Methyl 2,3-dibromo-2,3-diarylpropanoates. Debromination and dehydrobromination reactions

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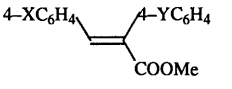
Rate and product studies of the iodide- and methoxide-mediated reactions of methyl (*R*,*R*)- and (*R*,*S*)-2,3-dibromo-2,3-diarylpropanoates and some of their 2- and 3-(4-substitutedphenyl)-derivatives have been carried out. The results indicate that the reaction of iodide with most of the substrates affords only debrominated olefins, whereas the course of the methoxide-promoted reactions seems to depend mainly on the configuration of the starting substrate. Thus, in the eliminations induced by methoxide ion most of the (*R*,*R*)-compounds led exclusively to dehydrobrominated olefins. On the other hand, the dehydrobrominations of most of the (*R*,*S*)-isomers can be accompanied by debromination. Mechanistic aspects are discussed.

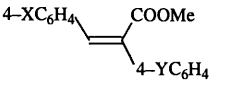
We have previously reported stereochemical and kinetic results for the methoxide-induced dehydrobromination of (*R*,*R*)-PhCHBrC(Ar)HCOOMe in methanol which were interpreted in terms of a reaction taking place by way of an irreversible E1cB mechanism.[1] In view of the structural similarity between these compounds and those derived from replacement of the 2-hydrogen by a bromine atom [PhCHBrC(Ar)BrCOOMe] and the fact that each pair of substrates should produce an identical carbanionic species by separation of the 2-hydrogen or the 2-bromine, respectively, the operation of a carbanionic mechanism for the elimination of the latter substrates was considered as a possibility. It was of interest, therefore, to obtain kinetic and stereochemical evidence of the behaviour of the latter reaction induced by the methoxide ion in methanol.

Results

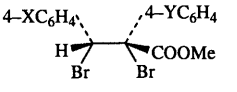
The reaction of methyl (*E*)-2,3-diarylpropenoates (**1**) with bromine in acetic acid afforded the corresponding methyl (*R*,*R*)- and (*R*,*S*)-2,3-dibromo-2,3-diarylpropanoates (**2**). The isomeric composition of the crude product was determined by ^{1}H NMR analysis from the relative intensity of the signals arising from the 3-H resonances (see Experimental section). Owing to the failure to separate these diastereoisomers, their purified mixtures were used as such. For the elimination reactions one of the dibromo-substrates was freed from its corresponding diastereoisomer by allowing the reaction of the mixture of isomers to proceed to complete conversion of the more reactive isomer into the reaction product. The elimination of the partially unreacted isomer (*i.e.* *R*,*R*) was then carried out on an impure sample containing *ca.* 40% of the olefin but since this impurity was also a reaction product this was taken into account in both the kinetic and product analysis. Under these conditions, the proportion of the olefin furnished by the elimination of the remaining diastereoisomeric dibromide of the mixture (*R*,*R*) was calculated from the increased areas under the methoxycarbonyl resonance peaks of the products and confirmed by following the decrease of its H-3 resonance intensity. The rate coefficient corresponding to the reaction of the second diastereoisomer (*R*,*S*) was estimated from a combination of the already determined rate constant ($k_{R,R}$) with the corresponding $k_{R,R}/k_{R,S}$ value calculated by estimation of the ratio of the unchanged starting isomers during the initial course of the reaction. Second- or first-order plots were obtained from the normal integrated rate equations and the rate coefficients were reproducible to within ±3.8%. For the substrate **2c**, the close similarity in the rates of elimination of the isomers precluded the application of this procedure. However, a rough evaluation of the rate coefficients was carried out on the basis that the average values were estimated to be equal within an experimental error of ±4.1%.



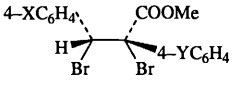
(*E*) - **1**



(*Z*) - **1**



(*R*,*R*) - **2**



(*R*,*S*) - **2**

ArCBr=C(Ar)COOMe

3

	X	Y
a	H	H
b	H	Me
c	H	OMe
d	H	Cl
e	H	NO_2
f	Cl	H
g	OMe	H
h	NO_2	H

The observed rate constants corresponding to the methoxide-promoted reaction of *R*,*S* **2a**, **b**, **d**, **e** and **g** were found to be composite quantities which include dehydrobromination and debromination rates. The dehydrobromination ($k_{dehydrobr}$) and debromination (k_{debr}) components of the overall reaction were calculated from the product ratio of the brominated (**3**) to unbrominated (**1**) olefin which were sufficiently resolved for analysis.

