

Debromination of *meso*- and (\pm)-1,2-Dibromo-1,2-diphenylethane by 9-Substituted Fluorenone Ions. Correlation between Stereochemical Results and Redox Potentials

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The ratio between (*E*)- and (*Z*)-1,2-diphenylethene, (*E*:*Z*), has been obtained for the reaction of ten 9-substituted fluorenone ions with 1,2-dibromo-1,2-diphenylethane in dimethyl sulfoxide. It has been demonstrated that both the redox potential of the fluorenone anion and the bulkiness of the 9-substituent are important parameters in the interpretation of the observed variation (0.08–1.64) of the *E*:*Z* ratio.

meso and (\pm)-dihalo-1,2-diphenylethanes have been used as model compounds in numerous mechanistic investigations of the reductive elimination of vicinal dihalides by various reagents. Two types of reductive elimination have been described. Classical nucleophiles such as iodide,^{1–3} thiolate¹ and cyanide⁴ reduce stereospecifically with both *meso*- and (\pm)-1,2-dihalo-1,2-diphenylethanes in a second-order elimination which here will be termed E2(R), (R for reduction), to distinguish it from the base-promoted E2 elimination of HX. E2(R) involves an inner-sphere electron transfer from the nucleophile to the substrate; the developing double bond in the transition state creates a barrier for the rotation around the central C–C bond.

One-electron reagents such as Cu(I),⁵ Cr(II),⁶ Fe(II)¹ and aromatic anion radicals^{7–10} react with vicinal dibromoethanes by an electron transfer (ET) mechanism involving radical intermediates. In general, the stereospecificity of the reaction is low; however, *meso*-1,2-dichloro-1,2-diphenylethane (*meso*-SCl₂), *meso*-SBr₂ and (\pm)-SCl₂ are reduced to 100% (*E*)-stilbene by one-electron reagents, while the reaction of (\pm)-SBr₂ gives slightly different results: 85–100% (*E*)-stilbene and 0–15% (*Z*)-stilbene are formed.

meso-SBr₂ is converted by both two-electron and one-electron reductants into (*E*)-stilbene and is therefore not very useful as a stereochemical probe in mechanistic investigations. Stereochemical information of the reaction of (\pm)-SBr₂ may, however, be used to distinguish between a polar *anti* reductive elimination mechanism E2(R) and an ET process. From an E2(R) mechanism

(*Z*)-stilbene is obtained while predominantly (*E*)-stilbene is expected if an ET mechanism is followed.

In the reaction of the enolate anion of 1,4-dihydro-4-methoxycarbonyl-1-methylpyridine (**1**[–]) with (\pm)-SBr₂ 100% (*E*)-stilbene was obtained indicating an outer-sphere ET mechanism.⁹ Ion **1**[–] has a very negative redox potential, (*E*^o = –1.3 V vs. NHE), and is therefore expected to be an efficient electron donor. The nucleophiles I[–] and PhS[–] are rather poor electron donors with estimated redox potentials in water of +1.4 V and +0.4 V vs. NHE, respectively.¹¹

The enolate anion of **1** has been shown to react with sterically hindered alkyl halides through an initial outer-sphere ET mechanism^{12,13} while I[–] reacts as a nucleophile in the Finkelstein reaction by a polar S_N2 two-electron mechanism.¹¹

At the extremes of the potential interval +0.4 V to –1.3 V, two different reductive debromination mechanisms are operative. In this interval there is a change from predominantly E2(R) to predominantly ET resulting in a mixed stereochemical product composition.

A systematic investigation of the correlation between redox potentials of nucleophiles and the stereochemistry of debromination reactions of vicinal dihalides has, to our knowledge, not been performed. This might partly be due to the fact that only very few reversible redox potentials of nucleophiles are known.

9-Substituted fluorenone ions, however, are nucleophiles for which reversible redox potentials can be obtained from a combination of normal cyclic voltammetry¹⁴ and fast CV techniques at an ultramicroelec-

trode.¹⁵ The redox potentials of fluorenone ions cover a wide range from +0.5 V to -0.8 V vs. NHE and these compounds therefore seem well suited to an investigation of the influence of redox potential vs. stereochemistry in the debromination reaction of (\pm)-SBr₂. Recently Bordwell *et al.* have investigated the reactions of the 9-substituted fluorenone ions in S_N2 reactions of aliphatic and benzyl halides.¹⁶⁻¹⁹

Results and discussion

The analysis of the product mixtures of the reactions of (\pm)- and *meso*-SBr₂ with 9-substituted fluorenone ions in dimethyl sulfoxide (DMSO) are shown in Tables 1 and 2.

A fluorenone anion may react as a base, as a polar reductant and/or as a one-electron donor (Scheme 1). The monobromostilbenes are obtained by a base-catalysed E2 mechanism with elimination of HBr while the stilbenes are formed by a reductive debromination of *meso*- and (\pm)-SBr₂ either by a polar reductive elimination E2(R) or a radical mechanism (ET).

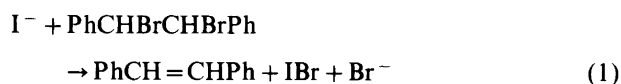
Stoichiometry. The ratio between (*E*)- and (*Z*)-stilbene in the debromination reaction depends in some cases upon the overall stoichiometry. A brief discussion of the stoichiometry is therefore required.

Two series of experiments were performed, in one of which the initial ratio between Nu⁻ and SBr₂ was 1 : 1 and the reaction time 1-2 days (the A series). In the second series (the 'B experiments') the starting ratio was 2 : 1 and the reaction time was approximately five minutes.

