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Triethylamine-induced Reactions of Methyl 2,3-Dibromo-2,3-diarylpropanoates in Methanol†

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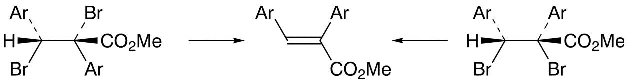
The title compounds undergo elimination with methanolic triethylamine to afford the corresponding debrominated olefins, most of them through an *E*2 stereoconvergent process.

In a previous paper we described the methanolic methoxide- and iodide-mediated reactions of methyl (*R*,*S*)- and (*R*,*R*)-2,3-dibromo-2,3-diarylpropanoates **1** and **2** respectively. As a continuation of this study we now report the results of the reaction of these compounds induced by triethylamine (TEA) in methanol.

The ^{1}H NMR spectra of the crude products of the elimination of the methyl (*R*,*S*)-2,3-dibromo-2,3-diarylpropanoates (**a**, **b**, **c**, **e**, **f** and **g**) (Table 1) showed only signals of the *E*-debrominated olefins.



1 **2**

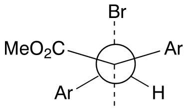
Pseudo-first-order kinetics were determined by using a large excess of the base. According to the data recorded in Table 1, electron-withdrawing groups such as those present in compounds **b**, **e**, **f** and **g**, as well as an electron-releasing group (compound **c**), increase the debromination rates only slightly. This modest influence may be taken as evidence indicating a rate-controlling transition state with little development of charge on either of the carbon atoms involved in the elimination and is compatible with the kinetic response of the iodide-induced debromination of the compounds in the same solvent. These results, associated with the stereochemical nature of the olefinic products, may satisfactorily be explained in terms of debromination proceeding by an *E*2 mechanism.[1]

As regards the corresponding diastereoisomeric substrates (*R*,*R*; **a**, **b**, **c**, **e**, **f** and **g**), Table 1 indicates that the relative magnitudes of the influence of the aryl substituent on the debromination rate are also typical of a concerted process. On this basis, the observation that these diastereoisomers lead exclusively to their corresponding *E* olefins seems to demand that the reactions should take place with *syn* elimination. Probably, in spite of the favourable orbital overlap accompanying *anti* elimination, the energetic increase arising from interaction between the 3-aryl and the CO_2Me groups in transition state **A** would be more important than that due to a eclipsing geometry of the two aryl groups (transition state **B**).‡

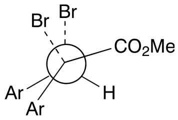
Table 1 Rate coefficients of the debromination of (*R*,*S*)- and (*R*,*R*)-ArCHBrCBrAr′CO_2Me (0.006 mol dm^{-3}) promoted by TEA (4.5 mol dm^{-3}) and TEA hydrochloride (2 mol dm^{-3}) in methanol at 30 °C

	Ar	Ar′	$k_{R,S}$[a]	$k_{R,R}$[a]
a	Ph	Ph	0.85	0.27
b	Ph	*p*-ClC_6H_4	1.58	0.60
c	Ph	*p*-MeC_6H_4	1.03	0.29
d	Ph	*p*-$MeOC_6H_4$[b]	*ca.* 75	*ca.* 75
e	Ph	*p*-$NO_2C_6H_4$	2.51	0.52
f	*p*-ClC_6H_4	Ph	1.19	0.47
g	*p*-$NO_2C_6H_4$	Ph	1.26	0.42
h	*p*-$MeOC_6H_4$	Ph[b]	>130	>130

[a]Second-order coefficients in dm^3 mol^{-1} min^{-1}. [b]First-order kinetics in min^{-1}.



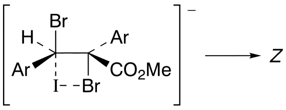
A



B

The total selectivity of TEA, also found for I$^-$, towards the debromination pathway might be attributed to a response of the 2-bromine to the effect of the adjacent carbonyl group which favours C-2—Br over C-3—H bond polarisation. However, the fact that the reactions induced by MeO$^-$ show a preference for dehydrobromination seems to argue against the former explanation. With the available evidence we do not see a justification of this behaviour and feel that more detailed investigation is required to uncover the factors which dictate the discrepancy.