Methyl (*E*)- and (*Z*)-3-bromo-2,3-diarylpropenoates (**3**) were geometrically assigned by ascribing the low field CO_2Me signal to the *Z*-isomer, according to the observation that an ester group in the *trans* orientation with respect to an aryl group always appears at lower frequencies compared with the isomer where the two groups are *cis* related.[2]

Discussion

Bromination of **1a** in acetic acid at 25 °C produced a mixture containing the two diastereoisomeric dibromides **2a** (**A** and **B**)†

† The isomers were initially identified by assigning the ^{1}H NMR chemical shift due to H-3 of the **A** compound to the singlet that appeared at a lower field (between 0.14 and 0.22 ppm) than that arising from the corresponding **B** isomer.

Table 1 Observed product yields for the additions of bromine to methyl (*E*)-2-(4-X-phenyl)-3-(4-Y-phenyl)propenoates[a] in acetic acid at 30 °C

X	Y	Reaction time/h	Yield (%)[b]
H	H	48	82
H	Me	33	79
H	OMe	24	82
H	Cl	52	81
H	NO_2	81	80
MeO	H	12	98
Cl	H	72	67
NO_2	H	288	83

[a] [Substrate] = 0.2 mol dm^{-3}; [Br_2] = 0.25 mol dm^{-3}. [b] As determined by ^1H NMR spectroscopy of the crude product mixture.

with isomer **A** predominating. The same reaction performed on substrates (*E*)-**1b–h**‡ does not lead to a significant variation of the resulting diastereoisomeric composition. Moreover, the isomeric product ratio of bromination of (*Z*)-**1g** and (*Z*)-**1h** under the same conditions proved to be quite similar to that arising from the (*E*)-olefins. Table 1 shows the yields and reaction times for bromination.

Although qualitative in nature, the pattern reported in Table 1 reveals that the magnitude of the reactivity response of the bromination to the presence of substituents in the 4-position of the 2-phenyl ring is not particularly large, since relative times of reaction (80%) increased only *ca.* 3.3-fold between the fastest and the slowest reacting substrate that were investigated. However, the reactivity is more noticeably affected by the nature of the 4-substitution in the 3-phenyl group. Thus, treatment of methyl (*E*)-2-phenyl-3-(4-methoxyphenyl)-propenoate with bromine in acetic acid at 25 °C gave virtually quantitative conversion into the dibromo-adduct in 12 h. Under the same conditions, methyl (*E*)-2-phenyl-3-(4-nitrophenyl)-propenoate showed 83% addition after 12 days. A likely explanation of these results might be a reaction pathway that involves a carbenium ion-like rate-controlling transition state with the positive charge located on the 3-carbon atom.

As regard the stereochemical outcome of these additions, the diastereoisomeric ratio of the products proved essentially independent of the influence of the 4-substituent in any of the phenyl rings. The reactions led to *ca.* 5:3 mixtures of diastereoisomeric products (**A** and **B** respectively) which strongly suggests that all the substrates are reacting by a mechanism that involves closely related product-determining pathways. Another interesting observation arises from the examination of the diastereoisomeric product provided by the reaction performed on substrates *Z*-(**1f**) and (*Z*)-**1h** which showed no dependence on the geometric nature of the starting olefin.

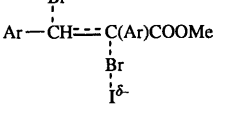
The analogy in the stereochemical results associated with the lack of stereospecificity and the effects of the aryl groups observed for these additions may reasonably be regarded as an indication of reactions proceeding by way of an open carbocationic intermediate produced by electrophilic attack of bromine prior to addition of the bromide ion to afford a product composition determined by the relative stability of the diastereoisomers. On this basis, it becomes apparent that isomers **A** (major) are thermodynamically more stable than the corresponding **B** isomers (minor).

It appears difficult, however, to reconcile the involvement of a 3-carbenium ion intermediate with the destabilising influence of the 3-(4-nitrophenyl) group, since such an ion might not have sufficient lifetime to exist as an intermediate. It would be more reasonable perhaps to speculate that in this case the reaction occurs through the formation of a bromonium ion in which the bridging is sufficiently weakened to allow C-2–C-3 bond rotation resulting in non-stereospecific addition.§

Consistent with the conclusions about reactions occurring through a carbenium ion intermediate is the observation that the diastereoisomeric product distribution of the bromination is not affected by the presence of varying [Br^-] in the reaction mixture. Apparent support for the above interpretation comes from the subsequent observation that whereas the reaction with methyl (*E*)-2-(4-methylphenyl)-3-phenylpropenoate produces dibromo-adducts exclusively, the addition of bromine to methyl (*E*)-2-phenyl-3-(4-methylphenyl)propenoate seems to be accompanied by methyl substitution forming 4-$CH_2BrC_6H_4$CHBrC(Ph)BrCOOMe and 4-$CHBr_2C_6H_4$CHBrC(Ph)BrCOOMe as follows from the disappearance of the 4-methyl group resonance and the appearance of two less intense signals at lower frequencies. This difference in behaviour is likely to be a reflection of an enhanced lability of the methyl hydrogens in the 3-phenyl ring of the presumed intermediate due to hyperconjugation with the positive charge density located on the 3-benzylic carbon atom.