The stoichiometry of the base-induced E2 is best illustrated by the B experiments. In these experiments the stoichiometric relationship between the disappearance of the nucleophile Δn_{Nu} and the products from the base-induced elimination, (*E*)- and (*Z*)-1-bromo-1,2-diphenylethene [(*E*)-SBr, (*Z*)-SBr] and diphenylethene (DPE) is given by the equations

$$\Delta n_{\text{Nu}} = n_{\text{NuH}} = n_{(\text{Z})\text{-SBr}} + n_{(\text{E})\text{-SBr}} + 2n_{\text{DPE}}.$$

In the classical reaction of iodide with SBr₂ a 2 : 1 stoichiometry is observed.



A similar 2 : 1 stoichiometry is observed in the B experiments. The 2 : 1 stoichiometry may be explained by eqns. (3)-(7).

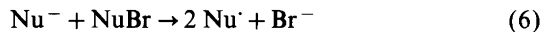
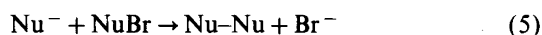
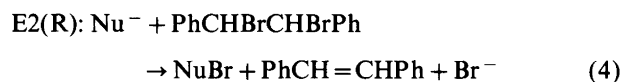
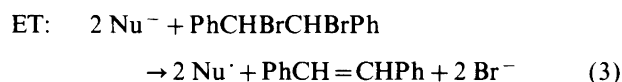


Table 1. Product yields (in μmol) of the reaction of 9-substituted fluorenone ions (9-G-FI⁻) and thiophenolate (PhS⁻) with (\pm)-1,2-dibromo-1,2-diphenylethane [(\pm)-SBr₂] in DMSO at room temperature.

G	Exp.	9-G-FI ⁻ (μmol)	(\pm)-SBr ₂ (μmol)	(<i>E</i>)-S	(<i>Z</i>)-S	(<i>E</i>)-SBr	(<i>Z</i>)-SBr	DPE	(\pm)-SBr ₂	9-G-FIH	<i>E</i> : <i>Z</i> ^a	R : B ^b	% yield ^c
Pyrrolidinyl	1A	350	350	94	73	0	31	50	120	102	1.3	2.06	108
Dimethylamino	2A	350	350	20	49	14	81	25	119	256	0.41	0.58	82
Piperidyl	3A	380	380	16	22	3	125	196	71	290	0.72	0.12	117
Diisopropylamino	4A	324	324	78	19	0	107	63	25	195	4.1	0.57	89
Methoxy	5A	119	199	5.7	17	0.03	90	65	10	112	0.34	0.15	94
Methyl	6A	199	199	11	66	1.1	31	74	42	57	0.17	0.73	117
<i>tert</i> -Butyl	7A	264	263	26	94	4.4	3.6	44	38	134	0.28	2.31	76
Phenyl	8A	199	199	4.8	17	0.6	117	74	0	87	0.28	0.11	107
Hydrogen	9A	380	380	18	97	0	149	85	72	180	0.18	0.49	113
Phenylthio	10A	380	380	13	165	1.9	45	67	122	46	0.08	1.56	113
PhS ⁻	11A	1339	1339	59	696	0	60	0	537	0	0.08	12.58	102
Pyrrolidinyl	1B	564	316	66	72	0	20	131	8.7	265	0.91	0.91	94
Dimethylamino	2B	590	286	34	83	0	0	166	0	298	0.41	0.70	99
Piperidyl	3B	584	290	35	69	0	0	171	0	338	0.51	0.61	95
Diisopropylamino	4B	611	291	61	37	0.6	91.5	56	21	398	1.64	0.66	91
Methoxy	5B	587	311	19	48	0	61	245	12	347	0.40	0.22	125
Methyl	6B	532	294	22	172	0	30	77	18	136	0.13	1.81	109
<i>tert</i> -Butyl	7B	532	294	12	66	0	28	203	17	478	0.18	0.34	112
Phenyl	8B	532	294	11	40	0	125	166	3	367	0.27	0.18	118
Hydrogen	9B	532	294	19	145	0	42	95	4	196	0.13	1.20	104
Phenylthio	10B	532	294	17	217	0	33	4.0	35	112	0.08	6.32	105
PhS ⁻	11B	1473	293	23	265	0	0	0	18	—	0.086	—	105

^aMolar ratio between (*E*)-S and (*Z*)-S. ^bR : B = $n_{(\text{E})\text{-S}} + n_{(\text{Z})\text{-S}} / (n_{(\text{E})\text{-SBr}} + n_{(\text{Z})\text{-SBr}} + n_{\text{DPE}})$. ^cYield = $n_{(\text{E})\text{-S}} + n_{(\text{Z})\text{-S}} + n_{(\text{E})\text{-SBr}} + n_{(\text{Z})\text{-SBr}} + n_{\text{DPE}} / (n_{\text{SBr}_2})_{\text{Start}} - (n_{\text{SBr}_2})_{\text{Final}}$.

Table 2. Product yields (in μmol) of the reaction of 9-substituted fluorene ions (9-G-Fl⁻) and thiophenolate (PhS⁻) with *meso*-1,2-dibromo-1,2-diphenylethane (*meso*-SBr₂) in DMSO at room temperature.

