concentrations of 5×10^{-2}—4×10^{-1} *M* for the product analyses and 1×10^{-5}—1×10^{-2} *M* for the rate measurements.

Product analyses show that addition to the olefinic linkage usually involves attack of electrophilic mercury exclusively at the carbon atom β to the phenyl group. However, in the case of *trans*-β-methylstyrene both orientations of addition were observed (see Experimental). Unlike alkylvinylferrocenes, where ring substitution competes with addition for some members of the investigated series, the similarly substituted styrene derivatives do not undergo any substitution at the benzene ring. This finding is in complete agreement with expectation, since the benzene ring is far less reactive than the Cp rings of ferrocene [7—9].

The reaction of the styrenes is first order in each reagent. The rate constants at 25°C are listed in Table 1, together with related data for alkylvinylferrocenes. There is a general similarity between the two series. In particular, an α-methyl group is moderately activating, whereas an α-*t*-butyl group is markedly deactivating. Also, the β-methyl and the β,β-dimethyl derivatives are both markedly deactivated. The observed analogies show that the steric requirements of the reaction are a major factor in determining the effects of alkyl substituents in both series and to a great extent at the β-position. The general reactivity pattern is therefore essentially independent of whether the unsaturated chain is linked to a ferrocenyl or to a phenyl group.

That the low reactivity of the β-methyl substituted substrates is caused by the large steric requirements of the mercurating reagent is confirmed by comparison with related data for other electrophilic reagents such as bromine, hydronium, etc., as reported in Table 2.

The literature data contained in Table 2 are of interest also in connection with several other points (vide infra). One of these concerns the effect of the α-methyl group, which is rate enhancing for the hydronium reagent (k_{rel} 550),

TABLE 1

SECOND-ORDER RATE CONSTANTS FOR THE METHOXYMERCURATION OF SOME STYRENES AND STILBENES IN METHANOL AT 25°C; COMPARISON WITH THE VINYLFERROCENE SYSTEM

Compound	k_2 (M^{-1} s^{-1})	k_{rel}	Compound	k_2 (M^{-1} s^{-1})	k_{rel}
Styrene	10.4 [a]	1	Vinylferrocene	230 [a]	1
α-Methylstyrene	24.0	2.1	α-Methylvinylferrocene	910 [a]	4.0
α-t-Butylstyrene	0.074	7.1×10^{-3}	α-t-Butylvinylferrocene	<0.024 [b]	$<1 \times 10^{-4}$
trans-β-Methylstyrene	0.020	1.9×10^{-3}	*trans*-β-Methylvinylferrocene	0.67	2.9×10^{-3}
cis-β-Methylstyrene	0.025	2.4×10^{-3}	β,β-Dimethylvinylferrocene	<0.026 [b]	$<1 \times 10^{-4}$
β,β-Dimethylstyrene	0.16	1.5×10^{-2}			
trans-Stilbene	1.6×10^{-4}	1.5×10^{-5}			
cis-Stilbene	2.9×10^{-4}	2.8×10^{-5}			
Allylbenzene	4.3 [c]	0.4			

[a] Ref. 7. [b] Upper limit given by 10% of the ring substitution rate coefficients [7]. [c] [$PhCH_2CH=CH_2$] 4.78×10^{-3} *M*, [$Hg(OAc)_2$] 9.2×10^{-4} *M*.

TABLE 2

SECOND-ORDER AND RELATIVE RATE CONSTANTS FOR SOME ELECTROPHILIC ADDITIONS TO THE STYRENE SYSTEM

Substrate	$HgOAc_2$ in MeOH at 25°C		Br_2 in AcOH at 25°C [10]		Br_2 in MeOH at 25°C [12]		Hydration in H_2SO_4 at 25°C [14]	
	k_2 (M^{-1} s^{-1})	k_{rel}	k_2 (M^{-1} s^{-1})	k_{rel}	k_2 (M^{-1} s^{-1})	k_{rel}	k_2 (M^{-1} s^{-1})	k_{rel}
$PhCH=CH_2$	10.4	1	11.2	1	1.53×10^{3}	1	2.4×10^{-7}	1
$PhC(CH_3)=CH_2$	24.0	2.1	680	61	1.38×10^{5}	90	1.33×10^{-4}	550
trans-$PhCH=CHCH_3$	0.020	1.9×10^{-3}	12.3	1.1	3.23×10^{3}	2.1	1.12×10^{-7}	0.47
cis-$PhCH=CHCH_3$	0.025	2.4×10^{-3}	8.9	0.8	—	—	—	—
$PhCH=C(CH_3)_2$	0.16	1.5×10^{-2}	14.7	1.3	—	—	—	—
trans-PhCH=CHPh	1.6×10^{-4}	1.5×10^{-5}	0.3 [11]	0.03	0.545 [13]	3.6×10^{-4}	7.1×10^{-11}	3×10^{-4}
cis-PhCH=CHPh	2.9×10^{-4}	2.8×10^{-5}	—	—	—	—	—	—

