Influence of Solvent and Cation on the Properties of Oxygen-containing Organic Anions. Part 4.† Mechanism and Reactivity of Tetraaryloxirane Cleavage with Alkali Metals

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Six tetraaryloxiranes **1a–f** (Scheme 4) were reduced (Schemes 1–3) with alkali metals (M = Li, Na, K, Cs) in eight polar aprotic solvents under an inert atmosphere. The organometallic solutions thus obtained were hydrolysed and the reaction products analysed. Similar experiments were carried out where the same solutions were quenched with D_2O or MeI. In some cases the same solutions were studied by NMR and ESR spectroscopy before quenching. A stepwise reduction mechanism was established where the transfer of a first electron produces CO-bond scission in the oxirane ring, yielding a short-lived radical anion **4** or **5** (Scheme 1), *i.e.* a tetraaryl-β-oxidoethyl radical. This intermediate can either eliminate oxygen as metal oxide (MO) to produce a tetraarylethylene **24** (Scheme 2) or be further reduced to a dianion **8** or **9** (Scheme 1). This anion yields, upon hydrolysis, low yields, if any, of the corresponding tetraphenylethanol **15** or **16** (Z = H). The larger proportion of the dianion, after the first protonation step, yielding anion **11** or **12**, undergoes CC-bond scission which leads eventually to the corresponding ketone and diarylmethane **19** + **20** or **21** + **23** (Z = H) (Scheme 2). Other possible pathways were excluded through experiments where other possible intermediates were generated. These led to different end products. A triparametric linear correlation as a function of solvent parameters E_T^N and *DN*, as well as the cationic radius, was established for the influence of the nature of the solvent and counter-ion on the ratio between the rates of formation of products stemming from metal oxide (MO) elimination by the ring-opened radical anion **4** or **5** (Schemes 1 and 2) and rates of formation of products stemming from further reduction of the same radical anion to the dianion **8** or **9**, thus confirming the mechanism established.

The mechanism of oxirane **1** reduction (Scheme 1) by stepwise electron transfer is less well understood than that of nucleophilic ring opening by means of a hydride ion.[1] Early reports on reactions of oxiranes with alkali metals refer mostly to either Birch reductions[1,2] (in liquid ammonia in the presence of a lower alcohol), or reactions in neat liquid ammonia,[2] or in an alkylamine.[3] Kaiser *et al.*[2] demonstrated for the reaction of styrene oxide **1** (R^1 = Ph; R^2–R^4 = H) and stilbene oxide **1** R^1 = R^4 = Ph; R^2 = R^3 = H) with M = Li, Na, or K in liquid ammonia that a short lived dianion **8** picks up a proton from ammonia to yield anion **11** (Z = H), which is converted into the 2-aryl substituted ethanol **15** (Z = H) by protolysis with ammonium chloride. The same experiment with styrene oxide and lithium, in a mixture of hexamethylphosphoramide (HMPA) and diethyl ether, revealed a stable dianion **8** (R^1 = Ph, R^2–R^4 = H, M = Li) through the formation of compound **15** (Z = D), deuteriated at the benzylic carbon, by deuterolysis with D_2O.

Similar dianions **8** or **9** were more recently prepared by Bartmann[4a] and Cohen and co-workers[4b–d] by reaction of various oxiranes **1** with species $Ar^{\cdot-}$ M^+ (M = Li, K, Mg) as electron-transfer agents in tetrahydrofuran (THF) [equations (XIX) and (XX)]. Reactions with electrophiles ZX [equations (XI), (XII), (XV) and (XVI)] yield the expected products **15** or **16**. Solutions of dianions such as **8** or **9** were also obtained by Barluenga *et al.* from organomercury compounds[5] or β-chlorohydrins[6] and yielded analogously products **15** or **16** after quenching with electrophiles.

Gurudutt *et al.*[7] also studied the reaction of oxiranes with alkali metals in aprotic solvents and found a variety of products after hydrolysis. Deoxygenation to olefins **24** (Scheme 2) was the major reaction in the case of lithium, whereas with sodium not only were the expected protonation products (alcohols **15**, **16**, Z = H) of dianions **8** and **9** obtained, but also such dimerisation products as dialcohols **32** or **34** (Z = H) (Scheme 3) which one would expect to be obtained from radical anions **4** and **5**. They rationalised all the reactions by proposing a mechanism involving an initial single-electron transfer leading through ring opening by CO-bond scission to the above mentioned radical anions **4** or **5**.

In the early stages of the work now being presented,[8,9] not only were reaction products resulting from CO-bond scission found, but also other products resulting from CC-bond scission (compounds **19**–**21**, and **23**) (Scheme 2), depending on the nature of the alkali metal and the solvent. In photolysis and thermolysis of oxiranes[10] the weakest bond of the oxirane ring, *i.e.* the CC-bond, is known to break. Therefore one is led to discuss:

(*a*) the possibility of ring opening by CC-bond cleavage in the reduction of oxiranes by stepwise electron transfer, leading first to radical anions **6** and **7** and later to dianion **10** [equations (V), (VI), (IX) and (X)] as precursors to products **19**, **20** [equations (XXII) and (XXIII)] and **21** and **23** [equations (XXV) and (XXVI)], and

(*b*) the alternative pathway involving CC-bond scission only after ring opening by CO-bond cleavage [equations (XXI), (XXIII), (XXIV) and (XXVI)].

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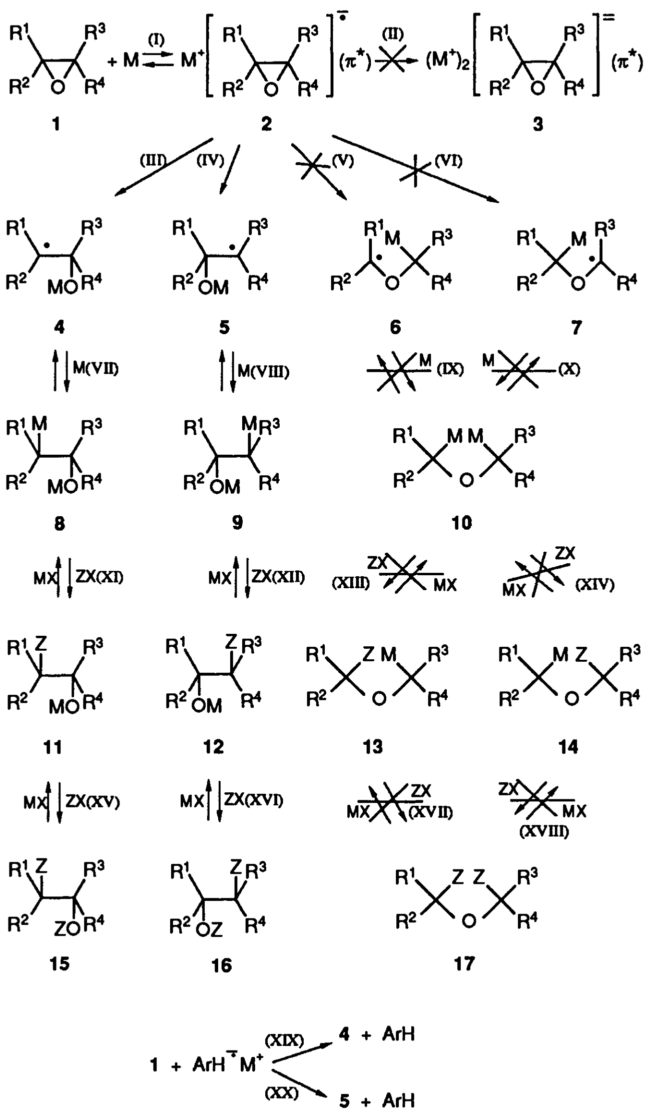
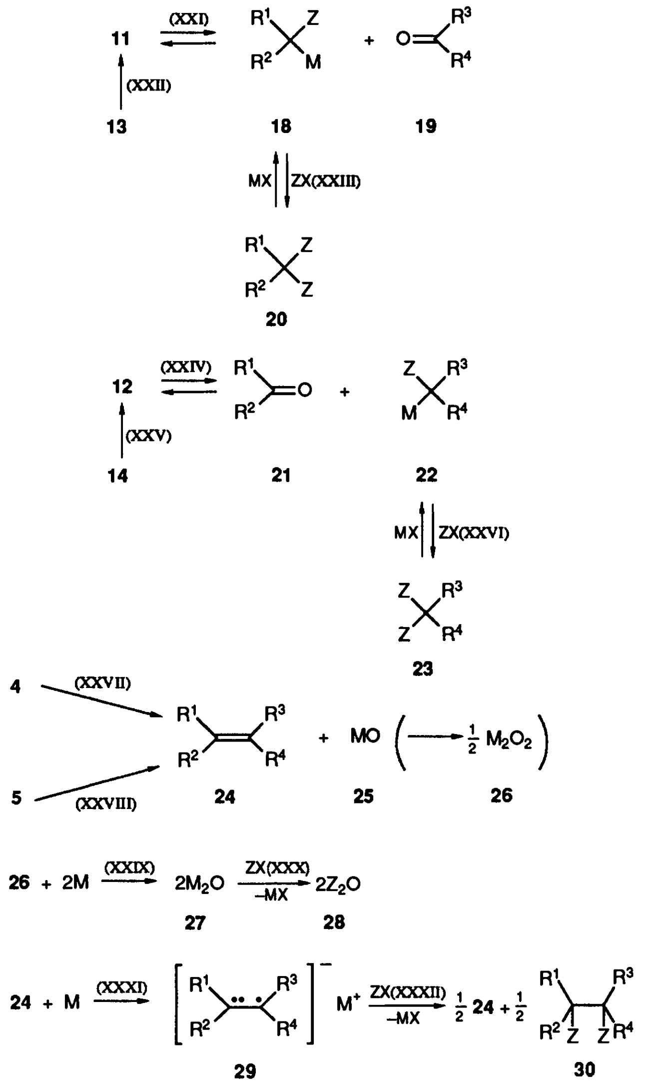
† Part 3 is ref. 24.