G	Exp.	9-G-Fl ⁻		<i>meso</i> -SBr ₂		(E)-S	(Z)-S	(E)-SBr	(Z)-SBr	DPE	<i>meso</i> -SBr ₂	9-G-FIH	E : Z ^a	R : B ^b	% yield ^c
		(μmol)	(μmol)	(μmol)	(μmol)										
PyrrolidinyI	21A	324	324	275	1.9	12	0	8.4	0	30	143	13.57	92		
Dimethylamino	22A	350	350	140	49	22	0	0	35	60	2.9	8.59	67		
Piperidyl	23A	380	380	232	9.1	53	0.5	20.5	0	95	25	3.26	83		
Piperidyl	23B	572	294	259	0	7	0	0	5	132	∞	37.00	92		
Diisopropylamino	24A	324	324	230	5.2	68	0	13	0	36	44	2.90	98		
Methoxy	25A	199	199	103	5	61	0.8	17.5	1.1	1.6	21	1.36	95		
Methyl	26A	294	317	183	2.7	11	1.4	0	106	11	68	14.98	94		
Phenyl	27A	199	199	138	0.4	34	1.1	8.6	0	30	345	3.17	92		
Hydrogen	28A	317	296	211	6	0	0	0	68	2.9	35	—	95		
Phenylthio	29A	380	380	190	15	18	0	12	65	57	13	6.83	75		
PhS ⁻	30A	518	518	359	7.5	0	0	0	124	—	48	—	93		

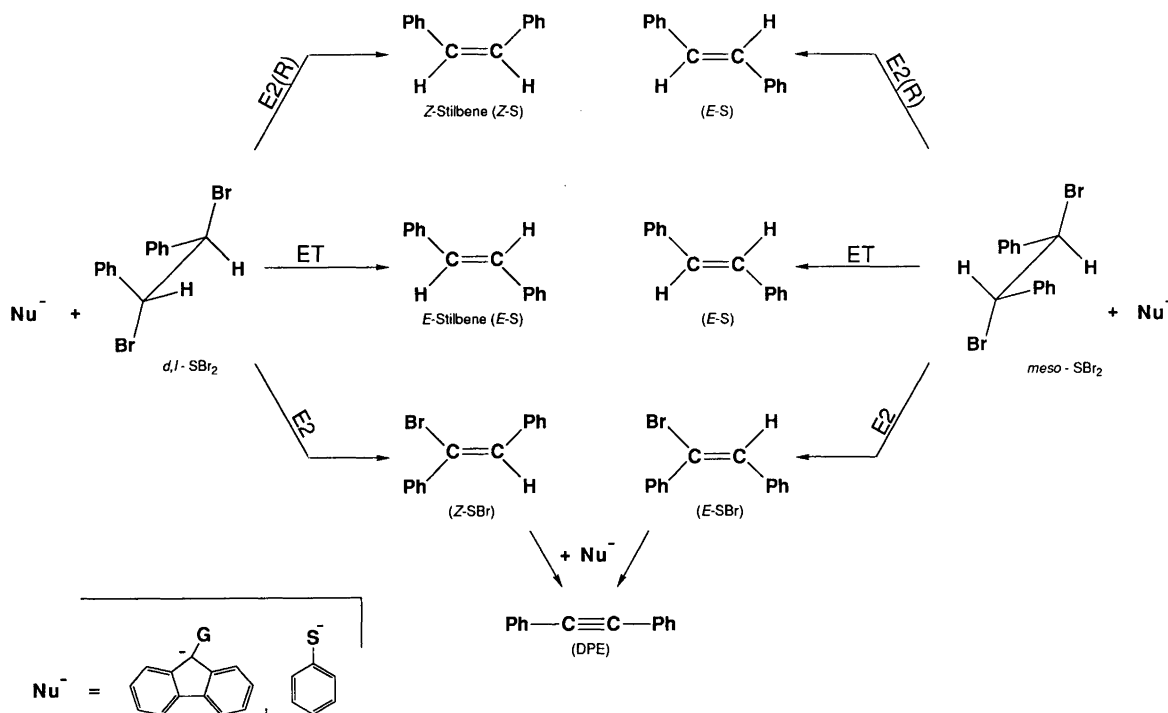
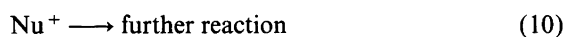
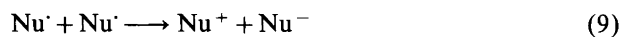
^a Molar ratio between (E)-S and (Z)-S. ^b R : B = $n_{(E)-S} + n_{(Z)-S} / n_{(E)-SBr} + n_{(Z)-SBr} + n_{DPE}$. ^c Yield = $n_{(E)-S} + n_{(Z)-S} + n_{(E)-SBr} + n_{(Z)-SBr} + n_{DPE} / (n_{SBr_2}^{\text{Start}} - n_{SBr_2}^{\text{Final}})$.

The dimeric product Nu-Nu (and Nu=Nu) has been observed only in the reactions between thiophenolate and the unsubstituted 9-fluorene anion with SBr₂ [diphenyl disulfide, 9,9'-bi-9H-fluorene and 9-(fluoren-9-ylidene)-fluorene]. No other dimeric products were detected, which might be attributed to the difficulties for dimers with high molecular weight to pass through the GC column. In the experiments in which the starting ratio between Nu⁻ and SBr₂ were 1 : 1 the overall stoichiometry after 24 h is 1 : 1 in most cases.