Substrate	2,4-Dinitrobenzenediazonium borofluoride in CH_3CN at 25°C [15]		NOCl in $CHCl_3$ at 0°C [16]		CH_3CO_3H in AcOH at 25.8°C [17]		ArSCl in TCE at 25°C [18]	
	k_2 (M^{-1} s^{-1})	k_{rel}	k_2 (M^{-1} s^{-1})	k_{rel}	k_2 (M^{-1} s^{-1})	k_{rel}	k_2 (M^{-1} s^{-1})	k_{rel}
$PhCH=CH_2$	2.33×10^{-4}	1	6.5×10^{-4}	1	1.9×10^{-4}	1	62.0	1
$PhC(CH_3)=CH_2$	1.42×10^{-2}	61	1.7×10^{-3}	2.6	—	—	265.0	4.3
trans-$PhCH=CHCH_3$	3.26×10^{-4}	1.4	2.6×10^{-3}	4	7.7×10^{-4}	4	118.3	1.9
cis-$PhCH=CHCH_3$	6.3×10^{-5}	0.3	—	—	—	—	43.0	0.69
$PhCH=C(CH_3)_2$	6.3×10^{-4}	2.7	—	—	—	—	26.0	0.42
trans-PhCH=CHPh	4.7×10^{-5}	0.2	2.9×10^{-4}	0.45	8.5×10^{-5}	0.45	—	—
cis-PhCH=CHPh	9.0×10^{-6}	0.04	6.4×10^{-5}	0.1	1.85×10^{-4}	0.97	—	—

less so for some of the other reagents, and only slightly rate enhancing for the ArSCl reagent (k_{rel} 4.3). These values may be taken as indicative for the nature of the intermediate cation, the highest degree of bridging (symmetrical) being attributed to the reactions characterized by low k_{rel} values. However, in the case of methoxymercuration (k_{rel} 2.1) no clear indication can be gained from the α-methyl effect because of the obscuring influence of steric hindrance, which tends to lower the k_{rel} value. Therefore, it is likely that for this reaction the intermediate cation is less symmetrically bridged than would appear from the α-methyl effect.

In the ferrocene series the reactivity order β-methyl > β,β-dimethyl reflects the expected order of the rate-depressing steric effect. However, the opposite order is observed in the styrene series and is probably due to the anomalous behavior of β,β-dimethylstyrene. PMR data [19] and ring current calculations [20] for this compound indicate that the double bond of the side-chain is not coplanar with the benzene ring, thus preventing maximum resonance stabilization in the conjugated system, $PhCH{=}CMe_2$. This seems to be reflected in the UV spectrum where the band at λ_{max} 245 nm of styrene suffers from a marked drop in intensity in going from the parent compound (ϵ, 15×10^3 [21]) and the *trans*-β-methyl derivative (ϵ, 16×10^3 [21]) to the β,β-dimethyl derivative (ϵ, 8.5×10^3 [21]). Such a change does not occur with the related band at λ_{max} 276 nm of vinylferrocene, whose intensity is essentially the same for the *trans*-β-methyl derivative (ϵ, 7.8×10^3) and for the β,β-dimethyl derivative (ϵ, 7.4×10^3). We suggest that a high degree of conjugation is maintained in the latter compound because the steric requirements of the 5-membered Cp ring are less severe than those of the phenyl group, other conditions being equal, and because the ferrocenyl group has a much greater electron-releasing capacity than the phenyl group [22].

A relatively high reactivity of β,β-dimethylstyrene can be found in other additions such as those involving bromine or the 2,4-dinitrobenzenediazonium ion as reagents (Table 2). In contrast, a relatively low reactivity in the addition with 4-chlorobenzenesulfenyl chloride has been observed by Schmid and Garratt [18]. Rolston and Yates [10] noted that there is no simple relationship between the number of methyl groups and the rate of bromine addition to styrene derivatives. Probably several factors contribute to the overall behavior of methyl-substituted styrenes including the molecular structure of the substrate, the steric and polar effects of the methyl groups as well as the nature of the electrophilic reagent, and play varying roles in the diverse reactions.

The loss of stability in the ground state is thought to be responsible for the anomalously high reaction rate of β,β-dimethylstyrene. The role of ground state stabilization by conjugation of the benzene ring with an unsaturated side chain has been recognized by Brown et al. [23] in recent years. That the observed anomalous reactivity is to be ascribed to the β,β-dimethyl rather than to the β-methyl styrene derivative seems to be further confirmed by a comparison of reactivity levels within the series PhCH=CHR, where the expected order H > Me > CHO ~ CO_2Et is observed, the lowest reaction rates being the result of a combination of steric and electronic effects (*trans*-PhCH=CHCHO, $k_2 = 5.0 \times 10^{-4}\ M^{-1}\ s^{-1}$; *trans*-PhCH=$CHCO_2Et$, $k_2 = 1.95 \times 10^{-4}\ M^{-1}\ s^{-1}$, reaction with $Hg(OAc)_2$ in MeOH at 25°C [24]). The contribution of the electronic

effect of the R group in the β position is presumably not very strong, as is apparent from the slight effect of the β-methyl group when reagents of more limited requirements are used (see Table 2).

The appearance of two orientations in the addition to *trans*-β-methylstyrene finds a reasonable explanation in the low reactivity of this compound. The *cis* isomer also shows relatively low reactivity, but only one orientation corresponding to β-attack. After allowance for the isomeric composition of the product from *trans*-β-methylstyrene, the k_{cis}/k_{trans} ratio turns out to be 2.0, i.e., somewhat lower than the values reported for related reactions, which range between 3 and 10 [25—27]. Some out of plane rotation of the phenyl group caused by some Ph/CH_3 repulsion may hinder α-attack as compared to the *trans* isomer. It is of interest to note that the *trans* isomer is more stable than the *cis* by about 2.8 kcal/mol [28], but that this ground state stability difference is reflected in the k_{cis}/k_{trans} value only to a minor extent.

