

Kinetics and Mechanism of Oxymercuration of $\alpha\beta$ -Unsaturated Carbonyl Compounds

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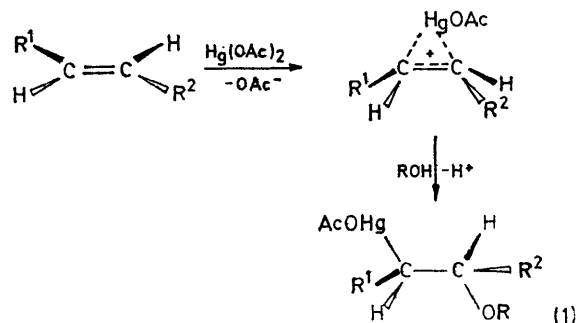
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The products and the kinetics of methoxymercuration of a series of $\alpha\beta$ -unsaturated ketones and esters have been studied. Whereas the methoxymercuration of $\alpha\beta$ -unsaturated esters is stereospecific, the methoxymercuration of the ketones leads to mixtures of diastereoisomers. The configuration of the products has been deduced from their ^1H n.m.r. spectra on the basis of chemical shifts and proton coupling constants. The results are consistent with the formation of a bridged 'mercurinium' ion intermediate. It is suggested that the mixtures of diastereoisomers obtained from the $\alpha\beta$ -unsaturated ketones are the result of equilibria established after the oxymercuration reaction.

THE addition of mercury(II) salts to olefins¹ is of interest both preparatively and mechanistically. In 1935 Wright² postulated that the reaction of mercuric salts with olefins in alcoholic solution occurred *via* a concerted *cis*-addition of an alkoxymercury(II) salt.³ In contrast, Lucas *et al.*⁴ suggested that the reaction involved the formation of an intermediate bridged cation [equation (1)] which was attacked from the rear by the alcohol to give an overall *trans*-addition. Most of the evidence from the reaction of simple unstrained olefins now indicates that a stereospecific *trans*-addition does occur,⁵ though detailed studies have only been carried out in a few cases. Moreover, in those cases for which a *trans*-addition was evident, interconversion between the diastereoisomeric alkoxymercuration products was shown not to occur.⁶

It was originally reported^{3a} that 1,3-diphenylpropene reacted with mercuric acetate in methanol to form a single diastereoisomeric 2-acetoxymercuri-3-methoxy-1,3-diphenylpropanone, as a result of a *cis*-addition of methoxymercuric acetate. However, no definite proof of configuration of the product was presented and the

stereochemistry of the reaction could only have been assumed. Recently, Bloodworth and Bunce⁷ have also studied the methoxymercuration of a number of $\alpha\beta$ -unsaturated carbonyl compounds from a preparative



aspect, but they did not investigate the configuration of the products. Since our initial studies indicated that the reaction of mercury(II) acetate with *trans*-1,3-diphenylpropene in methanol gave a mixture of diastereoisomeric adducts, a more detailed study of this and of related reactions seemed appropriate.

¹ J. Chatt, *Chem. Rev.*, 1951, **48**, 1.

² G. F. Wright, *J. Amer. Chem. Soc.*, 1935, **57**, 1993.

³ (a) A. M. Birk and G. F. Wright, *J. Amer. Chem. Soc.*, 1940, **62**, 2412; (b) J. Romeyn and G. F. Wright, *ibid.*, 1947, **69**, 697; (c) A. G. Brook and G. F. Wright, *Canad. J. Res.*, 1950, **28B**, 623; (d) A. G. Brook, A. Rodgman, and G. F. Wright, *J. Org. Chem.*, 1952, **17**, 988; (e) A. Rodgman and G. F. Wright, *ibid.*, 1953, **18**, 1617.

⁴ H. J. Lucas, R. F. Hepner, and S. Winstein, *J. Amer. Chem. Soc.*, 1939, **61**, 3102.

⁵ W. Kitching, *Organometallic Chem. Rev.*, 1968, **3**, 61.

⁶ G. F. Wright, *Ann. New York Acad. Sci.*, 1957, **65**, 436.

⁷ A. J. Bloodworth and R. J. Bunce, *J. Chem. Soc. (C)*, 1971, 1453.

This paper describes studies of the kinetics and products of reaction of mercury(II) acetate with several *cis*- and *trans*- $\alpha\beta$ -unsaturated ketones (4-XC₆H₄CH:CHCOPh or 4-X-C₆H₄CH:CHCOMe) and esters (4-XC₆H₄CH:CHCO₂Me), and the mechanisms of the addition reaction and of related side reactions are discussed.