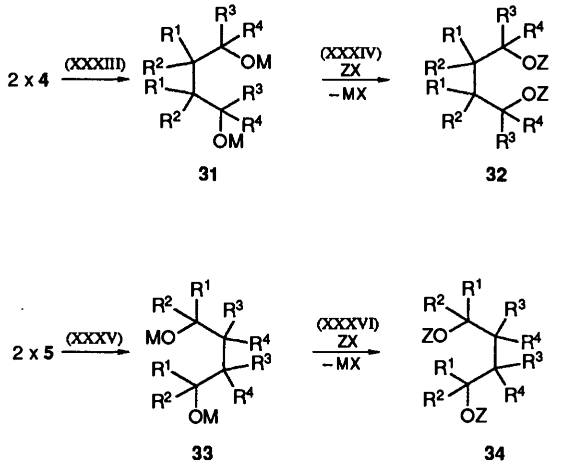
Scheme 1 Roman numerals denote equations

Results and Discussion

Synthesis of Tetraaryloxiranes.—Six tetraaryloxiranes **1a–f**, four of them new (compounds **1b**, **1c**, **1e** and **1f**), were synthesized according to Scheme 4 by reaction of chlorodiphenylmethyllithium **18** (Z = Cl, M = Li, $R^1 = R^2 = Ph$) or 9-chlorofluoren-9-yllithium **18** (Z = Cl, M = Li, R^1R^2 = o,o'-$C_6H_4C_6H_4$) with either benzophenone **19** ($R^3 = R^4$ = Ph) p,p'-dichlorobenzophenone **19** ($R^3 = R^4$ = p-ClC_6H_4), or p,p'-dimethoxybenzophenone **19** ($R^3 = R^4$ = p-$MeOC_6H_4$) [equations (XXXVIII), (XXXIX)]. The intermediate addition products, lithium 1,1,2,2-tetraaryl-2-chloroethoxides **11** (Z = Cl, M = Li) yielded directly the tetraaryloxiranes **1a–f**. The products were characterized by melting point, CH-analysis and ^1H NMR spectroscopy. The carbenoids used in these reactions were obtained from dichlorodiphenylmethane, 9,9-dichlorofluorene, and butyllithium [equation (XXXVII)]. Compound **1d** had already been synthesized by this procedure.[11]



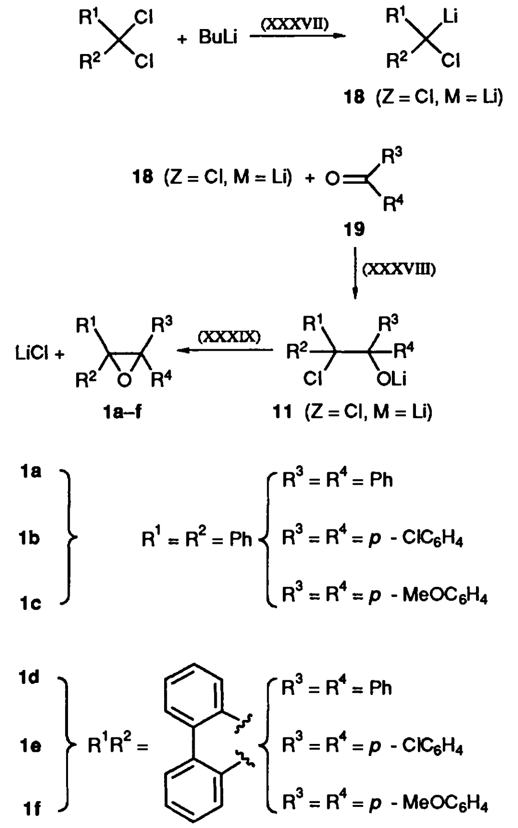
Scheme 2 Roman numerals denote equations



Scheme 3 Roman numerals denote equations

Cyclic Voltammetry.—The six oxiranes **1a–f** (Scheme 4) were studied by cyclic voltammetry in dimethylformamide (DMF) or acetonitrile–tetrabutylammonium perchlorate. Irreversible waves were observed in all cases within the range of sweeping rates used which are shown on Table 1 together with the peak potentials E_p.

The slopes of graphs of E_p *vs.* the logarithm of sweeping rate for oxiranes **1a** and **1c** were found to be situated between 30 and 40 units (used in Table 1) which indicates, according to a criterion used by Savéant *et al.*,[12,13] that the observed waves correspond to a single-electron transfer and that the irreversible reaction that follows is of first order. The nature of the irreversible reaction cannot be determined from the electrochemical data. As all the other evidence presented in this paper



Scheme 4 Roman numerals denote equations

Table 1 Peak potentials (E_p) and half-wave potentials ($E_{\frac{1}{2}}$) for the oxiranes **1a–f**

Oxirane	Scan rate/ mV s^{-1}	Solvent	E_p/V	$E_{\frac{1}{2}}$/V
1a	20	DMF	−2.61	
	100		−2.63	
	200		−2.64	
1b	100	DMF	−2.53	−2.095
1c	100	DMF	−2.73	−1.96
1d	100	DMF	−2.01	
	200		−2.02	−1.73
	500		−2.04	
	1000		−2.05	
1e	200	MeCN	−1.98	−1.56
1f	200	MeCN	−2.34	−2.1

refers to ESR spectral results and product analysis for alkali metal reductions of the same oxiranes, which differ considerably according to solvent and counter-ion, one should abstain from speculating too much on the nature of this irreversible process. Moreover, although care was taken to dry the solvents carefully, the possibility of the irreversible step being a protonation cannot be excluded completely. There cannot be any doubt, however, that the primary step is a single-electron transfer, leading to a radical anion. The peak potentials are lowered by electron-attracting substituents as would be expected. This effect can be expressed quantitatively by a linear correlation with Hammet's σ substituent parameters. For tetraphenyloxiranes **1a–c** eqn. (1) holds, and for 3′,3′-diphenylspiro[fluorene-9,2′-oxiranes] **1d–f** eqn. (2) holds.

$$E_p = -2.63 - 0.259\sigma \quad (n = 3, R = 0.998) \quad (1)$$

$$E_p = -2.14 - 0.861\sigma \quad (n = 3, R = 0.999) \quad (2)$$

Table 2 Percentages of recovered starting material and products obtained by the reaction of tetraphenyloxirane **1a** with alkali metals in aprotic solvents followed by hydrolysis, and values of log (Q_{el}/Q_{nel})

		Yield(%)					
Solvent[a]	Metal	**1a**	**20**[b,c]	**24**[b]	**30**[b]	**15**[b]	log(Q_{el}/Q_{nel})
METHF	Li	20	11	62	6	1	0.754
THF	Li	15	12	62	1	2	0.653
DME	Li	16	11	47		3	0.526
MeTHF	Na	20	3	48	3	15	0.452
THF	Na	13	12	54		10	0.389
DME	Na	35	14	37		6	0.267
DG	Na	36	21	30		3	0.097
Py	Na	39	29	22			−0.12
HMPA	Na	21	33	18	4		−0.176
DMF	Na	22	39	29			−0.129
DA	Na	1	80	10	3		−0.788
MeTHF	K	2	32	44	3	10	0.049
THF	K	3	32	40	2	14	−0.039
DME	K	6	51	29	4	1	−0.197
THF	Cs	24	33	21		12	−0.33
DME	Cs	20	46	12		2	−0.602

[a] For the meaning of solvent symbols see Experimental section, first paragraph. [b] R^1–R^4 = Ph, Z = H. [c] The percentages for benzophenone **19** were identical with those of diphenylmethane **20**.