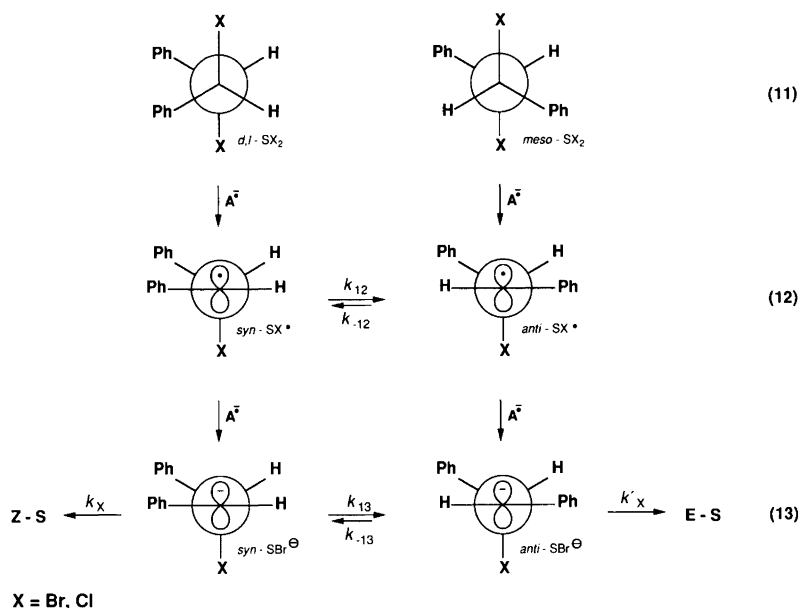
In experiment 11A, 22A, 28A and 30A, mixed stoichiometry was observed. The 1 : 1 stoichiometry is expected if the rate of the reactions (5) and (6) is slow compared with (4). No NuBr products, however, were identified in the reaction mixtures. This might be due to the instability of the NuBr products in the GC analysis

and/or the further reaction of NuBr during the work-up of the reaction mixture.

If the reaction proceeds through an ET mechanism an overall 2 : 1 stoichiometry is expected. However, the 1 : 1 stoichiometry may be explained if the radical Nu[•] generated in reaction (5) is able to react with the dibromide (8) or react in a slow disproportionation reaction (9).



Scheme 1.



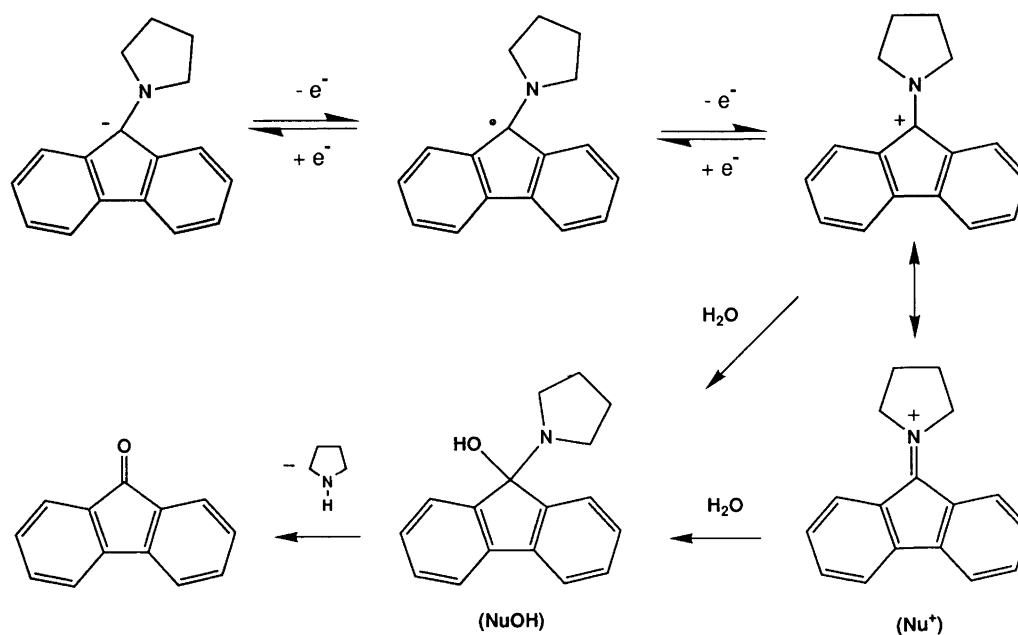
Scheme 2.

In all the reactions of the fluorenone ions containing a hetero atom, 9-fluorenone was observed in various amounts. The formation of 9-fluorenone may be explained by the reaction of water with NuBr or Nu⁺ with the formation of NuOH followed by the elimination of the hetero substituent (see Scheme 3). In the reactions of 9-phenyl- and 9-methylfluorenone anions no 9-fluorenone was obtained; however, 9-methylene-9*H*-fluorene was obtained in small amounts in the reactions of 9-methylfluorenone ion.

Base-induced elimination vs. reductive debromination. As seen from Tables 1 and 2 HBr is eliminated from both

(±)- and *meso*-SBr₂ by an almost 100% *anti* E2 mechanism. It cannot be excluded that the low yield (0–3%) of the *syn*-product, (*E*)-SBr, in the reaction of (±)-SBr₂ is due to a small contaminating amount of *meso*-SBr₂ in the (±)-SBr₂.

The ratio, R : B, between the debromination products (*E*)- and (*Z*)-stilbene [(*E*)-S and (*Z*)-S] and the base-elimination products (*E*)- and (*Z*)-bromostilbenes [(*E*)-SBr and (*Z*)-SBr] and diphenylethyne (DPE) is 6–50 times higher for the *meso*-SBr₂ than for the (±)-SBr₂. The base-induced elimination of hydrogen bromide (E2) prefers, as is usually assumed, an antiperiplanar transition state; in such a transition state



Scheme 3.

the phenyl groups are *anti* in (\pm)-SBr₂ whereas they are *gauche* in the *meso* compound. The rate of E2 would thus be higher for (\pm)-SBr₂ than for *meso*-SBr₂.