The least reactive substrates among the investigated compounds are the *cis*- and *trans*-stilbenes. This must be the result of a combination of conjugative and steric effects, which are both expected to be rate depressing. The steric effect of a phenyl group in hydroxymercuration has been found by Brown et al. [23] to be similar to that of an isopropyl group, and should be substantially greater than that produced by a methyl group. This is apparently one of the factors driving the attack to the β-position of β-methylstyrene away from the phenyl group. Conjugative stabilization of the ground state is greater than for styrene derivative because of the presence of a second phenyl group. The importance of this effect is supported by the relatively low reactivity of the stilbenes with reagents of smaller steric requirements (Table 2). The k_{cis}/k_{trans} ratio in the stilbene pair is also relatively low, and may again indicate larger steric hindrance of the *cis* isomer toward the reagent relative to the *trans* isomer and the greater importance of this effect in methoxymercuration than in other additions. It is noteworthy that the rate constant for the methoxymercuration of *cis*-stilbene was previously approximately evaluated ($1.61 \times 10^{-4}\ M^{-1}\ s^{-1}$ at 25°C [29]) from an early report by Wright [30] and is in fair agreement with the present data.

The reaction of *cis*- and *trans*-stilbene was found by product analysis to be stereospecific. The PMR spectra of the methoxymercuration products, $PhCH(OCH_3)CH(HgOAc)Ph$, obtained from *trans*- and *cis*-stilbene show similar patterns (see Experimental), but display a significant difference in the coupling constants of the benzyl protons (J 9.0 Hz and 3.8 Hz, respectively). Protons are expected to be coupled more strongly in the *erythro* than in the *threo* structure, with coupling constants in the range of 8.5—13 Hz and 4—6 Hz, respectively [31]. The coupling constants are found to be in good agreement with expectation, and enabled us to assign the *erythro* structure to the product obtained from *trans*-stilbene and the *threo* structure to that obtained from *cis*-stilbene. These results support the hypothesis of a bridged intermediate of some sort. It is noteworthy that PMR spectral differences are not observed in the products of reductive cleavage of the mercurated derivative, with $NaBD_4$, i.e., $PhCH(OCH_3)CHDPh$, probably because of the different stereochemistry of the reduction reaction and/or of the less marked sensitivity to spectral differences.

The reactivity of the sterically unhindered allylbenzene is quite high, though lower than that of styrene. The reaction leads exclusively to one product, 1-ace-

TABLE 3

ACTIVATION PARAMETERS FOR THE METHOXYMERCURATION OF SOME STYRENE AND STILBENES

Compound	E_a (kcal/mol)	$\Delta S^{\neq}$ (e.u.)
$PhCH{=}CH_2$	10.6 ± 0.5 [a]	−20 ± 1.5 [a]
$PhC(CH_3){=}CH_2$	9.2 ± 0.5	−23 ± 1.5
$PhC(t\text{-}Bu){=}CH_2$	11.5 ± 0.5	−27 ± 1.5
$PhCH{=}C(CH_3)_2$	10.3 ± 0.5	−30 ± 1.5
trans-$PhCH{=}CHCH_3$	14.1 ± 0.5	−21 ± 1.5
cis-$PhCH{=}CHCH_3$	15.0 ± 0.5	−17 ± 1.5
trans-PhCH=CHPh	14.1 ± 0.5	−30 ± 1.5
cis-PhCH=CHPh	11.7 ± 0.5	−37 ± 1.5

[a] Ref. 7.

toxymercuri-2-methoxy-3-phenylpropane (see Experimental), thus resembling the bromination reaction [32]. This regioselectivity is compatible with an appreciable carbocation character in both cases, but does not rule out some degree of unsymmetrical bridging.

The rate constants were determined at varying temperatures, as reported in the Experimental section. The activation parameters are shown in Table 3. The values for the *trans*-β-methylstyrene do not seem to be invalidated by the isomeric composition of the reaction product, which was found to be essentially independent of temperature.

The $\Delta S^{\neq}$ values are strongly negative as expected for a rate-limiting bimolecular mechanism. A mechanism involving a bridged cation should lead to extensive desolvation in the transition state and tend to raise the $\Delta S^{\neq}$ value. Whenever steric hindrance is expected to increase, the observed trend for the energy of activation is to increase and for the entropy of activation to become more negative. The latter effect may indicate less bridging interaction and increased carbocation character of the intermediate in some cases. The effects of reduced conjugation of β,β-dimethylstyrene and *cis*-stilbene, as discussed before, may be recognized in the relatively low E_a value for these compounds. The above interpretations can only be qualitative, because of the compensation effects between activation parameters and because of the limited set of data.

Concluding remarks

The steric requirements of methoxymercuration of the unsaturated side chain of styrene derivatives are a major controlling factor for the reactivity of these substrates. Except for the effect of β,β-dimethyl substitution, the behavior of the styrenes essentially parallels that of substituted vinylferrocenes.

The stereospecificity of the reaction as observed with the stilbenes is consistent with the idea that the addition involves a bridged intermediate of some sort. Stereospecificity via a non-bridged intermediate mechanism as suggested by Dubois et al. [12] is probably unlikely for a mercuration reaction [33]. In our case the intermediate may still retain an appreciable carbocation character, as suggested by the generally exclusive Markownikoff orientation. These data and

the activation parameters suggest that varying degrees of bridging interactions are possible.

