J. CHEM. SOC. PERKIN TRANS. 2 1994

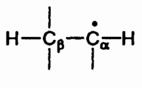
The Effects of β-Alkoxy Substituents on Radical Reactions: Halogen-atom Abstraction from Alkyl Chlorides

Brian P. Roberts* and Andrew J. Steel
Christopher Ingold Laboratories, Department of Chemistry, University College London, 20 Gordon Street, London, UK WC1H 0AJ

EPR spectroscopy has been used to measure the relative rates of halogen-atom abstraction from RCH_2Cl [R = Pr, $MeOCH_2$, $(MeO)_2CH$, $(MeO)_3C$, Me_3Si] by the metalloid-centred radicals $Me_3N\rightarrow\dot{B}HBu$, $Et_3N\rightarrow\dot{B}H_2$ and $Et_3Si^\bullet$ ($M^\bullet$) in cyclopropane and in oxirane solvents at 160–260 K. β-Methoxy substituents increase the rate of reaction, especially for chlorine abstraction by the highly nucleophilic amine–boryl radicals. The accelerating influence of the β-oxygen substituents is attributed to a polar effect which operates in the transition state and involves charge transfer from $M^\bullet$ to the CH_2–Cl group. The relative reactivities of the *cis-* and *trans-*isomers of 5-chloro-2-*tert*-butyl-1,3-dioxane indicate that the substituent effect of a β-alkoxy group does not depend markedly on the orientation of the β–C–O bond with respect to the rupturing C–Cl bond. It is concluded that the β–C–O bond dipole interacts electrostatically through space with the dipolar C••• Cl••• M grouping in the transition state and thus stabilises the latter relative to the reactants. This interpretation is supported by the results of *ab initio* molecular calculations for model systems. The EPR spectra of the β-alkoxyalkyl radicals are discussed in relation to their preferred conformations as deduced on the basis of the Heller–McConnell equation. The applicability of the latter equation is confirmed by *ab initio* calculations for the ethyl radical.

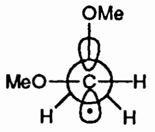
The measurement and interpretation of substituent effects in free radical chemistry are subjects of perennial interest and fundamental importance.[1] The detailed analysis of substituent effects on the rates of radical reactions, in terms of the interactions present in the reactants and in the transition state, can be complex and is often controversial.

For a carbon-centred radical **1**, the effects of replacing an α-hydrogen atom by another group are reasonably well understood for most types of substituent. However, interpretation of the effects which accompany replacement of a β-hydrogen atom in **1** by another substituent often presents a greater challenge. For β-substituent effects on radical reactions, questions as to the importance of hyperconjugative, negative hyperconjugative (*i.e.*, anomeric) and bridging interactions must be addressed.



$H{-}C_\beta{-}\dot{C}_\alpha{-}H$

1



2

In 1982 Barton, Hartwig and Motherwell[2] proposed that alkyl radicals are thermodynamically stabilised by β-alkoxy substituents and that this stabilisation results in the more ready formation of β-alkoxyalkyl radicals, as compared with unsubstituted analogues, in some related types of chain reaction mediated by trialkyltin hydrides. However, it should be noted that the *overall* rate of a radical chain reaction does not necessarily parallel the rate of any particular elementary step. For this reason, we consider that the magnitude (and even the existence) of the β-oxygen substituent effect remains to be confirmed for the key radical-fragmentation propagation steps of the chain processes discussed by Barton *et al.*[2]