RESULTS

Products of Methoxymercuration of $\alpha\beta$ -Unsaturated Ketones.—(a) *1,3-Diarylpropenones.* The crude products of methoxymercuration of three *trans*-(Ar¹ = Ph; Ar² = Ph, 4-NO₂C₆H₄, and 4-MeOC₆H₄) and one *cis*-(Ar¹ = Ar² = Ph) 1,3-diarylpropenones Ar¹COCH:CHAR² with mercury(II) acetate in methanol, with and without the addition of perchloric, nitric, hydrochloric, and acetic acid or their alkali metal salts (10⁻⁴–10⁻³M), were isolated and characterised by ¹H n.m.r. spectroscopy. In all cases the crude product was a mixture of two diastereoisomeric 2-acetoxymercuri-3-aryl-1-phenyl-1-methoxypropanones, the configurations of which are discussed below. In particular, the *same* mixture of diastereoisomers was obtained from the reaction of both

reported for 2-bromomercuri-3-methoxy-1,3-diphenylpropanone.⁷

The chemical shifts and coupling constants for the products are shown in Table 1. Attempts to isolate both pure *R,R*- and *S,R*-diastereoisomers were unsuccessful. In all cases the crude products were sticky semi-solid masses from which only the *S,R*-diastereoisomer could be isolated by recrystallisation from methanol, ethanol, or chloroform. When the remaining mother liquors from the crystallisations were either evaporated under reduced pressure, or poured into water and worked-up by the same procedure as was used for the isolation of the crude reaction mixtures, and analysed by n.m.r., they were shown to contain the same ratio of the corresponding *S,R*- and *R,R*-diastereoisomers as the original mixtures, namely 65–75 : 35–25. No product of destruction of one isomer was detected. Repetition of this operation gave identical results and in consequence the *R,R*-isomers could not be isolated. Moreover, when methanolic solutions of the pure *S,R*-2-acetoxymercuri-3-methoxy-1,3-diphenylpropanone, *S,R*-2-acetoxymercuri-3-methoxy-3-(4-methoxyphenyl)-1-phenylpropanone, or *S,R*-2-acetoxymercuri-3-methoxy-3-(4-nitrophenyl)-1-phenylpropanone, with and without the addition of acetic

TABLE 1

Chemical shifts (τ values) and proton coupling constants (Hz) for *R,R*- and *S,R*-4-XC₆H₄CH(OMe)CH(HgOAc)COY

Y	Ph						Me					
	H ^a		NO ₂ ^a		OMe ^b		H ^a		NO ₂ ^a		OMe ^b	
	<i>R,R</i>	<i>S,R</i>	<i>R,R</i>	<i>S,R</i>	<i>R,R</i>	<i>S,R</i>	<i>R,R</i>	<i>S,R</i>	<i>R,R</i>	<i>S,R</i>	<i>R,R</i>	<i>S,R</i>
α -H ^c	5.25	5.42	5.24	5.38	5.36	5.49	6.05	6.18	6.08	6.12	6.02	6.15
β -H ^c	4.76	4.82	4.64	4.68	4.85	4.92	5.00	5.06	4.84	4.86	5.08	5.12
β -OMe	6.80	6.72	6.75	6.66	6.85	6.75	6.82	6.76	6.74	6.70	6.84	6.80
OAc		8.14		8.08		8.24		8.02		8.12		8.00
$J_{\alpha,\beta}$	9.8	6.8	10.4	7.6	10.0	7.8	9.8	6.5	10.2	8.2	10.0	6.8

^a In CDCl₃ solution. ^b In CCl₄. ^c Doublet. Analysis based on the AB pattern.

cis- and *trans*-1,3-diphenylpropanone. Interruption of the latter reactions and recovery of the unreacted propenone showed that no isomerisation of the reactant had taken place. In all cases studied, the ratio of the two diastereoisomeric products was within the range 65–75 : 35–25, and we ascribed these proportions to the *S,R*- and *R,R*-diastereoisomers,* respectively.