Experimental

Materials

α-Methylstyrene, allylbenzene, *cis*- and *trans*-stilbene were commercially available reagents of analytical grade and were used without further purification. The remaining alkenes were based on modified procedures of earlier reports.

trans-β-Methylstyrene was obtained in a 71% yield by isomerization of allylbenzene with 20% KOH in butanol at reflux [34] (b.p. 60—65°C at 20 mmHg). The alkene resulted to be essentially the *trans* isomer (97% at least) on the basis of PMR and VPC analyses.

cis-β-Methylstyrene was prepared by catalytic hydrogenation of 1-phenylpropyne with 10% $Pd/BaSO_4$ at 1 atm and room temperature, until the equivalent amount of hydrogen was consumed (b.p. 68°C at 25 mmHg; yield 61%). VPC analysis showed the *cis* isomer to be more than 97% of the total amount. 1-Phenylpropyne was obtained in a 62% yield by treating phenylacetylene with CH_3MgI and dimethylsulfate (b.p. 83—85°C at 24 mmHg) [35].

α-t-Butylstyrene was prepared by shaking 2-phenyl-3,3-dimethyl-2-butanol with a freshly prepared solution of 20% v/v sulphuric acid in acetic acid [36] (b.p. 100°C at 25 mmHg; yield 47%). 2-Phenyl-3,3-dimethyl-2-butanol was obtained by treating pivalophenone with a large excess of methyllithium in anhydrous diethyl ether (b.p. 118°C at 30 mmHg; yield 60%). (Methylmagnesium iodide was found to be ineffective as a methylating reagent.) Pivalophenone was prepared according to the literature [37], by adding phenylmagnesium bromide [38] to pivaloyl chloride in anhydrous diethyl ether at —6 to —10°C (b.p. 107—108°C at 20 mmHg; yield 50%).

The preparation of β,β-dimethylstyrene gave some problems, since dehydration of 1-phenyl-2-methyl-1-propanol with KOH [39] gave polymerization products and dehydration with oxalic acid [40] gave low yields. Dehydration with concentrated sulfuric acid [41] proved to be the best method (yield 67%). 1-Phenyl-2-methyl-1-propanol was prepared in a 90% yield by reducing phenyl isopropyl ketone with $LiAlH_4$ and phenyl isopropyl ketone was obtained by acylation of benzene with isobutyrylchloride and $AlCl_3$ (yield 70%) [42].

Product analysis

This was usually carried out by treating the alkenes with equimolar amounts of mercuric acetate in methanol and isolating and identifying the products. The stilbenes were treated with a large excess of the mercurating reagent.

The analyses were confirmed by reductive cleavage of the C—Hg bond with $NaBH_4$ in basic aqueous solutions [43].

α-Methylstyrene. $Hg(OAc)_2$ (10.0 g, 0.031 mol) in 70 ml of methanol was added dropwise during ca. 45 min to a stirred solution of α-methylstyrene (3.7 g, 0.031 mol) in 10 ml of methanol. After stirring overnight, the mixture was poured into water and extracted repeatedly with CH_2Cl_2. The organic layer was washed with water, dried, and evaporated, to yield a viscous oil, which crystal-

lized to give 7.8 g (0.019 mol) of a white solid. This solid decomposed on standing to release mercury (yield 62%).

The PMR spectrum in $CDCl_3$ is in accord with the formulation 1-acetoxymercuri-2-methoxy-2-phenylpropane $PhC(CH_3)(OCH_3)CH_2HgOAc$: δ 7.35 ppm, 5 H, singlet due to the aromatic protons; δ 3.15 ppm, 3 H, singlet due to the OCH_3 protons; δ 2.3 ppm, 2 H, singlet due to the methylene protons; δ 2.0 ppm, 3 H, singlet due to the $HgOCOCH_3$ protons; and δ 1.7 ppm, 3 H, singlet due to the α-methyl protons.

To confirm the above structure, $NaBH_4$ (0.27 g, 7.0×10^{-3} mol) in 25 ml of 2 *N* NaOH was added dropwise to a stirred, ice-cooled suspension of the mercurated product (5.8 g, 1.4×10^{-2} mol) in 50 ml of methanol and 25 ml of 1 *N* NaOH, causing an immediate precipitation of a grey powder. After stirring overnight, the mixture was poured into CCl_4 and water was added. The organic layer was separated and the aqueous phase was extracted with several portions of CCl_4. The combined organic layers were washed with water, dried over anhydrous sodium sulfate and evaporated. The colorless liquid obtained was found to be pure to VPC analysis and its PMR spectrum in CCl_4 is in agreement with the formulation 2-phenyl-2-methoxypropane: δ 7.2 ppm, 5 H, complex signal due to the aromatic protons; δ 2.95 ppm, 3 H, singlet due to the OCH_3 protons; δ 1.45 ppm, 6 H, singlet due to the methyl protons.

α-t-Butylstyrene. $Hg(OAc)_2$ (4.2 g, 1.3×10^{-2} mol) in 130 ml of methanol was added dropwise to a stirred solution of α-*t*-butylstyrene (1.6 g, 9.9×10^{-3} mol) in 20 ml of the same solvent. The mixture was stirred overnight, filtered, poured into water, and extracted with CH_2Cl_2. After separation of the organic layer, washing with water, drying over anhydrous sodium sulfate, and evaporation of the solvent, a viscous oil was obtained, and this crystallized to give a yellow-white solid, m.p. 80—82°C.