The inner-sphere ET reductive elimination [E2(R)] of the dibromide also prefers an antiperiplanar transition state owing to the double bond developing during the reaction; this is also reflected in the slightly more negative reduction potential of (\pm)-SBr₂ compared with *meso*-SBr₂.⁸ In accordance with this the rate of electron transfer to *meso*-SBr₂ has been found to be slightly higher than that to (\pm)-SBr₂.⁹ The differences in rate for the base-induced elimination explains why the ratio R : B is higher for *meso*-SBr₂ than for (\pm)-SBr₂.

The rate constants k_{ET} and, to a lesser degree, $k_{E2(R)}$ would depend on E°_{Nu} and the ratio R : B would be expected to depend on E°_{Nu} , if the base strength of the nucleophiles in a series were constant. The pK_a -values of 9-pyrrolidinyl-, 9-dimethylamino- and 9-piperidinyl-fluorene are 22.5,²⁰ so k_{E2} would be expected to be constant as steric factors are to a first approximation equal. The standard potentials of the fluorenyl anions increase in the series from -0.785 V through -0.660 V to -0.635 V vs. NHE, and $k_{ET} + k_{E2(R)}$ and thus R : B should then decrease through the series, which is in accordance with the experimental results (see experiments 1B, 2B and 3B in Table 1.)

The ET reaction. It is generally accepted that aromatic anion radicals react with sterically hindered alkyl halides and vicinal dihalides by an outer-sphere ET process.⁸⁻¹⁰ Therefore, in order to establish the expected *E* : *Z* stilbene ratio for *meso*-SBr₂ and (\pm)-SBr₂ in DMSO of an ET-process these two compounds were reacted with a number of electrogenerated anion radicals. The results are shown in Table 3. *meso*-SBr₂ is reduced to 99.8–100% (*E*)-stilbene, (*E* : *Z* > 500), while (\pm)-SBr₂ is converted into 88–95% (*E*)-stilbene and 5–12% (*Z*)-stilbene, with an average value of *E* : *Z* = 11. This value is very similar to the *E* : *Z* = 10–11 obtained in the direct reduction of (\pm)-SBr₂ at a mercury electrode in *N,N*-dimethylformamide⁸ and in acetonitrile at not too negative reduction potentials.^{21a,b}

In order to test whether the *E* : *Z* ratio depended on the concentration of the anion radical, solutions with dif-

Table 3. The ratio between (*E*)- and (*Z*)-stilbene, *E* : *Z*, obtained in the 2 : 1 reactions of aromatic anion radicals, A^{•-}, with (\pm)- and *meso*-1,2-dibromo-1,2-diphenylethane.

A	SBr ₂	Method ^a	E°/V vs. NHE	<i>E</i> : <i>Z</i>
Perylene	\pm	1	-1.37	10
Diacetylbenzene	\pm	1	-1.16	17.9
4-Methoxycarbonylazobenzene	\pm	1	-0.77	7.0
1-Nitronaphthalene	\pm	2	-0.40	10.3
4-Methoxycarbonylazobenzene	<i>meso</i>	2	-0.77	633

^aMethod 1: SBr₂ added after the completion of the reduction of A to A^{•-}. Method 2: A was reduced in the presence of SBr₂.

ferent concentrations of the anion radicals of diacetylbenzene and (\pm)-SBr₂ were made according to Table 4. Two syringes containing the solution of the anion radical and the (\pm)-SBr₂, respectively, were injected simultaneously into a reaction tube. The results in Table 4 show a minor non-systematic variation in *E* : *Z* as a function of the anion radical concentration.

The fact that different anion radicals, and different concentrations of these, give approximately the same *E* : *Z* ratio suggests that they transfer electrons to the dibromide in an outer-sphere ET reaction in accordance with previous assumptions, and that an outer-sphere ET reductive elimination of (\pm)-SBr₂ would give *E* : *Z* \cong 10.

The mechanism of the reaction between one-electron reagents like aromatic anion radicals and aliphatic vicinal dihalides and 1,2-dichloro-1,2-diphenylethanes (SCl₂) has been discussed by Savéant,¹⁰ Garst⁷ and Lund.⁸ In Scheme 2, a possible reaction mechanism is depicted. The initial step is a rate-determining ET from the anion radical to the dibromide [eqn. (11)]. As discussed above, the ET to the dibromide occurs most favourably to the conformer in which the two bromine atoms are antiperiplanar. Therefore, (\pm)-SBr₂ is transformed in the ET step into the *syn*-SBr[•] where one phenyl group is between the other phenyl group and the bromine (see Scheme 2). The initial ET is followed by two competing reactions [eqns. (12) and (13)]. In eqn. (12) (Scheme 2), the *syn*-SBr[•] radical is transformed into *anti*-SBr[•] by a rotation around the central carbon-carbon bond. Alternatively, the *syn*-SBr[•] may react with the anion radical in a diffusion-controlled ET step with formation of the carbanion *syn*-SBr⁻.

The rate of rotation for *syn*-SBr[•], k_{12} , from the less favored *syn* conformation to the preferred *anti* conformation is not known; for SBr₂ a barrier of rotation of at least 6 kcal mol⁻¹ seems reasonable as butane has a barrier of that size between the *anti* and eclipsed forms. This would give a lifetime of a rotational conformer of about 10⁻⁸ s; the barrier in SBr[•] is probably somewhat higher owing to a coupling between the unpaired electron and the bromine²² and the lifetime of the conformer somewhat longer.²²

In all the experiments performed in this work, the initial anion radical concentration was between 5–50 mM and so $k_d[A^{\bullet-}] > k_{12}$. Therefore most of the *syn*-SBr[•] radicals will be reduced to *syn*-SBr⁻ and the *E* : *Z* ratio is predominantly determined by the ratio between the rate

Table 4. *E* : *Z* ratios obtained for the reaction of (\pm)-SBr₂ with *p*-diacetylbenzene anion radicals A^{•-} (Method 3) as a function of [A^{•-}].