The configurations of each pair of diastereoisomers were assigned on the basis of the coupling constants between the protons attached to the adjacent carbon atoms (α - and β -C). In view of the relatively small conformational preference of mercury⁸ and taking into account the fact that steric repulsion should normally demand that the phenyl and the carbonyl groups be located as far away from each other as possible, it seems reasonable to expect that each diastereoisomer would show preference for that conformation in which these substituents have a *trans*-orientation [(1a and b), equations (2) and (3)]. Further, as the Karplus equation⁹ has been shown to be applicable to cyclohexene methoxymercureals for which maximum coupling constants of ca. 10 Hz were observed for two vicinal axial protons,^{5,10} it seems reasonable to assign the higher value of the coupling constant $J_{\alpha,\beta}$ to the *R,R*- rather than the *S,R*-diastereoisomer. The chemical shifts of these products are consistent with those

acid in the same concentrations as result from the oxymercuration reactions, were allowed to stand for intervals shorter than the reaction period, they were shown to contain mixtures of the corresponding diastereoisomers of the same composition as the original reaction products (*S,R* : *R,R* = 65–75 : 35–25). The characteristics of the *S,R*-diastereoisomer are shown in Table 2.

TABLE 2

Products of methoxymercuration, 4-XC₆H₄CH(OMe)CH-(HgOAc)COY, of $\alpha\beta$ -unsaturated carbonyl compounds

Y	X	Configur- ation	Analysis (%)			M.p. (°C)
			Found	(calc.)	C	
Ph	H	<i>S,R</i>				113–115 (lit., ^{3a} 115)
Ph	NO ₂	<i>S,R</i>	39.7 (39.8)	3.5 (3.8)		121.5–124
Ph	OMe	<i>S,R</i>	43.0 (43.1)	4.0 (3.8)		133–135
Me	H	<i>S,R</i>	36.0 (35.8)	3.6 (3.7)		134–136
Me	NO ₂	<i>S,R</i>	32.4 (32.5)	3.1 (3.2)		142–145
Me	OMe	<i>S,R</i>	35.7 (35.9)	3.7 (3.9)		148–150
OMe	H	<i>R,R</i>				139–141 (lit., ² 142)
OMe	NO ₂	<i>R,R</i>	33.0 (33.2)	3.0 (3.2)		260–265
OMe	OMe	<i>R,R</i>	36.3 (36.6)	3.8 (3.9)		230–234
OMe	OMe	<i>S,R</i>				190–193

* For simplicity only one enantiomer of each pair (*R,R*-*S,S* and *R,S*-*S,R*) will be mentioned.

⁸ E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, 'Conformational Analysis,' Interscience, New York, 1965, p. 442.

⁹ M. Karplus, *J. Chem. Phys.*, 1959, **30**, 11.

¹⁰ M. M. Anderson and P. M. Henry, *Chem. and Ind.*, 1961, **50**, 2053.

(b) 4-Arylbut-3-en-2-ones. Similar methoxymercuration of three *trans*- (Ar = Ph, 4-NO₂C₆H₄, and 4-MeOC₆H₄) and one *cis*- (Ar = Ph) 4-arylbut-3-ene-2-ones, ArCH:CHCOCH₃, gave mixtures of the two diastereoisomeric 4-acetoxymethyl-3-methoxy-4-phenylbutan-2-ones in the proportions 65—75 : 35—25, which we ascribe, in the manner described above, to the *S,R*- and *R,R*-diastereoisomers, respectively. As with the products from the diarylpropenones, only the *S,R*-diastereoisomer could be isolated by crystallisation of the crude product from methanol, ethanol, or chloroform, and the mother liquor remaining was shown by ¹H n.m.r. spectroscopy to contain the original proportions of the two diastereoisomers, namely 65—75 : 35—25. Studies of the unreacted butenones isolated from interrupted methoxymercuration reactions showed that neither *cis*- nor *trans*-4-phenylbut-3-en-2-one underwent isomerisation during the reaction. The ¹H n.m.r. spectra of the reaction products are shown in Table 1, and other characteristics of the *S,R*-diastereoisomer are shown in Table 2.