Ab initio molecular orbital calculations by Sosa and Schlegel[3] indicate that $DH^\circ(HOCH_2CH_2{-}H)$ is essentially the same as $DH^\circ(CH_3CH_2{-}H)$ (421 kJ mol^{-1} by experiment)[4] and thus that the C–H bond weakening effect of the β-OH substituent in ethanol is negligible. In contrast, on the basis of appearance energy measurements, Holmes *et al.*[5] concluded that $DH^\circ(HOCH_2CH_2{-}H)$ is 397 kJ mol^{-1}, corresponding to a significant bond weakening effect of the β-OH group. However, the same technique indicates that $DH^\circ(HOCMe_2{-}CH_2{-}H)$ is only 383 kJ mol^{-1} and thus that a C–H bond in *tert*-butyl alcohol is appreciably weaker than the tertiary C–H bond in Me_3CH (402 kJ mol^{-1}).[4] This remarkably large substituent effect of the β-OH group appears rather unreasonable and is out of line with the homolytic reactivity of the C–H bonds in *tert*-butyl alcohol.†

Beckwith and Brumby[7] have concluded that the β-MeO substituent has only a minor influence on the rate of hydrogen-atom abstraction by $Bu^tO^\bullet$ from $MeOCH_2CH_2OMe$ to give $MeOCH_2\dot{C}HOMe$, although it does confer on the latter radical a preference for the eclipsed conformation **2**. On the other hand, Dupuis *et al.*[8] have reported that a β-C–O bond influences not only the ground-state conformations of certain carbon-centred glycosyl radicals but, at least when an α-oxygen atom is also present, can increase the rate of their formation by chlorine-atom transfer to tributylstannyl radicals when the β-C–O bond is antiperiplanar to the C–Cl bond undergoing cleavage in the transition state. The rate-enhancing effect of the β-oxygen substituent was interpreted in terms of an orientation-dependent radical stabilising influence (*i.e.*, an enthalpic effect) of the β-C–O bond.[8,9]

In a preliminary communication,[10] we reported relative rates of chlorine-atom abstraction by the metalloidal radicals $Me_3N\rightarrow\dot{B}HBu$ and $Et_3Si^\bullet$ from RCH_2Cl [R = Pr, $MeOCH_2$, $(MeO)_2CH$, Me_3Si] [eqn. (1)]. The β-methoxy

$$M^\bullet + RCH_2Cl \longrightarrow MCl + RCH_2^\bullet \qquad (1)$$

---

† *tert*-Butyl alcohol and similar tertiary alcohols have been used as 'inert' solvents or co-solvents for reactions of *tert*-butoxyl radicals. If the C–H bond is as weak as suggested by Holmes *et al.*,[5] then the β-OH group would need to exert an unreasonably large destabilising polar effect on the transition state for hydrogen-atom transfer to the electrophilic $Bu^tO^\bullet$ from these alcohols in order to make the abstraction process so slow (see later).[6]

substituent was found to be slightly activating towards chlorine abstraction by $Et_3Si^\bullet$, but strongly activating towards abstraction by the more nucleophilic amine–boryl radical. We argued that polar effects, which act in the transition state, are responsible for the accelerating influence of the β-methoxy group, rather than any enthalpic effect of the type proposed by Barton, Hartwig and Motherwell.[2] This polar effect of the MeO group presumably operates through facilitating the build-up of negative charge on the RCH_2Cl moiety in the transition state, by an anomeric interaction[11–13] and/or by an 'inductive' mechanism (the term taken to include both the classical σ-inductive and electrostatic field effects).[14] We favoured the dominance of the anomeric effect,[10] by analogy with the interaction thought[7,15] to be responsible for locking the radical $MeOCH_2\dot{C}HOMe$ into the conformation **2**. In the present paper we give a full account of this work, together with the results of additional experiments and calculations which strongly indicate that it is the electrostatic field effect of the β-alkoxy substituent which is predominant.