Table 3 Percentages of recovered starting material and products obtained by the reaction of 3′,3′-diphenylspiro[fluorene-9,2′-oxirane] **1d** with alkali metals in aprotic solvents, and values of log (Q_{el}/Q_{nel})

		Yield(%)					
Solvent[a]	Metal	**1d**	**20**[b,c]	**24**[b]	**30**[b]	**15**[b]	log(Q_{el}/Q_{nel})
DO	Li	3	3	70	3	11	0.717
MeTHF	Li	6	5	67		12	0.595
THF	Li	4	7	60	10	15	0.502
DG	Li	15	17	50	3	14	0.23
HMPA	Li		50	20	25	3	−0.07
DO	Na	80	1	7		1	0.544
MeTHF	Na		32	55	5	8	0.176
DME	Na	1	40	39	8	6	0.013
DG	Na	5	39	38	5	3	0.0
DA	Na		56	13	12	10	−0.422
HMPA	Na		54	18	17	1	−0.204
DMF	Na		72	10	8		−0.602
MeTHF	K	38	19	36	3	2	0.269
THF	K	1	50	40	4	4	0.089
DME	K		60	30	7	1	−0.218
DG	K		63	20	7		−0.369
HMPA	K	1	70	1	20		−0.523
DA	K	13	71	10	3		−0.738
DMF	K	28	63	5			−1.100
MeTHF	Cs	11	66	15		2	−0.650
THF	Cs	9	70	10	13	2	−0.743

[a] For the meaning of solvent symbols see the Experimental section, first paragraph. [b] R^{1}R^2 = o-(C$_6$H$_4$)$_2$, R^3 = R^4 = Ph, Z = H. [c] The percentages for benzophenone **19** were identical with those for diphenylmethane **20**.

In some cases the irreversible wave is followed by a wave corresponding to the reversible reduction of the tetraarylethylene **24** ($E_{\frac{1}{2}}$ in Table 1).

Preparative Results.—Tetraphenyloxirane **1a** and 3,3′-diphenylspiro[fluorene-9,2′-oxirane] **1d** were treated with Li, Na, K, and Cs metal in various aprotic solvents (see Tables 2 and 3).

According to the nature of the alkali metal and solvent, variable yields of five different products were obtained after hydrolysis: in the case of tetraphenyloxirane **1a** there were 1,1,2,2-tetraphenylethanol **15** (R^1–R^4 = Ph, Z = H), benzophenone **19**, diphenylmethane (these two in equimolar proportion), tetraphenylethylene **24**, and 1,1,2,2-tetraphenylethane **30**. Starting from 3′,3′-diphenylspiro[fluorene-9,2′-oxirane] **1d** the other corresponding tetraaryl derivates were obtained, [compounds **15**, **19**, **20**, **24** and **30** [Z = H, R^1R^2 = $(o\text{-}C_6H_4)_2$, R^3 = R^4 = Ph]. In those cases where two possibilities exist, according to the compound being a derivative either of fluorene or of diphenylmethane, it should be noted that fluoren-9-yldiphenylmethanol **15** and not 9-(1,1-diphenylmethyl)fluorene-9-ol **16** was obtained, and also benzophenone **19** and fluorene **20** were obtained instead of fluorenone **21** and diphenylmethane **23**.

The sets of products obtained allow for several mechanistic interpretations: the tetraarylethanols **15** (Z = H) have as their most obvious precursor the dianion **8**. None of the solvents used is sufficiently acidic to justify the presence of a stable singly protonated species **11** in solution before hydrolysis. The obtention of substituted ethanol **15** instead of the fluorenol **16** [R^1R^2 = $(o\text{-}C_6H_4)_2$, R^3 = R^4 = Ph] is consistent with the better stabilization of the negative charge on the fluorene moiety in species **8**. This points to the presence of a stable dianion **8** in the solution before it undergoes hydrolysis.

An alternative pathway to the tetraarylethanols **15** (Z = H) has nevertheless to be discussed: as the weakest bond in radical anion **2** is the CC-bond, one has to consider the possibility of the ring-opening reaction occurring by reaction (V) yielding radical anion **6** [or (VI) yielding **7**] followed by further reduction to dianion **10** [reaction (IX) or (X)]. Then during the hydrolysis half-protonated anions such as **13** (or **14**) (Z = H) should occur [reactions (XIII) or (XIV)]. Such anions would undergo Wittig rearrangement and yield anions **11** or **12** respectively (Z = H), according to reaction (XXII) or (XXV).

That a Wittig rearrangement would actually take place, once a monometallated dibenzhydryl ether **13** = **14** (R^1–R^4 = Ph, Z = H and M = Li) or a monometallated benzhydryl fluoren-9-yl ether **14** [R^1R^2 = $(o\text{-}C_6H_4)_2$, R^3 = R^4 = Ph, Z = H, M = Li] has been generated, was confirmed by an NMR experiment, reported in detail below. This shows that obtention of tetraarylethanols **15** from hydrolysis of the solutions obtained by reaction of tetraaryloxiranes with alkali metals is not sufficient to allow us to find out whether the primary ring-opening reaction is a CO-bond scission [equation (III) or (IV)] or a CC-bond scission [equation (V) or (VI)].

The pathway which leads to benzophenone **19** and either diphenylmethane **20** (R^1 = R^2 = Ph, Z = H) starting from tetraphenyloxirane **1a** or fluorene **20** [R^1R^2 = $(o\text{-}C_6H_4)_2$, Z = H] from 3′,3′-diphenylspiro[fluorene-9,2′-oxirane] **1d** allows *a priori* several possibilities. If the primary ring-opening process is a CO-bond scission the half-protonated intermediate **11** would occur during hydrolysis, and would then dissociate, according to reaction (XXI), to yield benzophenone **19** and the diarylmethyl anion **18**, which would be further protonated to the corresponding diarylmethane **20** [reaction (XXIII), X = OH, Z = H].

We have, however, argued above that anion **11** could also originate from the CC-bond scission pathway through Wittig rearrangement (XXII) of species **13** (Z = H). Even if this rearrangement did not occur, the heterolytic dissociation of **13** in a single step might justify the CC-bond scission pathway (the corresponding homolytic dissociation is considered anyway to be a step in the mechanism established for the Wittig rearrangement). A closer examination of the concerted transformation of species **13** to products **18** and **19** shows, however, that it is symmetrically forbidden as a thermally activated process (Hückel transition state with four electrons), still leaving the Wittig rearrangement (XXII) of anion **13** as a possibility.

In order to show that, under the reaction conditions used, no protonation of any of the anions **8**–**10**, which might be present does occur before the reaction mixture is hydrolysed, the following experiments were performed.

The solution obtained from the reaction of 3′,3′-diphenylspiro[fluorene-9,2′-oxirane] **1d** with potassium was treated with D_2O. A small quantity of 9,9-dideuteriofluorene **20** [R^1R^2 = $(o\text{-}C_6H_4)_2$, Z = D] was isolated and shown by NMR spectroscopy not to contain any detectable amount of monodeuteriated or undeuteriated fluorene. With the same objective the solutions obtained from the reactions of both tetraphenyloxirane **1a** and 3′,3′-diphenylspiro[fluorene-9,2′-oxirane] **1d** with lithium, sodium, and potassium in THF were treated with methyl iodide (ZX, Z = Me, X = I), the solvent was evaporated off, and the NMR spectrum of the resulting crude product in $CDCl_3$ was recorded. In five cases the spectra revealed the absence of a 1,1-diarylethane R^3R^4CHMe (1,1-diphenylethane when starting from tetraphenyloxirane **1a**) and 9-methylfluorene, when starting from 3′,3′-diphenylspiro-[fluorene-9,2′-oxirane] **1d**. Only in the case of tetraphenyloxirane **1a** and lithium were such compounds, 1,1-diphenylethane (*ca.* 4–8%) and other products (2–4%), observed in the NMR spectrum; these compounds may have resulted from protonation prior to reaction with methyl iodide. In all cases the tetraarylethylene **24** was the main product. The next highest percentage yields were estimated for benzophenone **19** and the 2,2-diarylpropane **20**. For the reaction of tetraphenyloxirane with potassium these yields were estimated as 20–25% for both benzophenone **19** (R^3 = R^4 = Ph) and 2,2-diphenylpropane **20** (R^1 = R^2 = Ph, Z = Me), and with sodium the yields were 23–28%. For the reaction of 3′,3′-diphenylspiro[fluorene-9,2′-oxirane] **1d** with potassium a 30–35% yield and with sodium 15–20%, of both benzophenone and 9,9-dimethylfluorene **20** [R^1R^2 = $(o\text{-}C_6H_4)_2$, Z = Me] were estimated. With lithium the results were not so clear, but were still sufficient to show that from 3′,3′-diphenylspiro[fluorene-9,2′-oxirane] after quenching with methyl iodide no 9-methylfluorene had been obtained at all.

One can conclude thus, from the absence of protonation (except in one case) before quenching the solution with water D_2O, or MeI, that if any Wittig rearrangement (XXII) or (XXV) took place at all, it would not be before quenching of the solution.

The occurrence of tetraarylethylenes **24** among the reaction products, often as the main product after hydrolysis, again does not allow us to exclude CC-bond scission as a primary ring-opening process (as has already been pointed out with respect to the occurence of tetraarylethanols).

The non-occurence of dibenzhydryl ether **17** among the reaction products points rather to exclusive CO-bond scission, but also does not exclude CC-bond scission taking place with total conversion of anion **13** (Z = H) by Wittig rearrangement (XXII) during the hydrolysis.

The presence of tetraarylethane **30** (Z = H) among the reaction products can be easily explained as resulting from further reduction of the tetraarylethylene **24** by the alkali metal [reaction (XXXI)], followed by hydrolysis [reaction (XXXII), Z = H, X = OH] or another quenching process. There again, except for the case of the reaction of tetraphenyloxirane **1a** with lithium [where an estimated 1.5% of $Ph_2C(Me)OH$ and 1.5% of $Ph_2CH(OMe)$ could be assumed from the NMR spectrum of the solution after methylation with MeI], the methylation experiments showed that no protonation of anion **8** could have taken place before hydrolysis.