Products of Methoxymercuration of Methyl Cinnamates.—The crude products of methoxymercuration of three *trans*- (Ar = Ph, 4-NO₂C₆H₄, and 4-MeOC₆H₄) and one *cis*- (Ar = Ph) methyl cinnamates, ArCH:CHCO₂Me, were prepared and examined in the same manner as described above. In each case only one diastereoisomer could be detected, and different single diastereoisomers were obtained from methyl *cis*- and *trans*-cinnamate. From a consideration of the coupling constants in the manner described above, we ascribe the *R,R*-configuration to the product from the *trans*-esters and the *S,R*-configuration to the product from the *cis*-esters. The ¹H n.m.r. spectra of the products are shown in Table 3 and the other characteristics are shown

TABLE 3

¹H N.m.r. spectra (τ values; J /Hz) of the products of methoxymercuration of $\alpha\beta$ -unsaturated esters, 4-XC₆H₄-CH(OMe)CH(HgOAc)CO₂Me

X	H ^a	OMe ^b	NO ₂ ^a
Isomeric olefin	<i>trans</i>	<i>trans</i>	<i>cis</i>
Isomeric adduct	<i>R,R</i>	<i>R,R</i>	<i>S,R</i>
β -H ^c	5.02	5.14	4.98
α -H ^c	6.22	6.30	6.54
β -OMe	6.68	6.78	6.74
OAc	7.98	8.04	8.08
$J_{\alpha,\beta}$	10.2	10.0	9.8

^a In CDCl₃ solution. ^b In CCl₄. ^c Doublet. Analysis based on the AB pattern.

in Table 2. Interconversion of these diastereoisomers could not be effected under conditions more drastic than those in which the methoxymercurationals from the $\alpha\beta$ -unsaturated ketones were readily isomerised.

Kinetics.—The kinetics of methoxymercuration of thirteen *trans*- $\alpha\beta$ -unsaturated ketones and esters in methanol with and without the addition of perchloric, nitric, or hydrochloric acid or their lithium salts, were studied by observation of the decrease in the concentration of mercury(II) acetate during the reaction. The conditions were such that the concentrations of reagents (*ca.* 0.05M) were comparable with those used in the preparative studies. In all cases, good second-order kinetics were observed, according to the rate equation $-d[\text{Hg}(\text{OAc})_2]/dt = k_2[\text{Hg}(\text{OAc})_2][\text{Substrate}]$. The measured second-order rate coefficients are shown in Tables 4 and 5, and in Figures 1 and 2.

TABLE 4

Kinetics^a of reaction of methyl *trans*-cinnamate (0.040M) with mercury(II) acetate (0.048M) in methanol at 30°

Catalyst	Concentration of catalyst (M × 10 ⁵)				
	0	5	10	20	30
None	2.0				
HClO ₄		19	34	66	
HNO ₃			23	43	59
HCl			12	25	34
LiClO ₄			4	5.8	10
LiNO ₃			6	9.5	14
LiCl			1.7	1.3	1.2
None ^b	7.7				
None ^c	5.2				
None ^d	1.7				
None ^e	0.37				

^a Second-order rate coefficient; l mol⁻¹ s⁻¹ × 10⁴. ^b 4-Methoxy-derivative. ^c 4-Methyl derivative. ^d 4-Chloro-derivative. ^e 4-Nitro-derivative.

TABLE 5

Kinetics^a of reaction of 1,3-diphenylpropenone (0.040M) with mercury(II) acetate (0.048M) in methanol at 30°

Catalyst	Concentration of catalyst (M × 10 ⁵)						
	0	5	10	20	30	40	50
None	1.8						
HClO ₄			18	25		51	63
HNO ₃			11		29		48
HCl			67			23	32
LiClO ₄	2				3.6		4.7
LiNO ₃	3			6.5		11	13
LiCl					1.4	1.3	1.1
None ^b	10.6						
None ^c	4.1						
None ^d	1.5						
None ^e	0.4						

^a Second-order rate coefficient; l mol⁻¹ s⁻¹ × 10³. ^b 4-Methoxy-derivative. ^c 4-Methyl derivative. ^d 4-Chloro-derivative. ^e 4-Nitro-derivative (see Experimental section).

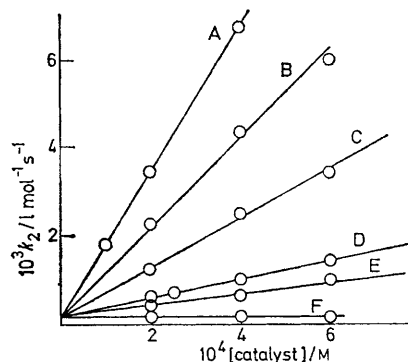


FIGURE 1 Influence of added reagents on the kinetics of reaction of methyl *trans*-cinnamate with mercury(II) acetate in methanol at 30°: A, HClO₄; B, HNO₃; C, HCl; D, LiNO₃; E, LiClO₄; F, LiCl

DISCUSSION

The formation of equilibrium mixtures of the diastereoisomeric methoxymercuration products from the $\alpha\beta$ -unsaturated ketones and their ready interconversion under mild conditions such as those used during the reaction show clearly that these products are thermodynamically controlled and hence are not relevant to the elucidation of the mechanism of the addition reaction.