[A ^{•-}]/mM	[(\pm)-SBr ₂]/mM	[(Bu) ₄ NBF ₄]/mM	<i>E</i> : <i>Z</i>
48	14.6	50	17.7
24	7.3	50	11.5
12	3.6	50	13.2
12	3.5	13	7.1

of rotation around the central C–C bond in the *syn*-SBr[−] to *anti*-SBr[−] (k_{13}) and the rate of *syn*-elimination of Br[−] from *syn*-SBr[−] (k_{Br}).

In the reactions of (±)-SCl₂ with aromatic anion radicals an *E*:*Z* ratio >200 was obtained. This might be explained by the decreased rate of Cl[−] elimination compared with the elimination of Br[−].

In Table 4 it is seen that the *E*:*Z* ratio depends slightly upon the concentration of the supporting electrolyte. As observed previously⁸ the cation of the supporting electrolyte may stabilize the carbanion *syn*-SBr[−] and thereby decrease the rate of Br[−] elimination. The *E*:*Z* ratio is therefore as expected and indeed is observed to increase with increasing supporting electrolyte concentration.

Fluorenyl radicals as electron donors. 9-Substituted fluorenyl ions generated from pyrrolidinyl-, diisopropylamino-, piperidyl- and methoxy-fluorene show two reversible waves in cyclic voltammetry at slow scan rates ($v_{scan} = 0.1 \text{ V s}^{-1}$).¹⁵ The redox behaviour of the 9-pyrrolidinylfluorenyl ion is shown in Scheme 3.

In the reaction of 9-pyrrolidinylfluorenyl ion with (±)-SBr₂ in the molar ratio 1:1, the color changes from deep red to brown/yellow over 1–2 minutes. After several hours the color of the reaction mixture changes to green. The fast color change may be attributed to the reaction of the pyrrolidinylfluorenyl anion ($E^\circ = -0.785 \text{ V vs. NHE}$)¹⁵ while the slow color change may be identified as the ET process of pyrrolidinylfluorenyl radicals ($E^\circ = -0.155 \text{ V vs. NHE}$)¹⁵ with the remaining (±)-SBr₂. If free fluorenyl radicals are involved in a slow follow-up reaction this will certainly have an important influence upon the measured *E*:*Z* ratio. In the B-experiments the influence of any free fluorenyl radicals would be eliminated owing to the short reaction time when a 2:1 ratio of Nu[−] and SBr₂ is used.

ET versus E2(R). The ratios between (*E*)- and (*Z*)-stilbene (*E*:*Z*) obtained from the reaction of ten

Table 5. The ratio between (*E*)- and (*Z*)-stilbene from the reaction of substituted fluorene ions and thiophenolate (PhS[−]) with (±)-1,2-dibromo-1,2-diphenylethane as a function of the redox potential of the fluorenes.

G	E°/V vs. NHE	CV	pK _a ^c	(<i>E</i> : <i>Z</i>) _A ^d	(<i>E</i> : <i>Z</i>) _B ^e
Pyrrolidinyl	−0.785	Rev. ^b	22.5 ²⁰	1.3	0.91
Dimethylamino	−0.660	Rev.	22.5 ²⁰	0.41	0.41
Piperidyl	−0.635	Rev.	22.5 ²⁰	0.72	0.51
Diisopropylamino	−0.463	Rev.	20.5 ¹⁴	4.1	1.64
Methoxy	−0.450	Rev.	22.1 ¹⁴	0.34	0.40
Methyl	−0.357	Irr.	22.3 ¹⁴	0.17	0.13
<i>tert</i> -Butyl	−0.325	Irr.	24.4 ¹⁴	0.28	0.18
Phenyl	−0.203	Irr.	17.9 ¹⁴	0.28	0.27
Hydrogen	−0.195	Irr.	22.6 ²⁴	0.18	0.13
Phenylthio	+0.031	Irr.	12.3 ¹⁴	0.08	0.08
PhS [−]	+0.400	Irr.	—	0.08	0.086

^aFrom Ref. 15. ^bReversible at scan rate 0.1 V s^{−1}. ^cpK_a in DMSO. ^d*E*:*Z* ratios from experiment series A: Nu[−]: (±)-SBr₂ = 1:1. ^e*E*:*Z* ratios from experiment series B: Nu[−]: (±)-SBr₂ = 2:1.

9-substituted fluorenyl ions with (±)-SBr₂ are shown in Table 5. The *E*:*Z* value of thiophenolate is included in order to have a stereochemical reference value of a nucleophile which reacts predominantly by an E2(R) mechanism. The reference value *E*:*Z* = 0.086 indicates that the reaction of thiophenolate with (±)-SBr₂ does not proceed by a pure anti E2(R) debromination mechanism. A contribution from an ET mechanism seems unlikely owing to the positive redox potential of the thiophenolate which has been estimated to +0.4 V vs. NHE. The slight deviation from a 100% stereospecific reaction might be attributed to a minor competition from an E1 mechanism involving free carbocations¹ or a *syn*-elimination.

The reproducibility of the *E*:*Z* values in Table 5, is typically ±0.05, regardless of minor changes in the starting concentrations of Nu[−] and (±)-SBr₂.