The formation of tetraarylethylenes **24** and tetraarylethanes **30** (Z = H) poses, however, another mechanistic problem: although Gurudutt *et al.*[7] have argued in favour of M_2O elimination from dianion **8** or **9** and did not even consider the elimination of MO from radical anions **4** or **5** [reactions (XXVII) or (XXVIII)], the latter hypothesis deserves to be

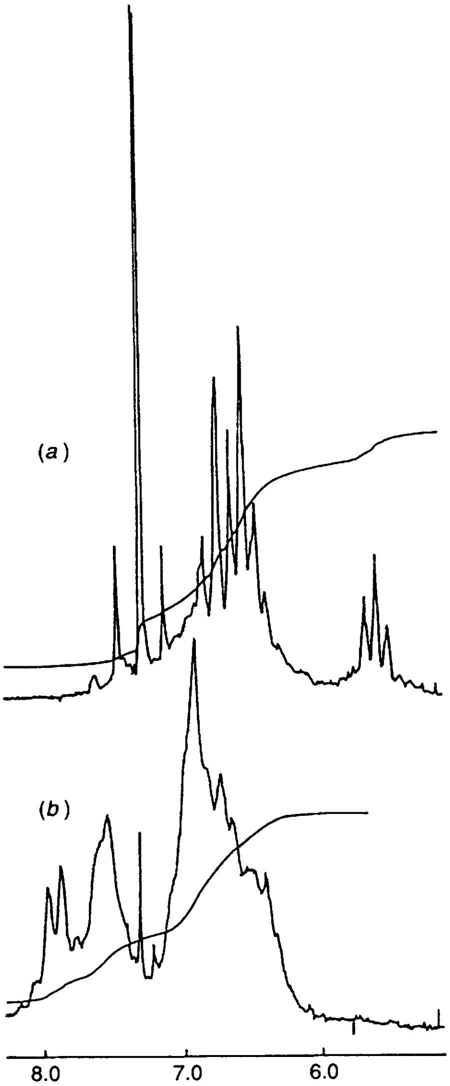


Fig. 1 NMR spectra of (*a*) solution obtained from reaction of potassium with tetraphenyloxirane **1a** in [$^2H_8$]THF, and (*b*) from reaction of the same metal with 3′,3′-diphenylspiro[fluorene-9,2′-oxirane] **1d** in the same solvent

discussed. This problem could not be solved by product analyses and had to be studied by kinetic experiments as reported below.

The correctness of the statement that the half-protonated dianions **13** and **14** would indeed undergo Wittig rearrangement under the reaction conditions was confirmed, unexpectedly, in the following way: in order to find out what would be the fate of the dianion **10**, resulting from primary CC-bond scission, we tried to generate this dianion by double deprotonation of dibenzhydryl ether **17** (R^1–R^4 = Ph, Z = H) or of benzhydryl 9-fluorenyl ether **17** [R^1R^2 = (o-C_6H_4)$_2$, R^3 = R^4 = Ph, Z = H]. Dilute solutions of these ethers in [$^2H_8$]THF were added slowly to a ten-fold excess of butyllithium in [$^2H_8$]THF. After quenching of the resulting solution with methyl iodide, the NMR spectra of these solutions showed that the starting product had disappeared and that, in the case of dibenzhydryl ether, *ca.* 50% had been converted into 1,1-diphenylethane Ph_2CHMe and the remaining 50% into a mixture of $Ph_2(C_4H_9)COH$, p-$(C_4H_9)C_6H_4COPh$, o-$(C_4H_9)C_6H_4COPh$ and $(C_4H_9)Ph_2COMe$. In the case of benzhydryl 9-fluorenyl ether, *ca.* 50% of the product was again 1,1-diphenylethane Ph_2CHMe. The remaining 50% could be identified by NMR spectroscopy as a mixture of (o-C_6H_4)$_2$(C_4H_9)COM and (o-C_6H_4)$_2$(C_4H_9)COMe.

In both cases, in spite of the manner in which the addition took place, the dimetallated ethers **10** had obviously not been obtained. Instead it seems that the deprotonation did not go further than to the monolithiated ether.

In the case of dibenzhydryl ether the only possible product is **13** = **14** (R^1–R^4 = Ph, Z = H, M = Li) being formed whereas with benzhydryl 9-fluorenyl ether the more stabilized of both possible anions **13** or **14**, *i.e.* compound **14** [R^1R^2 = (o-C_6H_4)$_2$, R^3 = R^4 = Ph, Z = H, M = Li] is expected. Wittig rearrangement (XXV) of compound **14** would yield **12** (Z = Me), which is then expected to dissociate heterolytically [reaction (XXIV)] to yield equimolar amounts of fluoren-9-one **21** and 1,1-diphenylethane **22**. As *ca.* 50% of the reaction product observed was actually 1,1-diphenylethane[22] and the other products can be explained as having fluoren-9-one as a precursor, this means that, if in the reaction of tetraaryloxiranes with alkali metals the dianion **10** were formed, the expected monoanions **13** and **14**, occurring as intermediates in the quenching reaction (either with water or MeI), would actually undergo Wittig rearrangement (XXII) and (XXV) and give monoanions **11** and **12**, respectively. This means that the product analysis *after* the quenching reaction would never allow us to find out whether, by reaction of the tetraaryloxirane with alkali metal, CC- or CO-bond scission has occurred, or a competition between both.

Owing to the difficulty of deciding, based solely on product analysis, between CO- or CC-bond scission as the primary ring-opening process, the solutions obtained from the reaction of tetraaryloxiranes with alkali metals were studied by NMR and EPR spectroscopy, in order to gather more evidence towards a solution of the problem.

NMR Spectra of Solutions obtained from the Reaction of Tetraaryloxiranes with Alkali Metals.—In order to find out whether, in the solutions obtained from the reaction of tetraaryloxiranes **1a–f** with alkali metals, dimetallated 1,1,2,2-tetraarylethanols **8** or **9** or dimetallated bis(diarylmethyl) ethers **10** are present as major components such solutions were prepared in [$^2H_8$]THF and studied by NMR spectroscopy. Fig. 1 compares the spectra of the solutions obtained from (*a*) the reaction of tetraphenyloxirane **1a** with potassium in [$^2H_8$]THF and (*b*) the reaction of 3′,3′-diphenylspiro[fluorene-9,2′-oxirane] **1d** with potassium in [$^2H_8$]THF.

In the first case it is possible to identify the well known[14] triplet originating from the *para*-protons of the phenyl groups shifted upfield (δ 5.6) by a negative charge on the carbon atom to which the phenyl groups are attached. This alone would, however, be consistent with any of the structures proposed for the dianion, whether it is **8** (=**9**) or **10**. Spectrum (*b*), however, does not show this triplet in the same region, which confirms that in the solution obtained from the reaction of 3′,3′-diphenylspiro[fluorene-9,2′-oxirane] **1d** with potassium no species exists in which there is a negative charge on a carbon atom attached to two phenyl groups. This rules out dianions with structures **9** or **10**, and leaves, as the only alternative consistent with this spectrum dianion structure **8** [R^1R^2 = (o-C_6H_4)$_2$, R^3 = R^4 = Ph in these cases].

It has been shown by deuteriolysis and reaction with methyl iodide that the half-protonated dianions, of whatever structure (**11**–**14**), cannot exist in solution before hydrolysis starts (except for a very small proportion in the case of lithium and tetraphenyloxirane where somehow a proton is picked up by 6–12% of the solute, even before hydrolysis takes place). Therefore a cross-over from CC-ring-opened species **13** or **14** by Wittig rearrangement (XXII) or (XXV) to CO-ring-opened species **11** or **12**, respectively, cannot have taken place before hydrolysis. The NMR evidence for the structure of the dianion **8** [R^1R^2 = (o-C_6H_4)$_2$, R^3 = R^4 = Ph] shows, therefore, without doubt,

Table 4 ^1H NMR chemical shifts for dianions **8**

8	Alkali cation	Positions ortho	meta	para	
R^1–R^4 = Ph	Na	6.85	6.65	5.7	
	K	6.75	6.55	5.6	
		1^a	2^a	3^a	4^a
$R^1R^2 = (o\text{-}C_6H_4)_2$	Na	6.6	7.3	6.9	7.8
$R^3 = R^4$ = Ph	K	6.25	8		

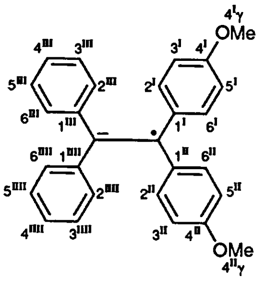
^{a} Numbering according to IUPAC rules for fluorene.

that the primary ring-opening process in the cleavage of aryl-substituted oxiranes by alkali metals is exclusively CO-bond scission. The occurrence of hydrolysis products where the CC-bond has been cleaved is therefore a consequence of reactions which occur during the reaction with ZX (hydrolysis: Z = H, X = OH; deuteriolysis: Z = D, X = OD; or methylation: Z = Me, X = I).