Stereochemical assignment of these adducts was based on their behaviour in elimination induced by iodide ion in methanol at 25 °C and its comparison with that of the 1,2-dibromostilbenes.[3] Under these conditions, substrates **2A** (**a**, **b**, **d**, **e**, **g** and **h**) produced the corresponding debrominated *E* compounds almost exclusively (> 97%), whereas **2B** (**a**, **b**, **d**, **e**, **g** and **h**) eliminated with high stereoselectivity for the *Z* olefins (*ca.* 88%). Similar results had been obtained for the reactions with *meso*- and *dl*-1,2-dibromostilbenes,[3] which led respectively to the exclusive and predominant formation of the corresponding products of *anti*-debromination.

The data listed in Table 2 reveal that Me, Cl and NO_2 substituents in the phenyl rings of the substrate molecule exert a modest accelerating influence on the iodide-mediated debromination reaction with respect to the unsubstituted compound. This increase in rates is in qualitative accord with the expectation that substituents, whether electron-attracting or -withdrawing, can stabilise an incipient π-bond in an E2 process, and is comparable to the kinetic response of the iodide-promoted debromination of *meso*-dibromostilbene in methanol.[3] The kinetic behaviour of the latter compounds along with the *anti*-stereospecificity of the reaction was interpreted as arising from an E2-type *anti*-elimination mechanism. Consequently, it seems reasonable to suggest that the elimination of compounds **a**, **b**, **d**, **e**, **g** and **h** proceeds by way of a concerted transition state that involves iodide-promoted removal of the 2-bromine according to the expected enhanced lability of the latter relative to 3-bromine due to the acidifying influence of the adjacent carbonyl group.



Alternatively, the lower reactivity of the **B** compounds compared with that of the corresponding **A** isomers (k_A/k_B = 36.2–49.5; Table 2) might be explained as elimination from the latter occurring *via* the concerted mechanism, whereas iodide-induced 2-bromine abstraction leading to a carbanionic intermediate stabilised by the adjacent carbonyl group could be

‡ **1a–e** represent different 4-substituents in the phenyl ring attached to the same carbon as the carboxymethyl group whereas **1f** and **1g** correspond to substituents in the ring attached to the unsubstituted carbon atom.

§ Owing to the electronic properties of the 4-phenyl substituent the results obtained with the 3-(4-nitrophenyl)olefin could alternatively be rationalised by invoking an open 2-carbanion arising from the nucleophilic addition of bromine to the 3-carbon atom, which subsequently gives the thermodynamically controlled products.

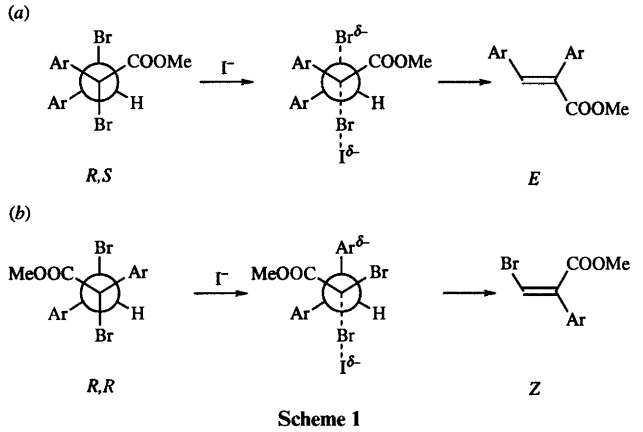
Table 2 Rates of the iodide-promoted reactions of diastereoisomeric 4-$XC_6H_4CHBrC(4\text{-}YC_6H_4)BrCOOMe$[a] in methanol at 25 ± 0.05 °C

	X	Y	$k_A/10^{-3}$ dm^3 mol^{-1} min^{-1}	$k_B/10^{-3}$ dm^3 mol^{-1} min^{-1}	k_A/k_B
a	H	H	9.4	0.19	49.5
b	H	Me	19.3	0.33	43.5
c	H	MeO[b,c]	*ca.* 93	*ca.* 93	*ca.* 1
d	H	Cl	10.1	0.23	43.9
e	H	NO_2	18.8	0.52	36.2
f	MeO	H[b]	*d*	*d*	
g	Cl	H	12.7	0.27	47.0
h	NO_2	H	15.6	0.40	39.0

[a] [Substrate] = [I^-] = 0.035 mol dm^{-3}. [b] First-order rate coefficient (min^{-1}). [c] Reaction leading to dehydrobromination. [d] Reaction leading to solvolytic products.

postulated as operative for the **B** isomer. This interpretation is compatible with the observed second-order kinetics and with the criterion[4] that a stepwise process should involve a higher energy of activation than a concerted pathway. It could also be compared with that of the methoxide-promoted dehydrobromination of the analogous methyl (*R,R*)-3-bromo-2-aryl-3-phenylpropanoates[1] for which an E1cB mechanism of the irreversible type was diagnosed. However, we believe that the remarkable similarity in the relative reactivity of each pair of diastereoisomeric substrates (k_A/k_B) (Table 2) for the set of substituents studied here, combined with the lack of influence of the 4-nitro-2-phenyl substituent and the stereochemical results, are manifestations of the same mechanistic behaviour for both isomers, *i.e.* the concerted pathway.