As seen from Table 5 there is a difference between the *E*:*Z* values for the A-experiments and the B-experiments.

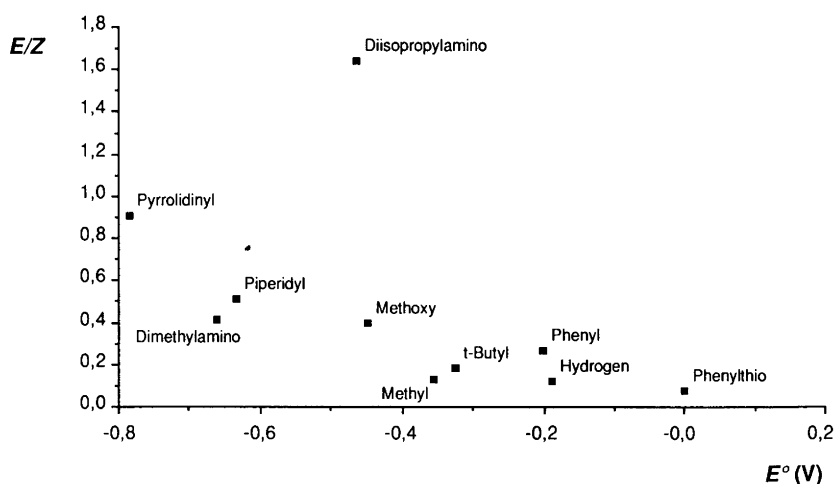
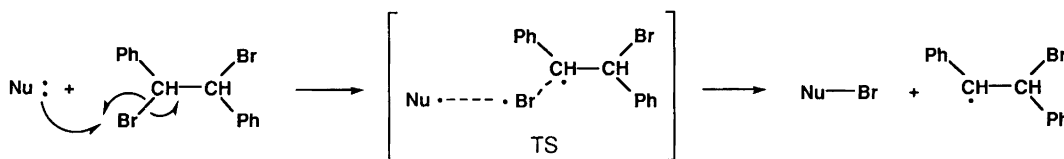


Fig. 1. The ratio between (*E*)- and (*Z*)-stilbene, *E*:*Z*, as a function of the redox potential (vs. NHE) of the 9-substituted fluorenyl ions. [9-G-FI[−]: (±)-SBr₂ = 2:1, 'B-experiments'].



Scheme 4.

The difference is largest in the experiments of pyrrolidinyfluorene (0.9 and 1.3) and diisopropylaminofluorene (1.64 and 4.1). According to the discussion above, this may indicate that free fluorenyl radicals are, to a certain extent, involved in reactions of *meso*- and (\pm)-SBr₂.

In Fig. 1 the *E*:*Z* values of the B-experiments (Table 5) are plotted as a function of E° of the anions. It is seen from Fig. 1 that the *E*:*Z* ratio decreases from 0.9 for 9-pyrrolidinyfluorene ($E^\circ = -0.785$ V) to the polar two-electron reference value 0.086 for 9-thiophenylfluorene ($E^\circ = +0.031$ V). However, the curve of *E*:*Z* vs. E° contains some irregular points which may be attributed to steric factors. A bulky substituent is expected to favor the ET mechanism relative to the E2(R) mechanism in which the steric constraints are much higher than for the ET reaction. The reaction of 9-diisopropylaminofluorene (*E*:*Z* = 1.64) demonstrates this clearly.

The reaction of 9-diisopropylaminofluorene and 9-phenylthiofluorene are examples of the two extremes of the mechanistic scenario, ET versus E2(R). The other 9-substituted fluorene ions listed in Table 5 show an intermediate stereochemical outcome which indicates a mixed mechanism. The mechanistic picture may simply be interpreted as a competition between two independent mechanisms ET and E2(R). However, a unified mechanism may also be suggested in which ET and E2(R) are the extremes of the same mechanism. The transition state (TS) might be described as shown in Scheme 4. The interaction between Nu \cdots Br \cdots C in the TS is <1 kcal in a pure outer-sphere ET process whereas it continuously increases in the direction of the E2(R) region of the ET-E2(R) mechanistic spectrum. In the reactions of 9-pyrrolidiny- and diisopropylamino-fluorene the inner-sphere interaction is probably so low that Nu \cdot may be able to escape from the solvent cage.

The ET-E2(R) mechanistic picture described above is very similar to the ET-S_N2 hybrid model of the nucleophilic substitution reactions suggested recently by Bordwell^{14,16-19} and Lund.^{12,13}

Conclusions

The ratio between (*E*)-stilbene and (*Z*)-stilbene (*E*:*Z*) in the reaction of ten substituted fluorene ions with (\pm)-SBr₂ in DMSO has been obtained. It is most likely that both the redox potential of the fluorene anion and the bulkiness of the 9-substituent are important in explaining the observed variation of the *E*:*Z* ratio. The results show that fluorene ions with redox potentials

more negative than -0.0 V vs. NHE react with (\pm)-SBr₂ by a non-stereospecific mechanism and fluorene ions with a more positive redox potential react by a stereospecific E2(R) mechanism. The redox limit -0.0 V may be used as a rough guideline in an attempt to predict the stereochemistry of the debromination reaction of (\pm)-SBr₂ by nucleophiles with known or estimated redox potential.