EPR evidence reported below also shows that tetraarylethylenes **24** (detected by their radical anions resulting from reaction with excess of alkali metal) are already present in the solutions before reaction with ZX takes place. The yields of quenching products also show that at least two-thirds of the starting tetraaryloxirane must have been converted by reaction with potassium into the respective dianion **8** and therefore that only a maximum of one-third can be present as tetraarylethylene (including products of further reactions of the tetraarylethylene with potassium). This allows us to identify and assign the NMR lines of the dianions **8** as shown in Table 4, in spite of the underlying spectra of *ca.* one-third of other components.

The solutions in [$^2H_8$]THF obtained by slow addition of dilute solutions of either dibenzhydryl ether or benzhydryl 9-fluorenyl ether to a ten-fold excess of butyllithium were also examined by NMR spectroscopy. They showed no evidence of the dilithiated species **10** and were consistent with a mixture of *ca.* 50% benzhydryllithium **22** ($R^3 = R^4$ = Ph, Z = H, M = Li) and another 50% as products from reaction of either benzophenone or fluoren-9-one with excess of butyllithium. This is consistent with the product analysis made by NMR spectroscopy after quenching of the solution with methyl iodide, reported in the paragraph 'Preparative Results' (*vide supra*). It reveals the following pathway for the reaction of bis(diarylmethyl) ethers **17** (Z = H) with butyllithium: the monolithiated ether **14** converts, by Wittig rearrangement (XXV), into alkoxide **12** and then by heterolytic dissociation (XXIV) into products **21** and **22**. Ketone **21** reacts further with butyllithium. The quenching reactions with methyl iodide substitute the metal cation by methyl groups.

EPR Spectra of Solutions obtained from the Reaction of Tetraaryloxiranes with Alkali Metals.—With the hope of obtaining the EPR spectra of 2-oxidotetraarylethyl radicals **4** or **5**, the solutions obtained from the reaction of tetraaryloxiranes **1a–f** with lithium and sodium in THF at room temperature were examined. None of the spectra obtained, however, showed evidence for the presence of species **4** or **5**. They all were identical with the known spectra of the alkene radical anions **29** obtained by reduction of alkenes **24** with the same alkali metals in the same solvent.[14,15] Among these, the only spectrum not yet reported in the literature is that obtained from either 1,1-bis-(*p*-methoxyphenyl)-2,2-diphenylethylene **24** ($R^1 = R^2$ = Ph, $R^3 = R^4$ = *p*-$MeOC_6H_4$) or 2,2-bis-(*p*-methoxyphenyl)-3,3-diphenyloxirane **1c**. The complex EPR pattern with numerous lines could only by unravelled after an ENDOR spectrum (of **1a** with sodium in THF) had been recorded. The nine coupling constants obtained from the ENDOR spectrum had to be further adjusted in order to obtain a satisfactory simulation of the ESR spectrum, changes in the last digit being critical for obtaining a good simulation (line-width used for simulation 2 μT). Hückel–McLachlan spin-density calculations were performed in order to assign the couplings to the various positions of species **29c**. The signs of the constants were determined by general TRIPLE and the multiplicities by special TRIPLE resonance.



29c

The hyperfine coupling constants/μT thus obtained are as follows: a_H −155.3 (calc. −155.2); $a_H(3',3'')$ 73.2 (calc. 55.8); a_H (4′-OMe 4″-OMe) −19.6; a_H $(5',5'')$ 89.2 (calc. 70.7); a_H $(6',6'')$ −190.1 (calc. −195.3); a_H $(2''',2'''')$ −120.0 (calc. −123.0); a_H $(3''', 3'''')$ 26.8 (calc. 34.0); a_H $(4''',4'''')$ −197.3 (calc. − 198.4); a_H $(5''',5'''')$ 49.0 (calc. 55); a_H $(6''',6'''')$ −155.3 (calc. −159.2).

By comparison with the known values for the radical anion of unsubstituted tetraphenylethylene and by taking into consideration the fact that the introduction of an OMe group will increase the electron spin density in the substituted phenyl rings, the above assignments can be confirmed.

The McConnell constant used for the spin-density calculations was Q^H_{CH} −3200 μT and the Hückel parameters were as follows: $\gamma_{1,1'} = \gamma_{1,1''} = 0.800$; $\gamma_{2,1'''} = \gamma_{2,1''''} = 0.707$; $\delta_{2'} = \delta_{2''} = \delta_{2'''} = \delta_{2''''} = -0.150$ (in order to take into account the topological non-equivalence of 'inner' and 'outer' *ortho*-hydrogens); $\delta_{COMe} = 0.900$; $\delta_O = 3.000$. A further adjustment of these parameters in order to obtain a better match between calculated and experimental values did not increase the reliability of the proposed assignments.

The observation of the spectra of the alkene radical anions **29** obtained from the reaction of tetraaryloxiranes with alkali metals shows that their precursors, the alkenes **24**, are formed *before* the quenching of the solution by protolysis or alkylation takes place.

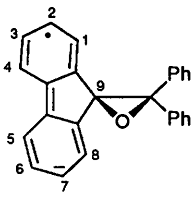
This rules out the hypothesis that the alkenes **24** found as final products after hydrolysis were being formed only during the hydrolysis. CC-bond scission [step (V) or (VI)] in the initial stage of the reaction, followed by further reduction of radical anion **6** or **7** to a dimetallated dibenzhydryl ether **10** [reaction (IX) or (X)], generating during the hydrolysis its half-protonated derivative **13** or **14** [Z = H, reaction (XIII) or (XIV)], followed by Wittig rearrangement [reaction (XXII) or (XXV)] to monoanions **11** or **12** can thus be ruled out altogether as a reaction path, leaving as the only other alternative the CO-bond scission path shown on the left-hand side of Scheme 1.

In the last attempt to obtain an EPR spectrum of a 2-oxidotetraarylethyl radical **4** or **5**, 3′,3′-diphenylspiro[fluorene-9,2′-oxirane] **1d** was reduced with Na/K-alloy in a THF–1,2-dimethoxyethane (DME) mixture in an EPR sample tube placed in the EPR cavity at 173 K. A different EPR spectrum was now obtained which could be unambiguously identified as that of the radical anion **2d** of **1d** before any bond scission had taken place. The experimental coupling constants (Table 5) were those used to simulate successfully the EPR spectrum with a line width of 15 μT.

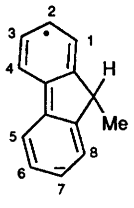
Table 5 EPR-hyperfine splitting constants (μT) of radical anion **2d** of 3′,3′-diphenylspiro[fluorene-9,9′-oxirane] compared with the radical anion **35** of methylfluorene and with 9,9′-bi(fluorenyl-9-yl) **36**

Positions	**2d**	**35**[16]	**36**[17]
1,8	96	100	385
2,7	500	502	76
3,6	96	100	350
4,5	409	412.5	76

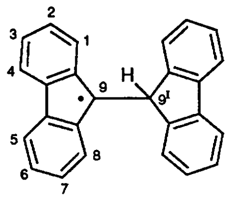
The published experimental values for the radical anion of 9-methylfluorene **35**,[16] and for that of 9,9′-bi(fluorenyl-9-yl) **36**,[17] which resemble most closely those of radical anion **2d** and **4** [$R^1R^2 = (o\text{-}C_6H_4)_2$, $R^3 = R^4 =$ Ph], respectively are listed in Table 5 and show clearly that the observed spectrum is that of radical anion **2d**, ruling out the other alternative.



2d



35



36

This result shows that, although the first cyclic voltammetric wave, observed in the reduction in DMF or acetonitrile was irreversible, it does not rule out a first, reversible electron-transfer step. Obviously, under these conditions of electrolytic reduction and with the scanning rate used the subsequent, irreversible CO-bond scission follows too soon to allow detection.

Kinetic Results.—In order to address the problem of at which stage of the reaction yielding an alkene is the oxygen eliminated, the following experiment was performed: degassed 10^{-2} mol dm^{-3} solutions of 3′,3′-diphenylspiro[fluorene-9,2′-oxirane] **1d** in dry THF were allowed to react with potassium mirrors at 25 °C. The reactions were interrupted after different intervals and the mixtures hydrolysed. After work-up the residues were analysed by HPLC. The percentages of recovered oxirane **1d**, and the percentage of 9-benzhydrylidenefluorene **24** [$R^1R^2 = (o\text{-}C_6H_4)_2$, $R^3 = R^4 =$ Ph] in relation to the initial quantity of oxirane **1d** are represented in the plot of Fig. 2, together with a third curve representing the percentage of dianion **8** [$R^1R^2 = (o\text{-}C_6H_4)_2$, $R^3 = R^4 =$ Ph] present in the solution before hydrolysis. The latter was calculated by adding the quantity of 9-fluorenyldiphenylmethanol **15** [$R^1R^2 = (o\text{-}C_6H_4)_2$, $R^3 = R^4 =$ Ph, Z = H] to the quantity of fluorene (which is identical with the quantity of benzophenone) expressed as a molar percentage in relation to the initial quantity of oxirane **1d**. This is based on the conclusion, drawn earlier, that these three products originate from the same dianion. The plot shows that after *ca.* 15 min the percentages remain constant.