On the basis of the fact that the geometry of the products of an E2 *anti*-elimination normally reflects that of the transition state and the assumption that the latter should be conformationally related to the starting substrate, it may be suggested that the (*E*)-olefins arise from debromination of the corresponding (*R,S*)-dibromo-substrates (Scheme 1) whereas



Scheme 1

the *R,R*-isomers are those which afford predominantly the corresponding (*Z*)-olefin. Thus, the *R,S* and *R,R* configurations were assigned to the isomers **A** and **B**, respectively.

The lower reactivity of the *R,R*-compounds may be taken to imply that the required conformation for *anti*-periplanar orientation of the C–Br bonds being broken in these diastereoisomers (*b*) is thermodynamically less favoured compared with that of the corresponding *R,S*-isomers (*a*). On these grounds it may be assumed that for these compounds, the interaction between the 3-Ar and COOMe in a *gauche* relationship (*b*) is energetically less favourable than that between the two aryl groups (*a*).

Regarding the dibromo-adducts containing a 4-MeO substituent in the 2-phenyl ring, the first-order kinetics coupled with the similarity in the rates of reaction of the isomers and the observation that elimination follows a different pathway to give

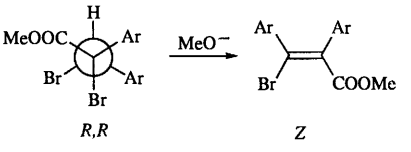
Table 3 Rate coefficients for the dehydrobromination of (*R,R*)-4-$XC_6H_4CHBrC(4\text{-}YC_6H_4)BrCOOMe$[a] with MeO^- [a] in MeOH at 25 ± 0.05 °C

	X	Y	$k_{dehydr}/10^{-3}$ dm^{3}mol^{-1} min^{-1} [b]
a	H	H	13.3
b	H	Me	9.8
c	H	MeO	96.5[c]
d	H	Cl	6.9
e	H	NO_2	8.1
f	MeO	H	*c,d*
g	Cl	H	14.2
h	NO_2	H	16.6

[a] [Substrate] = 0.035 mol dm^{-3}; [MeO^-] = 0.045 mol dm^{-3}. [b] Reactions leading to >97% (*Z*)-3-bromoolefin. [c] First-order rate constant. [d] Reaction leading to solvolysis products.

the products of dehydrobromination (Table 2) precludes an interpretation in terms of a concerted process and the application of mechanistic arguments to the assignment of configurations. In this case the stereochemistry of the dibromides was deduced from that of the remaining analogues, using the ^1H NMR 3-hydrogen signals and considering that the structural modification was not enough to invert the H-3 chemical shifts. A similar procedure was used for the diastereoisomeric identification of methyl 2,3-dibromo-2-phenyl-3-(4-methoxyphenyl)propanoates for which the first-order reaction for both isomers led to the formation of solvolytic products [4-$MeOC_6H_4CH(OMe)C(Ph)BrCOOMe$].

In contrast to the results for the iodide-mediated reactions, the (*R,R*)-dibromo-substrates **2a**, **b**, **d**, **e**, **g** and **h** reacted with sodium methoxide in methanol to provide dehydrobrominated olefins [ArCBr=C(Ar)COOMe] [reaction (1)]. Inspection of



(1)

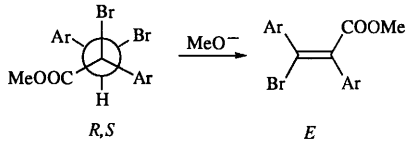
Table 3 reveals that a feature of the dehydrobromination of these compounds is that the reactions are not significantly influenced by the nature of the 4-phenyl substituents investigated indicating a process *via* a rate-determining transition state with a rather small charge build-up on the 2- and 3-carbon atoms. These observations, considered in conjunction with the high degree of *anti*-stereoespecificity of the elimination of this set of *R,R*-compounds, are characteristic of the usual E2 mechanism.[5,6] In this case, the proper geometry of 3-hydrogen and 2-bromine orientation for *anti*-elimination seems to be favoured in accordance with previous conclusions suggesting that repulsive interactions between *gauche* Ar–Ar are less pronounced that those arising between 3-Ar and COOMe.