The PMR spectrum in $CDCl_3$ shows the following signals: δ 7.25 ppm, 5 H, complex signal, aromatic protons; δ 3.3 ppm, 3 H, singlet, OCH_3 protons; δ 1.85 ppm, singlet, 2 H, CH_2Hg protons; δ 1.75 ppm, 3 H, singlet, $HgOCOCH_3$ protons; and δ 0.9—1.5 ppm, 9 H, complex signal due to the protons of the *t*-butyl group. This spectrum is in accord with the formulation 1-acetoxymercuri-2-methoxy-2-phenyl-3,3-dimethylbutane, $CH_3C(CH_3)_2C(OCH_3)$-$(Ph)CH_2HgOAc$.

The mercurated product (1.4 g, 3.1×10^{-3} mol) was treated with an aqueous basic solution of $NaBH_4$ (0.08 g, 2.1×10^{-3} mol) and the mixture was worked up as previously described. The PMR spectrum in CCl_4 corresponds to that expected for 2-phenyl-2-methoxy-3,3-dimethyl butane, $CH_3C(OCH_3)(Ph)C$-$(CH_3)_2CH_3$, except for the 12 protons in the region of aliphatic protons (δ 0.95 ppm and δ 1.35 ppm), which are not in the 3/1 ratio as expected for a *t*-butyl and a methyl group. However, VPC analysis confirms that there is a single product and ^{13}C NMR and mass spectrum are in complete agreement with the assigned structure.

β,β-Dimethylstyrene. $Hg(OAc)_2$ (4.9 g, 1.54×10^{-2} mol) in 160 ml of methanol was added dropwise to a stirred solution of β,β-dimethylstyrene (2.0 g, 1.5×10^{-2} mol) in 40 ml of methanol. The mixture was stirred overnight and worked up as described above. A viscous white oil was obtained (6 g; yield 93%). On the basis of the PMR spectrum in $CDCl_3$ the formulation 1-phenyl-1-meth-

oxy-2-acetoxymercuri-2-methylpropane, $PhCH(OCH_3)C(CH_3)_2HgOAc$ was assigned: δ 7.1 ppm, singlet, 5 H, aromatic protons; δ 3.55 ppm, singlet, 1 H, PhCH proton; δ 3.2 ppm, singlet, 3 H, OCH_3 protons; δ 1.8 ppm, singlet, 3 H, $HgOCOCH_3$ protons; and δ 1.15 ppm, doublet, 6 H, methyl protons. The mercurated product was reduced with basic aqueous $NaBH_4$ as previously described. 1-Phenyl-1-methoxy-2-methylpropane was obtained, as confirmed by the PMR spectrum in CCl_4: δ 7.1 ppm, singlet, 5 H, aromatic protons; δ 3.2 ppm, singlet, 3 H, OCH_3 protons; δ 2.75 ppm, doublet, 1 H, PhCH proton; δ 0.5—1.5 ppm, 7 H, complex signal due to the superposition of the multiplet of $CH(CH_3)_2$ and the methyl groups.

trans-β-Methylstyrene. $Hg(OAc)_2$ (5.8 g, 1.8×10^{-2} mol) in 200 ml of methanol was added dropwise to a stirred solution of *trans*-β-methylstyrene (2.1 g, 1.8×10^{-2} mol) in 40 ml of methanol. The reaction was carried on until VPC analysis showed the complete disappearance of the alkene. A viscous oil was obtained after usual work up. The PMR spectrum in CCl_4 showed the existence of two products, the following signals being particularly significant: two signals in the aromatic region (δ 7.2 ppm), two signals due to the OCH_3 protons (δ 3.15 and 3.25 ppm) and two doublets in the aliphatic region. ^{13}C NMR spectrum in $CDCl_3$ with TMS as an internal standard is in complete agreement with two products, i.e., 2-acetoxymercuri-1-phenyl-1-methoxypropane, $PhCH(OCH_3)CH(HgOAc)CH_3$ and 1-acetoxymercuri-1-phenyl-2-methoxypropane, $PhCH(HgOAc)CH(OCH_3)CH_3$, especially important being the presence of two signals due to the quaternary phenyl carbon at 141.78 ppm and 140.32 ppm.

Reductive cleavage on this mercurated mixture (4.0 g, 1.0×10^{-2} mol) with 0.23 g of $NaBH_4$ (6.0×10^{-3} mol) in aqueous basic solution and subsequent extraction with CCl_4 yielded a colorless liquid, the PMR spectrum of which was consistent with a mixture of 1-phenyl-1-methoxypropane and 1-phenyl-2-methoxypropane. VPC analysis also confirmed the existence of two products with ca. 60/40 ratio.

cis-β-Methylstyrene. $Hg(OAc)_2$ (3.2 g, 1.0×10^{-2} mol) in 200 ml of methanol containing 0.1% acetic acid was added to a stirred solution of *cis*-β-methylstyrene (1.2 g, 1.0×10^{-2} mol) in 20 ml of methanol. After 48 h, the reaction mixture was treated as described above, yielding 2.8 g (6.9×10^{-3} mol; yield 69%) of mercurated product, as a sticky white material.

The PMR spectrum in $CDCl_3$ is in agreement with a single addition product of structure $PhCH(OCH_3)CH(CH_3)HgOAc$, showing the following signals: δ 7.2 ppm, 5 H, signal due to aromatic protons; δ 3.4 ppm, 3 H, singlet, due to the OCH_3 protons; δ 3.2—3.9 ppm, 2 H, complex signal due to CHCH protons; δ 1.95 ppm, 3 H, singlet, $HgOCOCH_3$ protons; δ 1.18 ppm, doublet (*J* 6 Hz), methyl protons. The ^{13}C NMR spectrum in $CDCl_3$ confirms the existence of only one addition product.