The constancy of the percentages after 15 min allows only two interpretations: either the dianion and the alkene are in equilibrium or the alkene originates from an earlier branching of the reaction path. The first hypothesis can be discarded because of the following considerations: in order to obtain an alkene **24** from a dianion **8** M_2O **27** would have to be eliminated. These alkali metal oxides are insoluble in THF, and their precipitation would displace the equilibrium completely to the alkene side. An experiment was also performed by preparing dipotassium oxide K_2O according to the literature,[18] and sealing it off in high vacuum in a tube connected by a break-seal to another sealed tube which in turn contained a degassed solution of 9-benzhydrylidenefluorene **24** [$R^1R^2 = (o\text{-}C_6H_4)_2$, $R^3 = R^4 =$ Ph] in dry THF. The seal was broken and the solution was allowed to come into contact for several hours with the dipotassium oxide, but no reaction took place. Visually no dissolution of the oxide was detectable, and after hydrolysis 100% of the alkene was recovered.

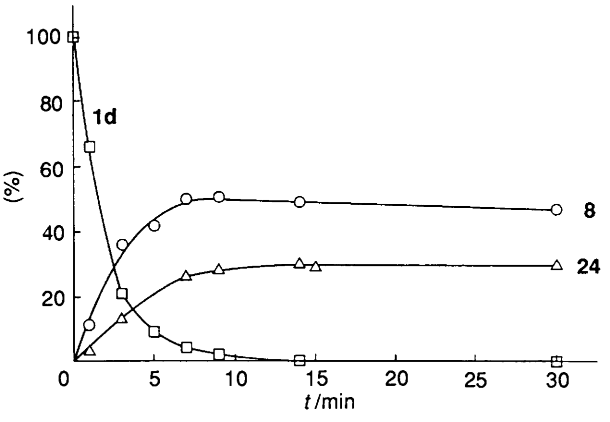


Fig. 2 Percentages of non-converted oxirane **1d**, 9-benzhydrylidenefluorene **24**, and dianion **8** [$R^1R^2 = (o\text{-}C_6H_4)_2$, $R^3 = R^4 =$ Ph, M = K] present in the reaction of 10^{-2} molar solutions of 3′,3′-diphenylspiro[fluorene-9,2′-oxirane] **1d** with a potassium mirror after several time intervals

This leaves as the only other interpretation the elimination of MO **25** at an earlier stage, specifically from the short-lived intermediate 2-oxidotetraarylethyl radical **4** as shown by reaction (XXVII). One might wonder why hydrogen peroxide could not be detected in the reaction mixture after hydrolysis since MO **25** should dimerise to M_2O_2 **26** and yield hydrogen peroxide upon hydrolysis. This fact can be easily explained by the presence of excess of alkali metal which will reduce M_2O_2 to M_2O according to reaction (XXIX) and yield water upon hydrolysis [reaction (XXX) yielding **28** (Z = H)]. This settles the last mechanistic question about the unexpectedly complicated reduction of tetraaryloxiranes in aprotic solvents and corrects a statement[7] which now appears as erroneous, that dianion **8** can be a precursor for an alkene in this reaction.

For the considerations of the next chapter on the influence of the nature of solvent and alkali cation on the molar ratio between metal oxide elimination products and those where no elimination took place (Q_{el}/Q_{nel}) the following experimental results are also important: the concentration of the oxirane **1d** decreases exponentially with time. A plot of log $[a/(a-x_t)]$, a being the initial concentration of the oxirane and x_t the concentration of oxirane at time t, *versus* t, is a straight line indicative of a first-order reaction in the oxirane.

For the reaction of a 10^{-2} mol dm^{-3} solution of compound **1d** in THF with potassium, the plot of the concentration of (**24** plus **30**) *versus* the concentration of (**20** plus **15**) is also a straight line passing through the origin, and with a slope of 0.55, possibly indicating two parallel reactions, though the mechanism may be more complex.

Since **24** plus **30** represent the products stemming from unimolecular metal oxide elimination, and **20** plus **15** are the products stemming from unimolecular CC-bond scission of the β-metallated alkoxide,[8] their quotient is indicative of the degree of metal oxide elimination *versus* the stability in solution of the β-metallated alkoxide.

For this purpose we consider as yields (which are proportional to the concentrations) Q_{el}, the sum of the yields of (**24** plus **30**), and as yields Q_{nel} the sum of the yields of (**20** or **19** and **15**); *i.e.*, eqn. (3) holds.

$$Q_{el}/Q_{nel} = ([\mathbf{24}] + [\mathbf{30}])/([\mathbf{20}] + [\mathbf{15}]) \qquad (3)$$

Table 6 Products obtained by reaction of compound **1d** with anthracene–potassium in THF, and the logarithm of the quotient Q_{el}/Q_{nel}

		Product yield(%)					
1d[a]	Anthracene–potassium[a]	**1d**[b]	**24**[b]	**30**[b]	**20**[b,c]	**15**[b]	$\log(Q_{el}/Q_{nel})$
20	10	62	1.5		13	4	−1.05
20	20	16	5		53	6	−1.07
20	40		6	0.3	65	9	−1.07

[a] Concentration in mmol dm^{-3}. [b] $R^1R^2 = o\text{-}(C_6H_4)_2$, $R^3 = R^4 = Ph$, Z = H. [c] The percentages for benzophenone **19** were identical with those of diphenylmethane **20**.

In view of the above considerations we will now study the dependence of the quotient of the rate constants of product formation on the temperature, the solvent, and the ionic radius of the counter-ion. This quotient is indicative of the degree of elimination of metal oxide or of the stability of the β-metallated alkoxides in solution.

Influence of the Solvent and Alkali Cation on the Ratio Q_{el}/Q_{nel}.—Tables 2 and 3 show the yields, expressed in molar percentages, of the recovered starting material and of the products resulting from the reaction of the tetraaryloxiranes **1a** and **1d** with alkali metals in different aprotic solvents followed by hydrolysis. The values for the logarithm of the quotient Q_{el}/Q_{nel} are shown in the last column. Table 6 shows the products obtained from homogeneous electron transfer to compound **1d** by the radical anion of anthracene–potassium instead of by the metal itself.

A brief examination of the data shows a dependence of the quotient Q_{el}/Q_{nel} on both the solvent and the counter-ion.

Linear regression analyses *vs.* various solvent parameters[19–21] and the cationic radius *r*, analogous to those used in Parts 1–3 of this work,[22–24] led eventually (see Appendix) to the following eqn. (4), where E_T^N is the normalized Dimroth–Reichardt solvent-polarity parameter[19] and *DN* the electron pair donicity according to Gutmann.[20] The numerical values for the coefficients are given in Table 7.

$$\log(Q_{el}/Q_{nel}) = \log(Q_{el}/Q_{nel})_o + a\,E_T^N + bDN + cr \qquad (4)$$

The application of a statistical analysis method specified in the Appendix led to the percentages of contribution of the three parameters given in Table 8.

From this Table, one can conclude that the stability of the β-metallated alkoxides obtained by reaction of tetraaryloxiranes with alkali metals in aprotic solvents depends both on the solvating power of the solvent and on the counter-ion. The larger the solvating power (dipolarity and electron-pair donicity) of the solvent and the larger the ionic radius of the counter-ion, the larger is the yield of the β-metallated alkoxide and the smaller is the yield of the alkene which results from elimination of the metal oxide. These results indicate that elimination of the metal oxide is favoured by a shorter interionic distance between the negatively charged oxygen atom and the alkali counter-ion. The larger yield of products stemming from the β-metallated alkoxide in the homogeneous electron transfer is consistent with an ion pair which is more separated by solvent.

The relative yield of products derived from β-metallated alkoxide depends largely on the ionic radius of the cation (~50%). The dependence on the solvating power of the solvent is not the same for both oxiranes. For the β-metallated alkoxide obtained from compound **1a**, the electron-pair donation described by the Lewis basicity parameter *DN* is roughly twice as important as the dipolar interaction described by Lewis acidity parameter (E_T^N) ($\bar{b} \simeq 2\bar{a}$); in contrast, the yield of β-metallated alkoxide obtained from compound **1d** is largely dependent on the dipolar interaction of the solvent.

The small importance of specific cation solvation on the quotient Q_{el}/Q_{nel} obtained from the oxirane **1d** is similar to that reported for the dependence of the spin density on the metal nucleus of *o*-diaroylbenzene ion pairs.[24] This points to a structure for the intermediate in which the metal is chelated by the negative charges on the oxygen atom and on the fluorenyl C-9 carbon. With tetraphenylethylene oxide the negative charge is spread over the two phenyl groups and the interionic distance is more strongly dependent on the specific solvation of the cation.