The data in Table 3 also indicate that the presence of a 4-methoxy substituent in the 2-phenyl ring causes a comparatively significant increase in the rate of elimination as well as a change towards first-order kinetics. The behaviour of this compound is similar to that observed for its iodide-promoted reaction and could reasonably be correlated with the known stability of α-COOR-substituted 4-methoxybenzyl carbocations.[7] It seems likely that both reactions proceed through a carbocationic intermediate resulting from expulsion of the 2-bromide ion followed by separation of the 3-proton with the consequent thermodynamically controlled formation of the 3-bromoolefin.

Deviation from the elimination route of these reactions was found for the methyl (*R,R*)-2,3-dibromo-2-phenyl-3-(4-methoxyphenyl)propanoate for which the reaction with sodium

methoxide provides the product of displacement of the 3-bromine by the methoxy group. As in the case of the reaction with I^-, this reaction does not show dependence on the base concentration and the result can be taken as a reflection of the increased electron-donating ability exerted by the MeO substituent which promotes the unimolecular expulsion of the 3-bromide ion with the subsequent formation of the corresponding product of solvolysis.

As regard the reactions of the (*R*,*S*)-dibromo-substrates induced by methoxide in methanol, the dehydrobromination of **a**, **b**, **e** and **g** was accompanied by debromination leading to the corresponding (*E*)-2,3-diarylpropenoate [reaction (2), Table 4].

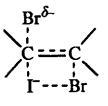


R,S *E* (2)

For compounds (*R*,*S*)-**2a**, **b**, **e** and **g**, the rather low sensitivity of the dehydrobromination rates to the effect of the sustituents might be understood on the basis of a concerted process which is compatible with the fact that the reaction produces almost exclusively the olefin arising from *anti*-elimination.

The effect exerted by the presence of the 4-methoxy substituent in the 2-phenyl ring on the *R*,*S* isomer is analogous to that on its *R*,*R* isomer (Tables 3 and 4), suggesting a similar elimination mechanism in both cases. The acceleration shown by the reaction with substrate (*R*,*S*)-**2d** probably reflects the capacity of a group such as 4-ClC_6H_4 to assist the rate-dependent ejection of the 2-bromine causing a change of the transition state structure towards the paenecarbonium side of the E2 spectrum.[8] The fact that the product provided by the dehydrobromination of this compound is the corresponding (*Z*)-3-bromoolefin (Table 4) could be associated with the conclusion[5] that the *anti*-geometrical requirement for an E1-like elimination does not seem to be as strict as for the case of a symmetrical transition state. Thus, the stereochemical result may be taken as an indication of the involvement of a product-controlling structure loose enough to attain a geometrical configuration leading to the thermodynamically preferred olefin. The behaviour exhibited by the (*R*,*S*)-dibromide having a 4-methoxy substituent in the 3-phenyl group is similar to that of its (*R*,*R*)-isomer (Tables 3 and 4). The results may indicate that the diastereoisomers share a common nucleophilic substitution mechanism in which the 3-carbenium ion intermediate formation is most likely to be the rate- and product-determining step.

For the debromination pathway, substrates (*R*,*S*)-**2a**, **b**, **d** and **g** (Table 4) display comparable rate coefficient values that could be accommodated, to a first approximation, within the framework of a concerted process promoted by MeO^-. This is the first evidence for the existence of a 1,2-debromination reaction induced by methoxide ion to the best of our knowledge. The similarity in the rate coefficient values as well as the degree of *anti*-stereoselectivity (*ca.* 96%) seem to point to



a mechanism which could be compared with that assigned to the iodide-mediated debromination of these substrates. An alternative interpretation of these facts might be in terms of a concerted process in which the 3-bromide expulsion is nucleophilically assisted by the base, resembling a typical E_2C reaction, which could also explain the *trans*-elimination

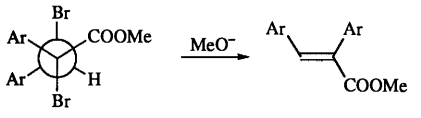
Table 4 Rate coefficients for the methoxide-promoted reaction of (*R*,*S*)-4-$XC_6H_4CHBrC(4\text{-}YC_6H_4)BrCOOMe$[a] in methanol at 25 ± 0.05 °C

	X	Y	$k_{dehydrobr}/10^{-3}$ dm^3 mol^{-1} min^{-1} [b]	$k_{debr}/10^{-3}$ dm^3 mol^{-1} min^{-1} [c]
a	H	H	1.94	0.65
b	H	Me	1.76	0.55
c	H	MeO	*ca.* 96[d,e]	
d	H	Cl	20.9[e]	0.69
e	H	NO_2	2.18	8.85
f	MeO	H	*d,f*	
g	Cl	H	1.95	0.71
h	NO_2	H	8.73	

[a] [Substrate] = 0.025 mol dm^{-3}; [MeO^-] = 0.035 mol dm^{-3}. [b] Reaction leading to the (*E*)-3-bromoolefin (> 97%). [c] Reaction leading to the (*E*)-2,3-diarylolefin (> 96%). [d] First-order kinetics (min^{-1}). [e] Reaction leading to the (*Z*)-3-bromoolefin (98%). [f] Products of solvolysis.

mechanism.¶ However, in the absence of more detailed information it is not justifiable to draw more definite conclusions.