The reductive debromination of (\pm)-SBr₂ (and *meso*-SBr₂) with fluorene anions may be considered as an inner-sphere ET reaction in which the strength of the inner-sphere interaction depends upon the redox potential and steric factors. A nucleophile with a negative redox potential is able to transfer the electron to SBr₂ in the TS from a greater distance than a nucleophile with a more positive redox potential. Therefore the inner-sphere interaction is expected to decrease as the redox potential becomes more negative. The inner-sphere interaction also decreases with increased bulkiness of the nucleophile. Therefore both a decrease in the redox potential and an increase of bulkiness of the nucleophile will increase the *E*:*Z* ratio until the outer-sphere ET *E*:*Z* ratio $\cong 10$ is reached.

Experimental

Materials. DMSO was stored under nitrogen (Sure-Seal bottle), potassium hydride, *meso*-SBr₂, (*Z*)-stilbene and fluorene were obtained from Aldrich. (\pm)-SBr₂ was synthesized according to the method of Fieser.²³ The purity of (\pm)-SBr₂ was >97% as determined by GC in different preparations.

The substituted aminofluorenes were synthesized by the method of Bordwell.²⁰ The 9-alkylsubstituted fluorenes were obtained by reduction of the corresponding 9-alkyl-substituted fluorenol in acetic acid containing I₂ and hypophosphorous acid.²⁴ The synthesis of 9-phenylthiofluorene was carried out according to Bavin.²⁵ Potassium dimsyl (KCH₂SOCH₃) was prepared by the method of Bordwell.²⁶

Apparatus. Products were identified by GC-MS run on a Hewlett Packard 5890 A gas chromatograph equipped with a 5971A MSD. Quantitative measurements were obtained by GC-FID. An HP1 12 m, 0.25 mm internal diameter non-polar GC-column was used, injection temperature 250°C, helium flow 1.0 ml min⁻¹, temperature program 70°C in 5 min to 300°C, rate 5°C min⁻¹. The following retention times (t_R /min) and response factors relative to diphenyl (R_x) were obtained. Diphenyl (15.34,

1.000); (Z)-S (19.04, 1.12); DPE (22.30, 1.175); (E)-S (23.39, 1.145); (E)-SBr (24.70, 1.10); (Z)-SBr (27.42, 1.10); (\pm)-SBr₂ (29.64, 0.94); *meso*-SBr₂ (30.2, 1.026).

Reaction of 1,2-dibromo-1,2-diphenylethane (SBr₂) with fluorene anions (1:1): 'A-experiments'. A solution of the 9-substituted fluorene (350 μ mol) was transferred to a test tube sealed with a tight rubber membrane. After deaeration with argon 2 ml of DMSO and the calculated amount of dimethylpotassium (2 ml) (total reaction volume of 4 ml) were transferred under argon to the test tube by the syringe technique. After completion of the acid-base reaction of dimethylpotassium the rubber membrane was removed and 350 μ mol of solid dibromide were added in a flow of argon. The test tube was protected from light with aluminium foil and placed in the dark. After one day 100 mg of diphenyl were added as an internal standard. The reaction mixture was poured into water and extracted with 50 ml of diethyl ether. The ethereal layer was washed three times with water and dried with 4 Å molecular sieves. The ether extract was analysed by GC-MS and GC-FID.

Reaction of SBr₂ with fluorene ions (1:2): 'B-experiments'. The same procedure as described above with a reaction time of 5 min but with double the concentration of anion.

Reaction of anion radicals with SBr₂: Method 1. *p*-Diacetylbenzene (87 mg, 0.538 mM) was reduced under argon in 29 ml DMSO/0.1 mol tetrabutylammonium tetrafluoroborate at -1.0 V vs. a silver wire in an H-cell containing a mercury pool cathode. After the consumption of 88 C (\pm)-SBr₂ (93.4 mg, 0.276 mmol) was added whereupon the blue color of the anion radicals disappeared. After addition of an internal standard, the electrolysis mixture was poured into water and extracted with diethyl ether and analysed as described above.

Method 2. 1-Nitronaphthalene (103.8 mg, 0.600 mM) was reduced under argon in DMSO/0.1 M TBABF₄ at -0.7 V vs. Ag in the presence of (\pm)-SBr₂ (104 mg, 0.308 mM) in an H-cell containing a mercury pool cathode (area 7 cm²). The reduction current was 100 mA. After 60 C (*n* = 1) diphenyl (98 mg) was added as an internal standard and the electrolysis mixture poured into water, extracted with diethyl ether and analysed as described above.

Method 3: E/Z as a function of the anion radical concentration. Three argon-deaerated solutions of (\pm)-SBr₂ in DMSO deaerated with argon were prepared at concentrations of 14.6 mM, 7.3 mM and 3.6 mM, respectively, in three tubes (1, 2 and 3) equipped with rubber septa. Three solutions, A, B and C, of diacetylbenzene anion radicals in DMSO/0.1 M TBABF₄ were prepared according to the following procedure. *p*-Diacetylbenzene (234 mg, 1.44 mM) was reduced under argon in 29 ml

DMSO/0.1 M TBABF₄ in an H-cell with a platinum net as cathode at -1.4 V vs. a silver wire. After the consumption of 133 C the concentration of diacetylbenzene anion radical was calculated to be 47.5 mM (solution A). Solutions B and C were prepared by dilution of 2 ml of solution A with 2 and 6 ml DMSO/0.1 M TBABF₄, respectively, in tubes well deaerated with argon. 2 ml of the (\pm)-SBr₂ and anion radical solutions were mixed (1A, 2B and 3C) by means of two syringes which were emptied simultaneously into a tube under argon. The reaction mixture was quenched with 1 drop of acetic acid and 25 ml of diethyl ether were added. The ether phase was washed with water, dried with MgSO₄ and reduced to 2-5 ml under reduced pressure and analysed by GC-FID.

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