Results and Discussion

Relative Rates of Chlorine-atom Abstraction.—EPR spectroscopy was used to monitor the radicals present during continuous UV irradiation of liquid samples positioned in the microwave cavity of the spectrometer.[16] The primary source of radicals in all experiments was the photolysis of di-*tert*-butyl peroxide (DTBP) [eqn. (2)]. *tert*-Butoxyl radicals produced in

$$\mathrm{Bu^tOOBu^t \xrightarrow{h\nu} 2Bu^tO^\bullet} \qquad (2)$$

this way abstract hydrogen rapidly from boron or silicon in amine–borane complexes[17] or in triethylsilane,[18] respectively, to form the corresponding metalloidal radical $M^\bullet$ [eqn. (3),

$$\mathrm{Bu^tO^\bullet + MH \longrightarrow Bu^tOH + M^\bullet} \qquad (3)$$

$MH = Me_3N{\rightarrow}BH_2Bu$, $Et_3N{\rightarrow}BH_3$ or Et_3SiH]. In the presence of an alkyl chloride RCH_2Cl, $M^\bullet$ abstracts halogen to generate the carbon-centred radical $RCH_2^\bullet$ [eqn. (1)]. Thus, a strong EPR spectrum of the butyl radical is detected during UV irradiation of a cyclopropane solution containing $Me_3N{\rightarrow}BH_2Bu$ (1.0 mol dm^{-3}), 1-chlorobutane (1.0 mol dm^{-3}) and DTBP (*ca.* 15% v/v) between 160 and 260 K.[19] The triethylamine–boryl radical $Et_3N{\rightarrow}\dot{B}H_2$ is somewhat less reactive than $Me_3N{\rightarrow}\dot{B}HBu$ in chlorine-atom abstraction and the triethylsilyl radical is appreciably less reactive.[19,20] Assuming an Arrhenius *A*-factor of $10^{8.7}$ dm^3 mol^{-1} s^{-1} (as found for similar abstraction from Bu^tCl),[20] the activation energy and rate constant at 200 K for chlorine-atom abstraction from 1-chloropentane by $Et_3Si^\bullet$ can be estimated to be *ca.* 18.4 kJ mol^{-1} and *ca.* 8×10^3 dm^3 mol^{-1} s^{-1}, respectively,[20] and the corresponding values for BuCl must be very similar.

Relative reactivities of pairs of chlorides R^1Cl and R^2Cl were determined in competition experiments.[21] UV irradiation of solutions containing DTBP (*ca.* 15% v/v), MH (0.6–1.0 mol dm^{-3}) and the two chlorides (total concentration *ca.* 0.9 mol dm^{-3}) afforded overlapping EPR spectra of $R^{1\bullet}$ and $R^{2\bullet}$ [eqns. (4) and (5)], from which the values of $[R^{1\bullet}]/[R^{2\bullet}]$ could be determined by double-integration and/or computer simulation.[16,21,*] The value of k_1/k_2 (k_{rel}) will be given by eqn. (6), provided that $R^{1\bullet}$ and $R^{2\bullet}$ are removed by radical–radical reactions which have effectively equal diffusion-controlled rate

$$\mathrm{M^\bullet + R^1Cl \xrightarrow{k_1} MCl + R^{1\bullet}} \qquad (4)$$

$$\mathrm{M^\bullet + R^2Cl \xrightarrow{k_2} MCl + R^{2\bullet}} \qquad (5)$$

$$k_1/k_2 = [R^{1\bullet}][R^2Cl]/[R^{2\bullet}][R^1Cl] \qquad (6)$$

constants.[23,†] The chlorides **3**–**7** were examined and the relative reactivities and Arrhenius activation parameters obtained from measurements between 160 and 260 K are given in Tables 1 and 2 for cyclopropane and oxirane solvents, respectively.

Table 1 Relative rate constants at 200 K and Arrhenius activation parameters for halogen-atom abstraction from the chlorides **3**–**7** in cyclopropane

	Abstracting radical $M^\bullet$					
	$Me_3N{\rightarrow}\dot{B}HBu$			$Et_3Si^\bullet$		
Chloride	k_{rel}	A_{rel}[a]	E_{rel}[b]	k_{rel}	A_{rel}[a]	E_{rel}[b]
3	(1)	(1)	(0)	(1)	(1)	(0)
4	5.5	0.82	3.2	1.4	1.4	0.1
5	17.2	0.52	5.8	2.2	1.4	0.7
6	45.0	0.60	7.2	2.4	1.5	0.8
7	46.3	0.78	6.8	38.2	0.66	6.8

[a] $A_{rel} = A(\text{chloride})/A(\text{BuCl})$. [b] $E_{rel} = E_a(\text{BuCl}) - E_a(\text{chloride})$ in kJ mol^{-1}.