In contrast, the single diastereoisomer formed from each cinnamic ester is clearly formed by a kinetically controlled *trans*-addition¹¹ consistent with the formation of an intermediate mercurinium ion (IIa or b) which

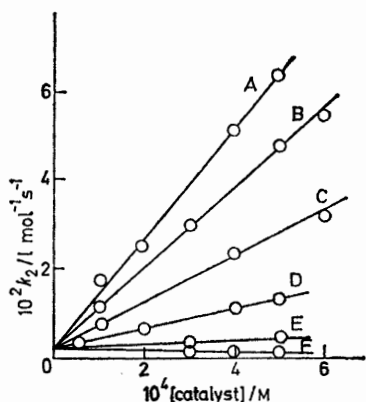
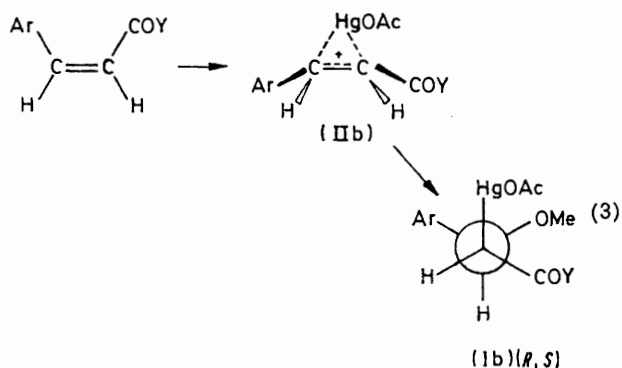
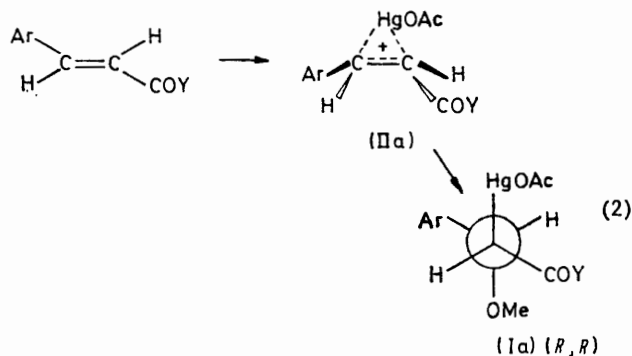


FIGURE 2 Influence of added reagents on the kinetics of reaction of *trans*-1,3-diphenylpropenone with mercury(II) acetate in methanol at 30°: A, HClO₄; B, HNO₃; C, HCl; D, LiNO₃; E, LiClO₄; F, LiCl

retains its configuration up to the time it reacts with the solvent to give the *trans*-addition product [equations (2) and (3)]. An interesting feature of this reaction is that



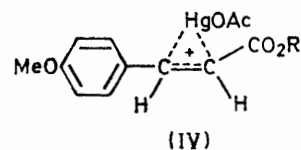
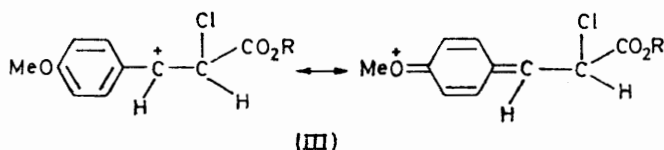
the *trans*-addition of the mercury(II) species and the solvent is total for both 4-nitro- and 4-methoxy-cinnamates, whereas in the electrophilic addition of chlorine to the same esters,¹² the *trans*-addition *via* a chloronium ion

¹¹ T. G. Traylor and A. W. Baker, *J. Amer. Chem. Soc.*, 1963, **85**, 2746.

¹² M. D. Johnson and E. N. Trachtenberg, *J. Chem. Soc. (B)*, 1968, 1912.

was only appreciable in the case of the less reactive 4-nitro-derivative, an open carbonium ion (III) being the intermediate in the case of the 4-methoxy-derivative. This suggests that the mercurinium ion (IV) is appreciably more stable than the corresponding chloronium ion.