Appendix.—In order to be able to interpret better the variations observed for the quotient Q_{el}/Q_{nel} *vs.* solvent and cation, linear regression analyses for the logarithm of Q_{el}/Q_{nel}, corresponding to the reaction of the oxiranes with each alkali metal in different solvents were tried against some empirical solvent parameters used in the literature to describe either polarity and Lewis acidity (E_T^N,[19] A_N,[20] π^*[21]) or solvent basicity (*DN*,[20] $\delta\nu_D$,[21] β[21]). The values of the empirical polarity–Lewis acidity and basicity parameters for the organic solvents are the same as those used and listed in the first part of this series.[22]

The results of the monoparametric regression analysis for compound **1d** in Table 9 show that, within each set of parameters, those which lead to better correlations are E_T^N and *DN*. The same conclusions were drawn from a similar analysis for compound **1a**, which is, however, less significant because there are fewer experimental points available.

Since solvent effects on chemical reactions generally involve both donor and acceptor interactions, these effects are best described by correlations which involve two parameters. The parameter chosen from the basicity set was *DN* and from the polarity–Lewis acidity set E_T^N. The results in Table 10 show that the correlations obtained are indeed better than any of the monoparametric ones.

The cation effect was then accounted for, by introducing in the regression analysis as a third parameter, the Goldschmidt radius of the alkali cation. A correlation with the reciprocal ionic volume ($1/r^3$) as the third parameter was also tried but for both oxiranes the correlations were poorer. The expression obtained [eqn. (4)] is the same as already reported by us to describe the solvent and cation effects on different properties of organic anions.[22–24] The numerical results are shown in Table 7.

The *R*- and *F*-values for the correlations reveal that they are statistically very significant. Nevertheless, Student's *t*-value for the parameter *DN* in the regression eqn. (4) corresponding to the oxirane **1d** is outside the critical range ([2, +∞] for α = 0.05). This may indicate the presence of multicollinearity.[25] E_T^N and *DN* have been considered in the literature to be linearly independent but within our set of solvents the correlation coefficient between E_T^N and *DN* is 0.706, indicating a small degree of multicollinearity between them, which can prevent an accurate determination of the sensitivity factors corresponding to each parameter in the regression equation.

One way to solve the problem is to drop *DN* from the model. We will have a diparametric correlation with E_T^N and *r*, with a higher *F*-value, but since the specific solvation of the cation is not taken into account the solvent effect will be described in an incomplete way. Thus, by dropping a variable from the model we may be committing a specification bias which may mislead us as to the true values of the parameters.

Another way to overcome the problem is by using the method of factor analysis with the transformation of the initial set of standardized explanatory variables* [$(E_T^N)^S$, $(DN)^S$, r_M^S], into

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* A standardized variable is obtained by subtracting the average value of the observation from each observation and dividing by the standard deviation of the observations.

Table 7 Parameters of regression analysis leading to correlations for $\log(Q_{el}/Q_{nel}) = \log(Q_{el}/Q_{nel})_o + aE_T^N + b\,DN + cr_M$ for the reaction of oxiranes **1a** and **1d** with alkali metals

Oxirane	$\log(Q_{el}/Q_{nel})_o$	$a(t)$	$b(t)$	$c(t)$	n	R	σ	F
1a	2.559	−1.875 (−5.01)	−0.025 (−9.86)	−1.32 (−21.40)	16	0.991	0.064	226.86
1d	2.358	−4.654 (−8.12)	0.001 (0.36)	−1.189 (−11.09)	22	0.968	0.136	87.9

Table 8 Percentage contributions from polarity ($\bar{a}$), Lewis basicity ($\bar{b}$), and cation ($\bar{c}$) effects in correlation (4) calculated by principal component analysis

Oxirane	$\bar{a}$(%)	$\bar{b}$(%)	$\bar{c}$(%)
1a	17	34	49
1d	51	2	47

Table 9 Parameters of regression analysis leading to correlations for $\log(Q_{el}/Q_{nel}) = \log(Q_{el}/Q_{nel})_o + aX$, for the reaction of **1d** with alkali metals

X	Metal	$\log(Q_{el}/Q_{nel})_o$	a	N[a]	R[b]	σ[c]	F[d]	t[e]
E_T^N	Li	1.549	−5.205	5	0.994	0.04	253.45	15.92
	Na	1.132	−4.395	8	0.981	0.08	154.13	12.41
	K	1.175	−5.607	7	0.976	0.11	102.1	10.10
AN	Na	1.126	−0.103	6	0.708	0.35	3.01	1.74
	K	1.127	−0.142	5	0.966	0.13	42.26	6.5
Π*	Na	1.340	−1.986	5	0.834	0.28	6.32	2.52
	K	1.177	−2.589	4	0.828	0.35	4.36	2.08
DN	Li	1.145	−0.033	5	0.965	0.10	41.30	6.43
	Na	0.538	−0.020	8	0.694	0.30	5.57	2.36
	K	0.220	−0.02		0.600	0.42	2.28	1.51
β	Na	0.651	−1.102	5	0.646	0.38	2.14	1.43
	K	0.207	−1.549	4	0.492	0.54	0.63	0.80
$\Delta\nu_D$	Li	0.928	−0.005	5	0.755	0.24	3.98	1.99
	Na	0.365	−0.003	8	0.574	0.34	2.94	1.72
	K	0.01	−0.003	7	0.463	0.46	1.36	1.16

[a] Number of experimental points. [b] Correlation coefficient. [c] Standard deviation. [d] Fisher parameter. [e] Student's *t*-parameter.

Table 10 Parameters of regression analysis leading to correlations for $\log(Q_{el}/Q_{nel}) = \log(Q_{el}/Q_{nel})_o + a\,E_T^N + bDN$ for the reaction of oxiranes **1a** and **1d** with sodium

Oxirane	$\log(Q_{el}/Q_{nel})_o$	a	b	n	R	σ	F
1a	1.206	−1.71	−0.025	8	0.987	0.077	93.13
1d	1.132	−4.253	−0.0014	8	0.982	0.086	66.3

For the meaning of symbols n, R, σ, and F see caption to Table 7.

linear combinations of these variables called principal components Z_i,[25] which are orthogonal. The principal components are calculated by eqn. (5).

$$Z_i = \alpha_i\,(E_T^N)^S + \beta_i\,(DN)^S + \gamma_i\,r_M^S \qquad (5)$$

This transformation allows us to express any property P to be studied as a function of Z_i. Substituting back in this expression Z_i by eqn. (5), it is possible to calculate more accurately the percentage contribution of each variable in the regression equation. The numerical values obtained for the principal components and the percentage contribution of each parameter in the triparametric regression equation are indicated, respectively, in Tables 11, 12 and 8. The computation required for this analysis was made with a package program from the scientific library of IBM.

Experimental

Solvents supplied by BDH were dried and freed from oxygen as follows. 1,4-dioxane (DO), 2-methyltetrahydrofuran (MeTHF), THF, diglyme (DG), and DME were dried with $LiAlH_4$, distilled from sodium benzophenone ketyl in a vacuum line, and stored over Na–K alloy (1:4) under vacuum. DMF, HMPA, pyridine (Py) and 1,2-diaminoethane (DA) were distilled under a reduced pressure of argon, kept over 3 Å molecular sieves (Fluka), and added to the sample tube with the help of a syringe.

Tetrabutylammonium perchlorate (BDH) was dried *in vacuo* at 100 °C over P_2O_5 as drying agent. Benzophenone, fluorene (BDH) 4′-dichlorobenzophenone and 4,4′-dimethoxytetraphenylethylene (Ega Chemie) were recrystallized before use.

^1H NMR spectra were determined with Bruker WP 80 (in Siegen) and Bruker 300 CXP (in Lisbon) instruments with Me_4Si as internal standard. M.p.s were measured on a Büchi apparatus and are uncorrected.

Synthetic Procedures.—Dichlorodiphenylmethane,[26] 9,9-dichlorofluorene,[27] fluoren-9-yl(diphenyl)methanol,[28] 1,1,2,2-tetraphenylethanol,[29] 9-methylfluorene,[30] 9,9-dimethylfluorene,[31] tetraphenylethane,[32] 9-benzhydrylidenefluorene,[25] and dibenzhydryl ether[33] were synthesized and purified as described in the literature.

The oxiranes **1a–f** were synthesized according to a procedure described in detail for compound **1d** with the adaptations quoted.

3′,3′-Diphenylspiro[fluorene-9,2′-oxirane] **1d**. *General Procedure for Oxiranes* **1a–f**.—A 250 cm^3, four-necked flask, fitted with a stirrer, a low-temperature thermometer, an argon inlet, and a rubber septum, was thoroughly cleaned, dried, and flamed out under vacuum and then cooled under a stream of dry argon immediately before use. 9,9-Dichlorofluorene (2.35 g, 10^{-2} mol) and deoxygenated, dry THF (100 cm^3) were introduced into the flask. The solution was cooled to −115 °C and 1.28 mol dm^{-3} butyllithium in hexane (7.8 cm^3; 10^{-2} mol) (as supplied by Merck and titrated by the method of Gilman and Haubein[34]) was slowly added during 30 min. After 30 min at −115 °C the mixture was treated with a solution of benzophenone (1.27 g, 0.7 × 10^{-2} mol) in THF (10 cm^{-3}). The mixture was kept for 1 h at −100 °C and then was allowed to warm up slowly. After reaching room temperature the solution was added to an excess of half-saturated aq. ammonium chloride. The organic layer was extracted with diethyl ether and the extract was dried over anydrous magnesium sulphate. The expected oxirane **1d** was obtained as crystals (1.81 g, 75%), m.p. 228 °C (from EtOAc) (lit.,[28] 228 °C) (Found: C, 90.0; H, 5.3. Calc. for $C_{26}H_{18}O$; C, 90.17; H, 5.20%); δ [$(CD_3)_2CO$] 6.103 (2 H, d, *J* 7.8 Hz), 6.909 (2 H, t, *J* 7.8 Hz), 7.553 (12 H, m) and 7.837 (2 H, d, *J* 7.8 Hz).