Comparison of the TEA-promoted debromination reactions of the *R*,*S* substrates with those induced by I$^-$ indicates that they show closely similar characteristics, both affording the product of *trans*-elimination (*E*). However, for the reactions with the corresponding *R*,*R* isomers the situation is quite the reverse. In this case, whereas the iodide-promoted reaction leads predominantly to the *anti*-debrominated olefin (*Z*), the stereochemical outcome of the reaction with TEA is the opposite (*E*). These results can be reconciled with the hypothesis that the iodide ion nucleophilicity might assist the separation of the 3-bromine in a transition state leading to *trans* elimination.[1]



In contrast to the former substrates, the introduction of a *p*-methoxyaryl substituent on C-2 causes the compounds to behave in a similar way to that exhibited by the reactions promoted by I$^-$ and MeO$^-$. Thus, the *R*,*S* and *R*,*R* **d** isomers led exclusively to the corresponding dehydrobrominated olefin through a first-order kinetic and relatively rapid process, which is explained as a reflection of the

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†This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1998, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

‡Consistent with this conclusion is the previously observed lower rate of the iodide-promoted debromination of *RR* relative to that of *RS* isomers.[1]

known stability of *p*-methoxybenzyl cations bearing an α-carbonyl substituent.[2]

In the case of the *R,S* and *R,R* **h** substrates, first-order rate coefficients of nearly the same value were observed (Table 1), together with stereoconvergent debromination leading to the *E* olefin. This is an expected consequence of the influence of the *p*-methoxy substituent on the 3-phenyl ring to enhance the leaving-group tendency of the 3-bromine, leading to a 3-carbonium ion which undergoes rotation before ejection of the 2-bromine to give the thermodynamically more stable olefin.§

Experimental

Triethylamine[3] and methanol[4] were purified according to reported procedures.

Methyl 2,3-dibromo-2,2-diarylpropanoates were obtained as described.[1] With the exception of (*R,R*)-**b** and (*R,R*)-**c**, all the diastereoisomers could be separated by repeated silica gel chromatography using light petroleum (bp 60–80 °C)–diethyl ether (49:1) as eluant. The substrates (*R,R*)-**b** and -**c** were obtained as mixtures containing 11% and 30% of their *R,S* isomers respectively. The mps of the solid compounds were as follows. **a**: (*R,S*) 104–106 °C, (*R,R*) 98–100 °C; **b**: (*R,S*) 65–68 °C; **d**: (*R,R*) 102–105 °C; **e**: (*R,S*) 153–156 °C, (*R,R*) 129–132 °C; **f**: (*R,S*) 72–74 °C; **g**: (*R,S*) 103–104 °C; **h**: (*R,S*) 130–133 °C.

Kinetic Procedures.—Rates were measured at 30 ± 0.05 °C. The reactions were initiated by adding a solution of the appropriate substrate in methanol (50 cm^3, 0.6 mmol) to a solution of triethylamine (0.50 mol)–triethylamine hydrochloride (0.20 mol) buffer in the same solvent (50 cm^3), which showed that the amine was the only reactive basic species. Aliquots were withdrawn periodically, quenched in water and extracted with dichloromethane. The solvent was removed by evaporation and the residue analysed by ^1H NMR spectroscopy, following the disappearance of the 3-proton resonance relative to the total methoxycarbonyl peak area. Second-order rate values were obtained as usual from those of pseudo-first-order ones. The kinetics of the impure (*R,R*)-**b** and -**c** compounds were also monitored by ^1H NMR spectroscopy in a similar way, except that the area corresponding to the methoxycarbonyl protons due to the *R,S* isomer was subtracted from the total methoxycarbonyl resonance intensity.

Product analysis.—The reactions were quenched after eight half-lives, worked up in the usual way and analysed by ^1H NMR spectroscopy.

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§A different result was obtained for the reaction of these substrates with MeO^- and I^-, since only solvolytic products were then formed. We tentatively assign the lack of solvolysis to the presence of the large excess of triethylamine which probably interacts with the carbonium centre precluding attack by the solvent.