According to the E2-type debromination mechanism suggested above, the configuration of the transition state for the methoxide-promoted dehydrobromination of the *R*,*S* compounds (**2a**, **b**, **e**, **g** and **h**) leading to the corresponding (*E*)-3-bromoolefin [reaction (2)] should be energetically less favourable than that for the *anti*-debromination producing the *E*-olefin [reaction (3)]. However, the preference for the former



R,S *E* (3)

pathway (Table 4) may stem from a greater tendency of the base to abstract the 3-proton relative to the 2-bromine, which should overshadow the effect of the energetically unfavourable geometry of the required *anti*-periplanar arrangement of the bonds involved in the dehydrobromination. This tendency seems to dominate completely the reaction for compound (*R*,*S*)-**2h** (Table 4) for which no debromination could be detected, most probably due to the acidifying influence exerted on the 3-proton by the 4-NO_2 group.

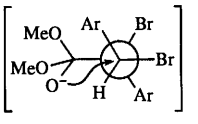
From the present observations it may be concluded that the nature of the base plays a key role upon the course of the reaction of the methyl 2,3-dibromo-2,3-diarylpropanoates investigated. It is also evident that the products, as well as the rate of the reactions, are dependent on the configurational properties of the substrates, although the electronic nature of the aryl substituents may have significant effects in determining the observed results.

Experimental

Materials

Methyl 2,3-diarylpropenoates[1] were prepared by esterification of the corresponding purified acids[9] with diazomethane in diethyl ether. Methanol was purified as described[10] and stored

¶ A referee has suggested an alternative interpretation which involves neighbouring group displacement of Br^- by the tetrahedral intermediate of the methoxycarbonyl substituent arising from addition of MeO^-:



under nitrogen. Sodium methoxide was prepared under nitrogen and stored in water- and carbon dioxide-free conditions. Solutions containing the required concentration of reagents were prepared immediately before use by dilution of stock solutions. Potassium iodide was dried according to the described technique.[3] Methyl 2,3-dibromo-2,3-diarylpropenoates were obtained from reaction of the corresponding methyl 2,3-diarylpropenoate (0.2 mol dm^{-3}) and bromine (0.25 mol dm^{-3}) in acetic acid at 30 °C. After the appropriate reaction period, the solvent was evaporated under *vacuo* and the residue examined by ^1H NMR spectroscopy. Chemical shifts were measured with a Varian EM 360L 60 MHz instrument. Tetramethylsilane was used as external reference. The crude product was then poured into water, extracted with dichloromethane and the solvent removed. Attempted separation of the diastereoisomers by consecutive recrystallisations or repeated column chromatography gave pure mixtures containing different amounts of the (*R,R*)- and (*R,S*)-substrates.

Methyl 2,3-dibromo-2,3-diphenylpropanoates. (Found: C, 48.6; H, 3.7. $C_{16}H_{14}Br_2O_2$ requires C, 48.27; H, 3.54%); $\delta_H(CCl_4)$ 7.4–6.6 (10 H, ArH, m), 5.77 (0.63 H, H-3, s), 5.56 (0.37 H, H-3, s), 3.78 (H, COOMe, s) and 3.70 (1.11 H, COOMe, s).

Methyl 2,3-dibromo-2-(4-methylphenyl)-3-phenylpropanoates. (Found: C, 49.8; H, 3.9. $C_{17}H_{16}Br_2O_2$ requires C, 49.54; H, 3.91%); $\delta_H(CCl_4)$ 7.3–6.5 (9 H, ArH, m), 5.68 (0.61 H, H-3, s), 5.47 (0.39 H, H-3, s), 3.70 (1.17 H, COOMe, s), 3.62 (1.83 H, COOMe, s), 2.23 (1.17 H, ArMe, s) and 2.12 (1.83 H, ArMe, s).

Methyl 2,3-dibromo-2-(4-methoxyphenyl)propanoates. (Found: C, 47.3; H, 3.9. $C_{17}H_{15}Br_2O_2$ requires C, 47.69; H, 3.77%); $\delta_H(CCl_4)$ 7.3–6.2 (9 H, ArH, m), 5.66 (0.64 H, H-3, s), 5.46 (0.36 H, H-3, s), 3.78 (1.92 H, COOMe, s), 3.72 (1.92 H, ArOMe, s), 3.68 (1.08 H, ArH, m) and 3.51 (1.08 H, ArOMe, s).