The role and stability of the mercurinium ion is also evident in the relatively small influence of the 4-substituent on the rate of the mercuriation reaction. Thus, the rate of the uncatalysed methoxymercuration of methyl *trans*-cinnamate changes by a factor of *ca.* 20 on going from the 4-nitro- to the 4-methoxy-substituent, which is equivalent to a ρ value of *ca.* -0.9 (using the Brown and Okamoto¹³ σ^+ substituent constants). The corresponding electrophilic addition of chlorine to the



cinnamates in acetic acid is much more susceptible to the nature of the 4-substituent, *i.e.* $\rho = -4.01$.¹⁴ This latter, larger value is a result of the ability of the methoxy and other electron-donating groups to accommodate the substantial positive charge which is generated on the β -carbon atom during the formation of the intermediate open cation. Little charge is generated on the β -carbon atom in the formation of a bridged mercurinium ion, and there is less scope for the electron donating-groups to stabilise the intermediate and the transition state leading to that intermediate.

Despite the fact that the methoxymercurations of the $\alpha\beta$ -unsaturated ketones are *ca.* 10 times faster than those of the corresponding esters, the ρ value (*ca.* -0.96) for the former reaction is very similar to that for the latter, and a similar mechanism seems likely. The corresponding electrophilic chlorine addition¹⁴ to the 1,3-diarylpropenones also has a much higher ρ value (-3.66) than the methoxymercuration.

The nature of the acid catalysis and the anion catalysis is more difficult to determine with certainty, but is probably a result of the influence of the several additives on the nature of the mercury(II) species in solution.

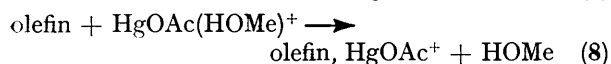
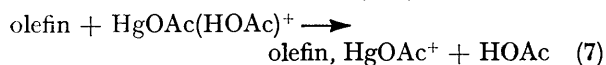
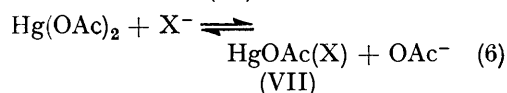
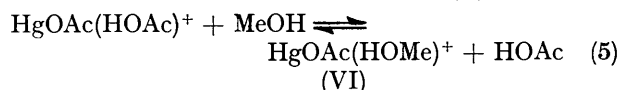
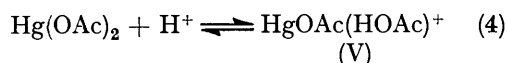
Thus, the addition of anions (as their lithium salts) which do not co-ordinate readily to mercury(II) would be expected to influence the reaction only in so far as they change the activity of the various reagents. However,

¹³ Y. Okamoto and H. C. Brown, *J. Org. Chem.*, 1957, **22**, 485.

¹⁴ H. P. Rothbaum, I. Ting, and P. W. Robertson, *J. Chem. Soc.*, 1948, 980.

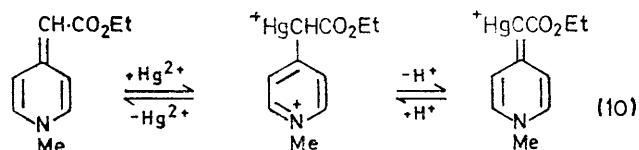
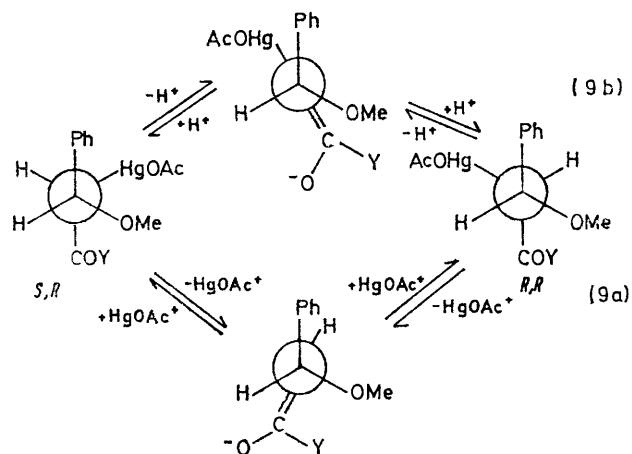
the actual catalysis by lithium nitrate and perchlorate is somewhat larger than would be expected for a simple salt effect when less than $5 \times 10^{-4}\text{M}$ -salt is added to *ca.* $5 \times 10^{-2}\text{M}$ -reagents. It seems possible that the lithium cation may also interact strongly with co-ordinated acetate in a manner similar to that described for the proton, below. The addition of chloride ion would result in the formation of chloromercury(II) species [e.g. (VII) equation (6)] which are known to be appreciably less reactive than the corresponding acetatomercury(II) species in electrophilic displacement reactions.¹⁵ The effect of adding small amounts of lithium chloride should therefore be slightly to reduce the apparent reactivity by the deactivation of a small proportion of the total mercury(II) species.