Reductive cleavage with $NaBH_4$ yielded a colorless liquid, the spectrum of which exhibits signals in agreement with the formula $PhCH(OCH_3)CH_2CH_3$: δ 7.2—7.0 ppm, complex signal, 5 H, aromatic protons; δ 3.2—3.4 ppm, triplet, 1 H, benzyl proton; δ 3.25 ppm, 3 H, singlet, OCH_3 protons; δ 1.6—0.8 ppm, complex signal, 5 H, due to the ethyl group protons.

Allylbenzene. Mercuric acetate (15 g, 4.7×10^{-2} mol) in 200 ml of methanol was added to a stirred solution of allylbenzene (2.5 g, 2.1×10^{-2} mol) in 50 ml

of the same solvent. The mixture was stirred until TLC analysis revealed that no more alkene remained. After filtration, evaporation to concentrated solution, pouring into water, and extraction with CH_2Cl_2, a very viscous oil was obtained (3.4 g, 8.3×10^{-3} mol; yield 42%), the PMR spectrum of which in $CDCl_3$ is in agreement with the Markownikoff addition product, $PhCH_2CH(OCH_3)CH_2HgOAc$, without rearrangement (δ 7.2 ppm, 5 H, singlet, due to aromatic protons; δ 3.75 ppm, 1 H, multiplet, due to the CH proton; δ 3.3 ppm, 3 H, singlet due to the OCH_3 protons; δ 2.5—3.2 ppm, 2 H, multiplet due to the CH_2Hg protons; δ 1.9 ppm, 5 H, signal due to the superposition of the $HgOCOCH_3$ singlet and the $PhCH_2$ doublet.

Reductive cleavage was performed with 3.4 g (8.5×10^{-3} mol) of mercurated product and 200 mg (5.3×10^{-3} mol) of $NaBH_4$ in aqueous basic solution. After extraction with CCl_4 and the usual work up, a pale yellow liquid was obtained (1.2 g, 8.0×10^{-3} mol; yield 96%). The PMR spectrum is as expected for 1-phenyl-2-methoxypropane: δ 7.15 ppm, 5 H, singlet, due to aromatic protons; δ 3.4 ppm, 1 H, multiplet, CH; δ 3.25 ppm, singlet, 3 H, OCH_3 protons; δ 2.4—2.9 ppm, 2 H, multiplet due to benzyl protons; δ 1.1 ppm, 3 H, doublet due to the CH_3 protons. This spectrum and VPC analysis enable us to assign the structure 1-phenyl-2-methoxypropane to the less abundant isomer obtained from *trans*-β-methylstyrene methoxymercuration.

trans-Stilbene. Mercuration of *trans*-stilbene was performed in methanol with 0.1% acetic acid, using a large excess of the mercuric acetate (20.0 g, 6.28×10^{-2} mol) with respect to the alkene (1.0 g, 5.56×10^{-3} mol), since the ratio 1/1 was found not to be satisfactory. After 48 h the mixture was worked up as described above and yielded 2.5 g of a white-yellow solid (5.32×10^{-3} mol; yield 95.5%), m.p. 82—84°C.

The PMR spectrum in $CDCl_3$ exhibits the following signals: δ 7.18—7.00 ppm, 10 H, aromatic protons; two doublets centered at δ 4.64 and 4.10 ppm, 2 H (J = 9.0 Hz) due to the benzyl protons; δ 3.15 ppm, singlet, OCH_3; δ 1.93 ppm, 3 H, singlet, $HgOCOCH_3$.

The reaction with $NaBH_4$ quantitatively yielded $PhCH(OCH_3)CH_2Ph$, as white crystals (m.p. 28—29°C). The structure of the product was confirmed by the PMR spectrum in CCl_4: δ 6.9—7.3 ppm, complex signal, aromatic protons; δ 4.10 ppm, 1 H, triplet (*J* 6 Hz), due to CH; δ 2.81 ppm, 2 H, doublet (*J* 6 Hz), CH_2 protons; δ 3.08 ppm, 3 H, singlet, OCH_3.

The reductive cleavage was also performed with $NaBD_4$. The PMR spectrum shows the following signals: δ 6.9—7.2 ppm, 10 H, complex signal, aromatic protons; two doublets centered at δ 4.2 ppm and δ 3.2 ppm, 2 H (*J* 6 Hz), benzyl protons; δ 3.10 ppm, 3 H, singlet, OCH_3.

cis-Stilbene. A large excess of mercuric acetate (20 g, 6.28×10^{-2} mol) was made to react 48 h with *cis*-stilbene (1.0 g, 5.56×10^{-3} mol) in methanol with 0.1% acetic acid.

After the usual work-up a white material was obtained (2.6 g, 99% yield), the PMR spectrum of which in $CDCl_3$ is as follows: δ 7.18—7.04 ppm, 10 H, aromatic protons; two doublets centered at δ 4.59 and 3.58 ppm, 2 H, *J* 3.8 Hz, due to the benzyl protons; δ 3.20 ppm, 3 H, singlet, OCH_3; δ 1.85 ppm, 3 H, singlet, $HgOCOCH_3$.

Reductive cleavage both with $NaBH_4$ and $NaBD_4$ yielded products with the same PMR spectra as those obtained from mercurated *trans*-stilbene.