$MeCH_2CH_2CH_2Cl$ **3** $MeOCH_2CH_2Cl$ **4** $(MeO)_2CHCH_2Cl$ **5**

$(MeO)_3CCH_2Cl$ **6** Me_3SiCH_2Cl **7**

UV photolysis of cyclopropane solutions containing dipentanoyl peroxide (*ca.* 10% v/v) and one of the chlorides **4**–**7** (*ca.* 1.0 mol dm^{-3}) afforded only a strong EPR spectrum of the butyl radical up to 250 K [eqn. (7)], irrespective of the nature of

$$\mathrm{Bu(O)OOC(O)Bu \xrightarrow{h\nu} 2Bu^\bullet + 2CO_2} \qquad (7)$$

the chloride, confirming that halogen-atom abstraction from **4**–**7** by a primary alkyl radical does not compete with radical–radical reactions under the conditions of our experiments.

The results presented in Tables 1 and 2 show that β-methoxy groups significantly activate RCH_2Cl towards chlorine-atom abstraction by amine–boryl radicals, but that the activating effect is small for abstraction by triethylsilyl radicals. As was pointed out before, $Me_3N{\rightarrow}\dot{B}HBu$ abstracts chlorine much more rapidly from 1-chlorobutane **3** than does $Et_3Si^\bullet$.[19] Thus, despite being the more *reactive* radical, $Me_3N{\rightarrow}\dot{B}HBu$ is more *selective* than $Et_3Si^\bullet$ in competitive abstraction of chlorine from **3** and **4**–**6**, indicating[24a] that 'polar effects',[6,19,24] which operate specifically in the transition state, are important in determining the activation energies for halogen abstraction.

The transition state for chlorine-atom transfer to a

---

[*] To take account of depletion of the reagents during UV irradiation, it was sometimes necessary to extrapolate the value of $[R^{1\bullet}]/[R^{2\bullet}]$ to zero photolysis time. Corrections were applied to take account of chemically induced dynamic electron polarisation (CIDEP) effects[22] whenever these were evident in the spectra.

[†] This assumption should be valid when $R^{1\bullet}$ and $R^{2\bullet}$ are unhindered primary and secondary carbon-centred radicals of similar size,[23] as in this work.

Table 2 Relative rate constants at 200 K for halogen-atom abstraction from the chlorides **3**–**6** in oxirane

Chloride	$k_{rel}(Me_3N\rightarrow\dot{B}HBu)$	$k_{rel}(Et_3N\rightarrow\dot{B}H_2)$	$k_{rel}(Et_3Si^{\bullet})$
3	(1)	(1)	(1)
4	4.7	4.0	1.6
5	16.4	12.8	2.1
6	30.1	16.6	2.3

nucleophilic metalloidal radical $M^{\bullet}$ can be described as a resonance hybrid of structures **8a**–**d** and the contributions from **8c** and **8d** will increase as the ionisation energy of $M^{\bullet}$ decreases and as the electron affinity of $RCH_2^{\bullet}$ increases.[6] Thus, for a