The addition of mineral acids may influence the reaction in two ways. First, through the effect of the anion as described above. Secondly, protonation of co-ordinated acetate ion should result in the formation of the solvated monoacetatomercury(II) complexes (V) and (VI) which are likely to be more reactive than the diacetatomercury(II) species.¹⁵ Since perchlorate ion co-ordinates the least readily to mercury(II), the greatest acceleration is with perchloric acid. Though nitric acid is weaker¹⁶ in acetic acid than is hydrochloric acid, the nitrate ion does not readily co-ordinate to mercury(II). Hydrochloric acid is also a surprisingly good catalyst in view of the ready formation of chloromercury(II) species. It seems probable that, though the small amount of added chloride ion reduces slightly the amount of the diacetatomercury(II) species, the proton is still able appreciably to activate the latter in its reaction with the olefin.



The isomerisation of the methoxymercuration products from the $\alpha\beta$ -unsaturated ketones is also of interest, for there are two likely routes by which this may occur. Reutov and Chzhu¹⁷ have suggested that the acetatomercury(II) group is 'enolisable' [equation (9a)] because of its position adjacent to the carbonyl group; but enolisation of the corresponding proton [equation (9b)] is also possible. In either case a reketonisation would lead to both *R,R*- and *R,S*-products. Indeed,

reversible loss of an α -proton and reversible loss of an α -mercury(II) species have both been shown¹⁸ readily to occur in the related α -mercuriated pyridioacetates [equation (10)]. However, since no hydrogen exchange



is evident when a mixture of *R,R*- and *R,S*-diastereoisomers of 2-acetoxymercuri-3-methoxy-1,3-diphenylpropanone is treated with an excess of MeOD or with a mixture of MeOD and $\text{CF}_3\text{CO}_2\text{D}$ (1 : 1 v/v) over several days at room temperature, a mercury-enolisation process seems the more likely. If the isomerisation does involve ionisation of the mercury(II) species, then this must be readily reversible and the reverse reaction must be competitive with the uptake of a proton by the intermediate. Uptake of a proton would lead to the formation of methanol adducts which are not observed. The lower rate of enolisation of the methoxymercuration products of the cinnamate esters is consistent with this mechanism.

The thermodynamic preference for the *R,S*-isomer must reflect the greater stability of the predominant conformations of that diastereoisomer relative to those of the *R,R*-diastereoisomer. Inspection of the two predominant conformations (Ia) and (Ib) shows that, though both have the two larger groups *trans* to each other, only the former (*R,R*) has the largest groups separated into two *gauche* pairs. However, it is believed that the *gauche*-arrangement of the methoxy- and acetatomercury-groups is more favoured than simple steric considerations would suggest.¹⁹ Consequently it is probable that conformation (Ib) is more stable than (Ia).

¹⁷ O. A. Reutov and L. T. Chzhu, *Doklady Akad. Nauk. U.S.S.R.*, 1956, **110**, 575.

¹⁸ D. Dodd and M. D. Johnson, *J. Chem. Soc. (B)*, 1970, 1337.

¹⁵ D. Dodd and M. D. Johnson, *J. Chem. Soc. (B)*, 1971, 662.
¹⁶ D. H. Murray-Rust and H. Hartley, *Proc. Roy. Soc.*, 1929, **A126**, 84.

¹⁹ M. M. Kreevoy, L. L. Schaleger, and J. C. Ware, *Trans. Faraday Soc.*, 1962, **58**, 2433.

EXPERIMENTAL

Materials.—Methanol was purified by the method of Lund and Bjerrum,²⁰ b.p. 64.5–65°. Mercuric acetate was Mallinckrodt grade. Perchloric, nitric, hydrochloric, and acetic acids, lithium perchlorate, lithium nitrate, lithium chloride, and sodium acetate were the best available qualities (Hopkin and Williams, Fluka, or C. Erba).