Kinetic measurements

The determination of the reaction rates was carried out spectrophotometrically in silica cells, provided with a septum for the faster reactions, in a thermostatted Beckman DB-GT self-recording spectrophotometer, with zero suppression and expansion scale, depending on the overall spectral change. The reaction was followed by the absorbance decrease due to the disappearance of the double bond signal: at 250 nm with α-methyl-, β,β-dimethyl-, *trans*-, and *cis*-β-methylstyrene; at 262 nm with α-*t*-butylstyrene; at 290 nm with *cis*-stilbene, and at 306 nm with *trans*-stilbene.

Pseudo-first order conditions were ensured by keeping the mercuric acetate concentration at least 10 times as high as that of the alkenes. With α-*t*-butylstyrene in some case it was the alkene concentration which was kept higher than that of mercuric acetate. With *cis*-β-methylstyrene the reaction starts after a few minutes and thereafter follows pseudo-first order kinetics.

The $Hg(OAc)_2$ concentration was checked by titration with 0.103 *N* KSCN. Stock solutions of mercuric acetate were prepared with methanol containing 0.2% v/v acetic acid, which turned out to be sufficient to avoid the decomposition of mercuric acetate which is normally observed in methanol [44].

The second-order rate constants reported in Table 1 are mean values from several runs carried out with substrate and mercuric acetate concentrations in the following ranges: $PhC(CH_3)=CH_2$: 1.95×10^{-5}—1.27×10^{-4} *M*, $Hg(OAc)_2$: 3.62×10^{-4}—2.27×10^{-3} *M*; $PhC(t\text{-}Bu)=CH_2$: 1.03×10^{-3}—1.03×10^{-2} *M*, $Hg(OAc)_2$: 4.55×10^{-4}—1.54×10^{-3} *M*; $PhCH=C(CH_3)_2$: 2.82×10^{-5}—1.34×10^{-4} *M*, $Hg(OAc)_2$: 1.12×10^{-3}—2.97×10^{-3} *M*; *trans*-$PhCH=CHCH_3$: 2.69×10^{-5}—5.99×10^{-5} *M*, $Hg(OAc)_2$: 1.17×10^{-3}—2.94×10^{-3} *M*; *cis*-$PhCH=CHCH_3$: 3.30×10^{-5}—1.06×10^{-4} *M*, $Hg(OAc)_2$: 1.37×10^{-3}—5.14×10^{-3} *M*; *trans*-PhCH=CHPh: 1.20×10^{-5}—4.00×10^{-5} *M*, $Hg(OAc)_2$: 3.11×10^{-2}—1.19×10^{-1} *M*; *cis*-PhCH=CHPh: 4.48×10^{-5}—1.34×10^{-4} *M*, $Hg(OAc)_2$: 6.53×10^{-3}—1.54×10^{-1} *M*.

Activation parameters. The rate measurements at various temperatures were duplicated. Good Arrhenius plots were obtained in all cases. The related data, in addition to the rate coefficients in Table 1, are as follows (temperatures given in parentheses).

[$PhC(CH_3)=CH_2$] 5.64×10^{-5} *M*, [$Hg(OAc)_2$] 2.27×10^{-3} *M*; $k_2(M^{-1}\ s^{-1})$: 15.5 (16.2°C), 18.5 (20.3°C), 21.0 (22.4°C), 22.4 (24.2°C), 25.0 (26.2°C), 30.2 (30.3°C).

[$PhC(t\text{-}Bu)=CH_2$] 1.03×10^{-3} *M*, [$Hg(OAc)_2$] 1.54×10^{-2} *M*; $k_2(M^{-1}\ s^{-1})$: 0.105 (30.5°C), 0.133 (34.2°C), 0.209 (40.0°C), 0.250 (44.6°C).

[$PhCH=C(CH_3)_2$] 6.05×10^{-5} *M*, [$Hg(OAc)_2$] 2.49×10^{-3} *M*; $k_2(M^{-1}\ s^{-1})$: 0.198 (30.3°C), 0.248 (34.2°C), 0.337 (40.0°C), 0.450 (44.2°C).

[*trans*-$PhCH=CHCH_3$] 7.05×10^{-5} *M*, [$Hg(OAc)_2$] 2.49×10^{-3} *M*; $k_2(M^{-1}\ s^{-1})$: 0.0276 (30.5°C), 0.044 (34.3°C), 0.056 (40.2°C), 0.074 (44.0°C). Product analysis carried out at these temperatures showed the same isomeric composition as at 25°C, within experimental errors, i.e., 60 ± 2% of the product from β-attack and 40 ± 2% of the product from α-attack.

[*cis*-$PhCH=CHCH_3$] 8.80×10^{-5} *M*, [$Hg(OAc)_2$] 2.28×10^{-3} *M*; $k_2(M^{-1}\ s^{-1})$: 0.0187 (22.5°C), 0.0262 (26.4°C), 0.0398 (30.8°C), 0.0677 (35.7°C), 0.0789 (39.9°C), 0.0846 (44.6°C).

[*trans*-PhCH=CHPh] 2.50×10^{-5} *M*, [$Hg(OAc)_2$] 1.09×10^{-1} *M*; $k_2(M^{-1}\ s^{-1})$: 1.24×10^{-4} (21.7°C), 2.79×10^{-4} (30.2°C), 4.07×10^{-4} (35.1°C), 8.47×10^{-4} (45.2°C).

[*cis*-PhCH=CHPh] 8.96×10^{-5} *M*, [$Hg(OAc)_2$] 9.79×10^{-2} *M*; $k_2(M^{-1}\ s^{-1})$: 2.10×10^{-4} (21.3°C), 4.31×10^{-4} (30.6°C), 6.09×10^{-4} (35.6°C), 8.31×10^{-4} (40.0°C), 1.17×10^{-3} (45.2°C).