Table 11 Principal components Z_i and percent variation λ_i absorbed by each component

$$Z_i = \alpha_i\,(E_{\mathrm{T}}^{\mathrm{N}})^S + \beta_i(DN)^S + \gamma_i\,(r_{\mathrm{M}})^S$$

Oxirane		α_i	β_i	γ_i	λ_i(s)
1a	Z_1	0.682	0.679	0.270	59.6
	Z_2	0.178	0.203	0.963	36.7
	Z_3	0.709	−0.705	0.017	36.7
2d	Z_1	0.707	0.706	0.040	57.9
	Z_2	−0.019	−0.038	0.999	38.4
	Z_3	0.707	−0.707	−0.013	3.7

Table 12 Parameters of regression analysis leading to correlations for $\log(Q_{\mathrm{el}}/Q_{\mathrm{nel}}) = \log(Q_{\mathrm{el}}/Q_{\mathrm{nel}})_o + \alpha'\,Z_1 + \beta'\,Z_2 + \gamma\,Z_3$, and for $\log(Q_{\mathrm{el}}/Q_{\mathrm{nel}}) = \log(Q_{\mathrm{el}}/Q_{\mathrm{nel}})_o + a'\,(E_{\mathrm{T}}^{\mathrm{N}})^S + b'\,(DN)^S + c' r_m{}^S$

Oxirane	α'	β'	γ'	a'	b'	c'
1a	−0.513	−0.642	0.520	−0.27	−0.54	−0.77
2d	−0.345	−0.902	0.177	−0.72	0.03	0.65

2,2,3,3-*Tetraphenyloxirane* **1a**. According to the above general procedure butyllithium in hexane (10^{-2} mol) was added to a solution of dichlorodiphenylmethane (2.37 g, 10^{-2} mol) in THF (100 cm^3). A solution of benzophenone (1.27 g, 0.7 × 10^{-2} mol) in THF (10 cm^3) was then added. Compound **1a** was obtained as crystals (2.26 g, 65%), m.p. 208 °C (from EtOH) (lit.,[28] 202–203 °C) (Found: C, 89.6; H, 5.7. Calc. for $C_{26}H_{20}O$: C, 89.66; H, 5.75%); δ $[(CD_3)_2CO]$ 7.3 (20 H, m).

2,2-*Bis*-(4-*chlorophenyl*)-3,3-*diphenyloxirane* **1b**. According to the above general procedure butyllithium in hexane (10^{-2} mol) was added to a solution of dichlorodiphenylmethane (2.37 g, 10^{-2} mol) in THF (100 cm^3). A solution of 4,4′-dichlorobenzophenone (1.76 g, 0.7 × 10^{-2} mol) in THF (10 cm^3) was then added. Compound **1b** was obtained as crystals (2.41 g, 60%), m.p. 161 °C (from EtOH) (Found: C, 74.5; H, 4.4. $C_{26}H_{18}Cl_2O$ requires C, 74.82; H, 4.35%); δ $[(CD_3)_2CO]$ 7.2 (10 H, m) and 7.49 (8 H, m).

2,2-*Bis*-(4-*methoxyphenyl*)-3,3-*diphenyloxirane* **1c**. According to the above general procedure butyllithium in hexane (10^{-2} mol) was added to a solution of dichlorodiphenylmethane (2.37 g, 10^{-2} mol) in THF (100 cm^3). A solution of 4,4′-dimethoxybenzophenone (1.69 g, 0.7 × 10^{-2} mol) in THF (10 cm^3) was then added. Compound **1c** was obtained as crystals (1.63 g, 40%), m.p. 137 °C (from EtOH) (Found: C, 82.5; H, 5.8. $C_{28}H_{24}O_3$ requires C, 82.35; H, 5.88%); δ ($CDCl_3$) 3.87 (6 H, s), 6.95 (4 H, d, *J* 6 Hz), 7.256 (10 H, m) and 7.785 (4 H, d, *J* 6 Hz).

3′,3′-*Bis*-(4-*chlorophenyl*)*spiro*[*fluorene*-9,2′-*oxirane*] **1e**. According to the above general procedure butyllithium in hexane (10^{-2} mol) was added to a solution of 9,9-dichlorofluorene (2.35 g, 10^{-2} mol) in THF (100 cm^3). A solution of 4,4′-dichlorobenzophenone (1.76 g, 0.7 × 10^{-2} mol) in THF (10 cm^3) was then added. Compound **1e** was obtained as crystals (3.26 g, 80), m.p. 204 °C (from EtOAc) (Found: C, 75.4; H, 4.2. $C_{26}H_{16}Cl_2O$ requires C, 75.18; H, 3.86%); δ $[(CD_3)_2CO]$ 6.17 (2 H, d, *J* 8.3 Hz), 7.046 (2 H, t, *J* 8.3 Hz), 7.36 (8 H, m), 7.64 (2 H, m) and 7.86 (2 H, d, *J* 8.3 Hz).

3′,3′-*Bis*-(4-*methoxyphenyl*)*spiro*[*fluorene*-9,2′-*oxirane*] **1f**. According to the above general procedure butyllithium in hexane (10^{-2} mol) was added to a solution of 9,9-dichlorofluorene (2.35 g, 10^{-2} mol) in THF (100 cm^3). A solution of 4,4′-dimethoxybenzophenone (1.69 g, 0.7 × 10^{-2} mol) in THF (10 cm^3) was then added. Compound **1f** was obtained as crystals (2.45 g, 60%), m.p. 236 °C (from EtOAc) (Found: C, 83.0; H, 5.1. $C_{28}H_{22}O_3$ requires C, 82.30; H, 5.88%); δ $[(CD_3)_2CO]$ 3.78 (6 H, s, Me), 6.19 (2 H, d, *J* 7.5 Hz), 6.9 (6 H, t, *J* 7.5 Hz), 7.38 (6 H, m) and 7.69 (2 H, d, *J* 6 Hz).

Benzhydryl Fluorenyl Ether **17** [$R^1R^2 = (o\text{-}C_6H_4)_2$, $R^3 = R^4 = \mathrm{Ph}$).—A mixture of benzhydrol (1.5 g, 8.21 × 10^{-3} mol), fluorenol (3.5 g, 19.2 × 10^{-3} mol) and toluene-*p*-sulphonyl chloride (1.9 g, 10^{-2} mol) in benzene (35 cm^3) was refluxed for 2 h. The solution obtained was washed successively with distilled water and then with aq. sodium hydrogen carbonate until neutral, dried with sodium sulphate, and evaporated to dryness. *Benzhydryl fluorenyl ether* was obtained as crystals (1.4 g, 40%), m.p. 116–117 °C (from EtOAc), (Found: C, 89.6; H, 5.8. $C_{26}H_{20}O$ requires C, 89.66; H, 5.75%); δ ($CDCl_3$) 5.65 (1 H, s), 5.75 (1 H, s), and 7.23 (18 H, m); *m*/*z* 348 (M^+, 2.4%), 183 (15), 181 (20), 167 (30), 165 (100), 105 (10) and 77 (10).

Other Procedures.—Cyclic voltammetry experiments were performed on a Princeton Applied Research potentiostat–galvanostat model 173 at room temperature using 10^{-3} mol dm^{-3} solutions of the compounds in DMF. Tetrabutylammonium perchlorate (0.1 mol dm^{-2}) was used as a support electrolyte, the working electrode was a mercury drop electrode, and the reference electrode was a saturated calomel electrode.

The reactions of the oxiranes with alkali metals were run in vacuum-sealed double Schlenk tubes, with the two arms joined by a break-seal. The samples were prepared in a high-vacuum line by known techniques.

The NMR experiments were run under argon in the apparatus already described.[35]

Product analysis was by high-pressure liquid chromatography (HPLC) with a 10 μm particle size silica gel Lichrosorb, Si60 column of 4 mm inner diameter and 250 mm length. Hexane with 0.5–1.5% of DO was used as mobile phase. A UV detector was used, tuned to 230 nm. For the determination of concentrations in the analysed solutions of reaction products the method of internal standards was used.

EPR spectra were run on a Bruker ER 200 D spectrometer equipped with an ER400 vt variable-temperature unit.

Acknowledgements

Financial support from the *Instituto Nacional de Investigação Científica* through *Centro de Processos Químicos da Universidade Técnica de Lisboa* is gratefully acknowledged. M. L. T. M. B. F. thanks DAAD, *Deutscher Akademischer Austrauschdienst*, for a travel and subsistence grant to Siegen.

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Paper 0/02196B
Received 17*th May* 1990
Accepted 7*th August* 1990