$\alpha\beta$ -Unsaturated Ketones.—The *trans*-4-phenylbut-3-en-2-ones and *trans*-1,3-diphenylpropenones were prepared by condensation of the corresponding 4-substituted benzaldehydes with acetone or acetophenone respectively. Their n.m.r. spectra indicated absence of the respective *cis*-isomers. *cis*-4-Phenylbut-3-en-2-one was separated from the mixture formed by irradiation of the *trans*-isomer in ether with a mercury vapour arc lamp,²¹ $J_{\alpha,\beta}$ 12 Hz. *cis*-1,3-Diphenylpropenone was prepared from the mixture formed on exposing to direct sunlight a solution of the *trans*-isomer²¹ in *n*-pentane, m.p. 45–46° (lit.,²² 45–46°), $J_{\alpha,\beta}$ 12 Hz.

$\alpha\beta$ -Unsaturated Esters.—Methyl *trans*-cinnamate and methyl *trans*-4-methoxy-, 4-methyl-, 4-chloro-, and 4-nitrocinnamates were obtained by esterification of the corresponding acids with diazomethane in ether.¹² They were shown by n.m.r. to be free from the corresponding *cis*-isomers. Methyl *cis*-4-methoxycinnamate was prepared by esterification with diazomethane of the *cis*-4-methoxycinnamic acid obtained from the mixture formed on irradiation of the sodium salt of the *trans*-isomer in water with a mercury arc lamp for 100 h,²³ $J_{\alpha,\beta}$ 14 Hz.

Oxymercuration Reactions.—The reactions were carried out at 30°. In a typical experiment a solution of the corresponding $\alpha\beta$ -unsaturated ester or ketone in methanol was added to a solution of mercuric acetate in the same solvent such that the initial concentration of each reactant was ca. 0.05M and the reaction was allowed to proceed to completion. The mixture was then added to an excess of water and extracted with chloroform. The chloroform solution was washed with water and the solvent was removed from the dried extract (Na_2SO_4) under reduced pressure (40°). The residual oil was dissolved in chloroform (10% w/v) and examined by n.m.r. spectroscopy.

²⁰ H. Lund and J. Bjerrum, *Ber.*, 1931, **64**, 210.

²¹ H. O. House, *J. Org. Chem.*, 1959, **24**, 1374.

Product proportions were calculated from the n.m.r. spectra by measuring the areas under the α -proton doublets and confirmed from the areas of the corresponding methoxy-proton resonance signals. Thus the ratio of the total area found under the peaks at τ 5.25 (d) to that area under the peaks at τ 5.42 (d) gave the proportion of *R,R*- to *S,R*-2-acetoxymethyl-3-methoxy-1,3-diphenylpropanone and a check of this value was obtained from the ratio of the areas under the signals at τ 6.80 and 6.72 (OMe).

All ¹H n.m.r. spectra were recorded on a Varian A-60 instrument with tetramethylsilane as internal reference. The *S,R*-methoxymethylmercurials arising from 1,3-diphenylpropenone, m.p. 113–115°, 1-(4-methoxyphenyl)-3-phenylpropenone, m.p. 133–135°, and 1-(4-nitrophenyl)-3-phenylpropenone, m.p. 121.5–124°, crystallised from their respective diastereoisomeric mixtures upon standing and were purified by recrystallisation from methanol, chloroform, or carbon tetrachloride.

Kinetic Measurements.—A solution of mercuric acetate in methanol (25 ml; 0.096M) at 30° was added to a solution of the $\alpha\beta$ -unsaturated carbonyl compound in methanol (25 ml; 0.080M) at 30°, with or without the appropriate amount of added electrolyte. Aliquot portions were removed at suitable intervals and quenched by pouring into water. The oxymercuration contained in each fraction was extracted with chloroform and the unchanged mercuric acetate in the aqueous solution was titrated with potassium thiocyanate using ferric ammonium sulphate as indicator. In the case of 1-(4-nitrophenyl)-3-phenylpropenone the insolubility of the olefin in methanol made impossible the determination of the reaction rate. It was therefore measured in the presence of sufficient perchloric acid to dissolve the substrate.

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²² W. B. Black and R. E. Lutz, *J. Amer. Chem. Soc.*, 1953, **75**, 5990.

²³ T. A. Wittstruck and E. N. Trachtenberg, *J. Amer. Chem. Soc.*, 1967, **89**, 3803.