Methyl 2,3-dibromo-2-(4-chlorophenyl)-3-phenylpropanoates. (Found: C, 44.7; H, 3.1; Cl, 8.0. $C_{16}H_{13}Br_2ClO_2$ requires C, 44.43; H, 3.03; Cl, 8.20%). $\delta_H(CCl_4)$ 7.3–6.7 (9 H, ArH, m), 5.80 (0.64 H, H-3, s), 5.58 (0.36 H, H-3, s), 3.72 (1.92 H, COOMe, s) and 3.68 (1.07 H, COOMe, s).

Methyl 2,3-dibromo-2-(4-nitrophenyl)-3-phenylpropanoates. (Found: C, 43.1; H, 3.1; N, 3.3. $C_{16}H_{13}Br_2NO_4$ requires C, 43.37; H, 2.96; N, 3.16%); $\delta_H(CCl_4)$ 8.2–6.5 (9 H, ArH, m), 5.70 (0.63 H, H-3, s), 5.52 (0.37 H, H-3, s), 3.70 (1.89 H, COOMe, s) and 3.65 (1.11 H, COOMe, s).

Methyl 2,3-dibromo-2-phenyl-3-(4-methoxyphenyl)propanoates. (Found: C, 47.9; H, 3.9. $C_{17}H_{16}Br_2O_3$ requires C, 47.69; H, 3.77%); $\delta_H(CCl_4)$ 7.1–6.1 (9 H, ArH, m), 5.58 (0.65 H, H-3, s), 5.38 (0.35 H, H-3, s), 3.68 (1.95 H, ArOMe, s), 3.62 (3 H, COOMe, s), 3.58 (1.05 H, ArOMe, s).

Methyl 2,3-dibromo-2-phenyl-3-(4-chlorophenyl)propanoates. (Found: C, 44.6; H, 3.1; Cl, 7.9. $C_{16}H_{13}Br_2ClO_2$ requires C, 44.43; H, 3.03; Cl, 8.20%); $\delta_H(CCl_4)$ 7.3–6.6 (9 H, ArH, m), 5.84 (0.63 H, H-3, s), 5.70 (0.37 H, H-3, s), 3.80 (1.89 H, COOMe, s) and 3.72 (1.11 H, COOMe, s).

Methyl 2,3-dibromo-2-phenyl-3-(4-nitrophenyl)propanoates. (Found: C, 43.6; H, 2.7; N, 3.2. $C_{16}H_{13}Br_2NO_4$ requires C, 43.37; H, 2.96; N, 3.16%); $\delta_H(CCl_4)$ 8.1–6.8 (9 H, ArH, m), 5.72 (0.65 H, H-3, s), 5.53 (0.35 H, H-3, s), 3.66 (1.95 H, COOMe, s) and 3.60 (1.05 H, COOMe, s).

Kinetic procedure

Rates were measured at 25 ± 0.05 °C. The reactions were initiated by adding methanolic sodium methoxide or potassium iodide to the solution of the corresponding substrate in methanol. Aliquots of the reaction with potassium iodide were withdrawn at various time intervals and mixed with water containing $Na_2S_2O_3$. In the case of sodium methoxide, samples were prepared by quenching the reaction with water containing a slight excess of hydrochloric acid. The products were removed by extraction with dichloromethane, the solvent evaporated off and a solution (10%) was made with carbon tetrachloride for ^1H NMR analysis. The rates were measured using the intensity of the methoxycarbonyl and the 3-proton signals of the starting material relative to the methoxycarbonyl peak areas of the product. Each result is the mean of six to eight experiments. For the relative rate coefficients of the eliminations, the ratio was calculated using eqn. (4). The agreement of triplicate rate

$$k_{R,R}/k_{R,S} = \frac{\log [\text{fraction of unchanged } R,R]}{\log [\text{fraction of unchanged } R,S]} \quad (4)$$

constant values was generally better than ± 3.8%.

Product analysis

The iodide- and methoxide-induced reactions were quenched after 10 half-lives, worked up as usual and the residues examined by ^1H NMR spectroscopy. The products of the reactions with iodide consisted of mixtures of the corresponding methyl (*E*)- and (*Z*)-2,3-diarylpropenoates and their compositions were determined by comparing the intensity of the H-3 signal (between δ 7.7 and 7.2) arising from the *E* isomer with the area due to the total COOMe resonance of the mixture. For the product of the reactions containing mixtures of methyl (*E*)-2,3-diarylpropenoates and methyl (*Z*)-3-bromo-2,3-diarylpropenoates (Table 4), the proportions of the olefins were estimated from the relative areas under the respective COOMe resonances. For the cases where the signals due to the (*E*)-propenoate and (*Z*)-3-bromopropenoate were not sufficiently separated, the relative proportions of these olefins were estimated by substraction from the total methoxycarbonyl peak area that corresponded to the former calculated from the H-3 olefinic signal (in the δ 7.7–7.2 region).