The activation parameters as calculated from the above data are reported in Table 3.

References

1 I.C. Ambidge, S.K. Dwight, C.M. Rynard, and T.T. Tidwell, Can. J. Chem., 55 (1977) 3086.
2 H.C. Brown and J.H. Kawakami, J. Amer. Chem. Soc., 95 (1973) 8665.
3 S. Bentham, P. Chamberlain, and G.H. Whitham, J. Chem. Soc. D, (1970) 1528.
4 W.L. Waters, W.S. Linn, and M.C. Caserio, J. Amer. Chem. Soc., 90 (1968) 6741.
5 D.J. Pasto and J.A. Gontarz, J. Amer. Chem. Soc., 92 (1970) 7480; ibid., 93 (1971) 6902, 6909.
6 H.J. Bergmann, G. Collin, G. Just, G. Müller-Hagen, and W. Pritzkow, J. Prakt. Chem., 314 (1972) 285.
7 B. Floris and G. Illuminati, J. Organometal. Chem., 168 (1979) 203.
8 G. Cerichelli, B. Floris, G. Illuminati, and G. Ortaggi, 39 (1974) 3948.
9 B. Floris and G. Illuminati, J. Organometal. Chem., 150 (1978) 101.
10 J.H. Rolston and K. Yates, J. Amer. Chem. Soc., 91 (1969) 1483.
11 I. Ting and P.W. Robertson, J. Chem. Soc., (1947) 628.
12 M.F. Ruasse, A. Argile, and J.E. Dubois, J. Amer. Chem. Soc., 100 (1978) 7645.
13 M.F. Ruasse and J.E. Dubois, J. Org. Chem., 37 (1972) 1770.
14 W.K. Chwang, V.J. Nowlan, and T.T. Tidwell, J. Amer. Chem. Soc., 99 (1977) 7233.
15 H. Marxmeimer and E. Pfeil, Chem. Ber., 97 (1964) 815.
16 T. Beier, H.G. Hauthal, and W. Pritzkow, J. Prakt. Chem., 26 (1964) 304.
17 J. Böeseken and J. Stuurman, Rec. Trav. Chim. Pays Bas, 56 (1937) 1034.
18 G.H. Schmid and D.G. Garratt, Can. J. Chem., 52 (1974) 1807.
19 H. Rottendorf, S. Sternhell, and J.R. Wilmshurst, Aust. J. Chem., 18 (1965) 1759.
20 N. Inamoto, S. Masuda, Y. Nagai, and O. Simamura, J. Chem. Soc., (1963) 1433.
21 Organic Electronic Spectral Data 3 (1966); 4 (1963) Interscience, New York.
22 G. Cerichelli, B. Floris, G. Illuminati, and G. Ortaggi, Gazz. Chim. Ital., 103 (1973) 911.
23 H.C. Brown and P.J. Geoghegan jr., J. Org. Chem., 37 (1972) 1937.
24 A.K. Chaudhuri, K.L. Mallik, and M.N. Das, Tetrahedron, 19 (1963) 1981.
25 J. Halpern and H.B. Tinker, J. Amer. Chem. Soc., 89 (1967) 6427.
26 F. Asinger, B. Fell, G. Hadik, and G. Steffan, Chem. Ber., 97 (1964) 1568.
27 M.H. Thomas and F.E.W. Wetmore, J. Amer. Chem. Soc., 63 (1941) 136.
28 G.H. Schmid, V.M. Csizmadia, V.J. Nowlan, and D.G. Garratt, Can. J. Chem., 50 (1972) 2457.
29 R. Bolton, in C.H. Bamford and C.F.H. Tipper (Eds), Comprehensive Chemical Kinetics, Vol. 9, Elsevier, Amsterdam, 1973.
30 G.F. Wright, J. Amer. Chem. Soc., 57 (1935) 1993.
31 H.B. Koogan (Ed.), Stereochemistry Fundamental and Methods, Vol. 1, Georg Thieme, Stuttgart, 1977.
32 K. Meinel, Justus Liebigs Ann. Chem., 516 (1935) 231.
33 G. Freeman, Chem. Rev., 75 (1975) 441 and ref. therein.
34 T.W. Campbell and W.C. Young, J. Amer. Chem. Soc., 69 (1947) 688.
35 M.J.S. Dewar and R.C. Fahey, J. Amer. Chem. Soc., 85 (1963) 3645.
36 E.W. Garbisch, J. Org. Chem., 26 (1961) 4165.
37 H.J. Ford, C.D. Thompson, and C.S. Marvel, J. Amer. Chem. Soc., 57 (1935) 2619.
38 H. Gilman Ed., Organic Synthesis, Coll. Vol. I, John Wiley, New York, 1932, p. 221.
39 A.J. Vogel, Practical Organic Chemistry Including Qualitative Organic Analysis, 3rd ed., Longmans, London, 1962, p. 1024.
40 M. Tiffeneau, Ann. Chem., 10 (1907) 365.
41 R.S. Sandler and W. Karo, Organic Functional Groups Preparations, Academic Press, New York, 1968.
42 C. Schmidt, Chem. Ber., 22 (1889) 3250.
43 F.G. Bordwell and M.L. Douglass, J. Amer. Chem. Soc., 88 (1966) 993.
44 I.M. Kolthoff and R. Belcher, Volumetric Analysis, Interscience, New York, Vol. 3, 1957.