The new methyl (*E*)- and (*Z*)-3-bromo-2,3-diarylpropenoates were isolated from their mixtures with the corresponding methyl (*E*)-2,3-diarylpropenoates by chromatography on a silica gel column with hexane–ethyl acetate (10:1). Separation of the isomers was not attempted.

Methyl 3-bromo-2,3-diphenylpropenoates. (Found: C, 60.8; H, 4.3. $C_{16}H_{13}BrO_2$ requires C, 60.59; H, 4.13%); $\delta_H(CCl_4)$ (*Z*) 7.3–6.7 (10 H, ArH, m), 3.58 (3 H, COOMe, s); (*E*) 7.3–6.7 (10 H, ArH, m) and 3.30 (3 H, COOMe, s).

Methyl 3-bromo-2-(4-methylphenyl)propenoates. (Found: C, 61.9; H, 4.8. $C_{17}H_{15}BrO_2$ requires C, 61.65; H, 4.57%); $\delta_H(CCl_4)$ (*Z*) 7.4–6.7 (9 H, ArH, m), 3.60 (3 H, COOMe, s), 2.18 (3 H, ArMe, s); (*E*) 7.4–6.7 (9 H, ArH, m), 3.36 (3 H, COOMe, s) and 2.10 (3 H, ArMe, s).

Methyl 3-bromo-2-(4-methoxyphenyl)-3-phenylpropenoates. (Found: C, 59.2; H, 4.5. $C_{17}H_{15}BrO_3$ requires C, 58.80; H, 4.35%); $\delta_H(CCl_4)$ (*Z*) 7.4–6.3 (9 H, ArH, m), 3.62 (3 H, COOMe, s) and 3.60 (3 H, ArOMe, s); (*E*) 7.4–6.3 (9 H, ArH, m), 3.78 (3 H, ArOMe, s) and 3.30 (3 H, COOMe, s).

Methyl 3-bromo-2-(4-chlorophenyl)-3-phenylpropenoate. (Found: 54.9; H, 3.6; Cl, 9.8. $C_{16}H_{12}BrClO_2$ requires C, 54.65; H, 3.44; Cl, 10.08%); $\delta_H(CCl_4)$ 7.3–6.7 (9 H, ArH, m) and 3.20 (3 H, COOMe, s).

Methyl 3-bromo-2-(4-nitrophenyl)-3-phenylpropenoates. (Found: C, 53.2; H, 3.5; N, 3.8. $C_{16}H_{12}BrNO_4$ requires C, 53.06; H, 3.34; N, 3.87%); $\delta_H(CCl_4)$ (*Z*) 8.1–6.6 (9 H, ArH, m), 3.52 (3 H, COOMe, s); (*E*) 8.1–6.6 (9 H, ArH, m) and 3.21 (3 H, COOMe, s).

Methyl 3-bromo-2-phenyl-3-(4-chlorophenyl)propenoates. (Found: C, 54.9; H, 3.5; Cl, 9.9. $C_{16}H_{12}BrClO_2$ requires C, 54.65; H, 3.44; Cl, 10.08%); $\delta_H(CCl_4)$ (*Z*) 6.9 (9 H, ArH, br s) and 3.68 (3 H, COOMe, s); (*E*) 7.2 (9 H, ArH, br s) and 3.34 (3 H, COOMe, s).

Methyl 3-bromo-2-phenyl-3-(4-nitrophenyl)propenoates. (Found: C, 53.4; H, 3.5; N, 3.7. $C_{16}H_{12}BrNO_4$ requires C, 53.06; H, 3.34; N, 3.87%); $\delta_H(CCl_4)$ (*Z*) 8.1–6.8 (9 H, ArH, m) and 3.65 (3 H, COOMe, s); (*E*) 8.1–6.8 (9 H, ArH, m) and 3.16 (3 H, COOMe, s). For the reactions with methyl 2,3-dibromo-2-

phenyl-3-(4-methoxyphenyl)propanoates, only mixtures of methyl (*R*,*R*)- and (*R*,*S*)-2-bromo-3-methoxy-2-phenyl-3-(4-methoxyphenyl)propanoates were obtained which were not diastereoisomerically identified (Found: C, 57.4; H, 4.9. $C_{18}H_{19}BrO_4$ requires C, 57.00; H, 5.05%); $\delta_H(CCl_4)$ 7.4–6.2 (ArH, m), 4.82 (H-3, s), 4.55 (H-3, s), 3.70 (ArOMe, s), 3.68 (ArOMe, s), 3.68 (COOMe, s), 3.65 (COOMe, s) and 3.15 (COMe, s).

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