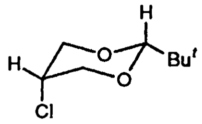
$[RCH_2\text{–}Cl\ ^{\bullet}M] \longleftrightarrow [RCH_2^{\bullet}\ Cl\text{–}M] \longleftrightarrow$
8a **8b**
$[RCH_2^{\bullet}\ Cl\bar{:}\ ^{+}M] \longleftrightarrow [R\dot{C}H_2^{-}\ Cl^{\bullet}\ ^{+}M]$
8c **8d**

given chloride this charge transfer stabilisation of the transition state should be more important for abstraction by the very nucleophilic[17,19-21] amine–boryl radicals than by the less nucleophilic trialkylsilyl radical (see Table 8 and the discussion below). In accord with this analysis, the β-methoxy groups in **4**–**6** exert only a relatively small activating effect on chlorine abstraction by $Et_3Si^{\bullet}$, but a large effect for abstraction by the amine–boryl radicals, with $Me_3N\rightarrow\dot{B}HBu$ somewhat more selective than the less nucleophilic $Et_3N\rightarrow\dot{B}H_2$ (see Table 2).†

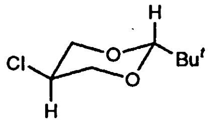
The ability of trialkylsilyl groups to stabilise an adjacent carbanionic centre is well known.[25] Wilt *et al.*[26] have interpreted the very high reactivity of Me_3SiCH_2Cl compared with 1-chloropentane towards chlorine abstraction by nucleophilic tributylstannyl radicals in terms of charge transfer stabilisation of the transition state in the manner described here. Likewise, Me_3SiCH_2Cl is very reactive towards halogen-atom transfer to both amine–boryl and trialkylsilyl radicals. While Me_3SiCH_2Cl is only slightly more reactive than $(MeO)_3CCH_2Cl$ towards $Me_3N\rightarrow\dot{B}HBu$, $Et_3Si^{\bullet}$ abstracts chlorine much more rapidly from the former chloride (see Table 1). It is likely that the activation energies for chlorine abstraction by $Me_3N\rightarrow\dot{B}HBu$ are very small for both halides, resulting in compression of the relative reactivities, while the activation energies are larger for abstraction by $Et_3Si^{\bullet}$.

The question remains as to how the β-MeO groups stabilise the transition state by facilitating charge transfer from $M^{\bullet}$ to the RCH_2Cl moiety. The effect could be a classical σ-inductive one in which the electronegative oxygen atom polarises the bonding electrons to delocalise negative charge from the CH_2Cl group.[14] Alternatively, the β-C–O bond dipole could interact electrostatically through space to stabilise the negative charge building up on the CH_2Cl group.[14] Thirdly, this negative charge could be delocalised into the β-C–O σ* orbital (negative or reverse hyperconjugation), an example of the generalised anomeric effect.[11] The degree of anomeric delocalisation and stabilisation of the transition state could be critically dependent on the orientation of the β-C–O bond with respect to the C–Cl bond and should be maximised when these bonds are antiperiplanar.

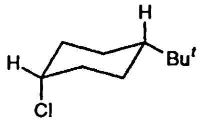
In an attempt to distinguish the mechanism of action of the β-oxygen substituent effect, we have examined chlorine-atom abstraction from the isomerically pure *cis*- and *trans*-dioxanes **9** and cyclohexanes **10**. The *tert*-butyl group serves as a conformational lock and the chlorine atom is axial in the *cis*-isomers and equatorial in the *trans*-isomers. The *cis*- and *trans*-isomers of the dioxane **9**, which were separated by preparative HPLC, could be equilibrated in $CDCl_3$ in the presence of a polymer-bound sulfonic acid catalyst (Amberlyst-15). At 293 K, the equilibrium value of [*trans*-**9**]/[*cis*-**9**] was 5.3, corresponding to $\Delta G_{c\rightarrow t}$ = −4.1 kJ mol^{-1}.‡ The difference in stabilities of *cis*- and *trans*-**10** is similar ($\Delta G_{c\rightarrow t}$ *ca.* −1.8 kJ mol^{-1}).[28] In *cis*-**9**, the β-C–O and C–Cl bonds will be synclinal (*gauche*), while in the *trans*-isomer they will be antiperiplanar (see structures **11a** and **11b**). The rates of chlorine-atom abstraction from *cis*- and *trans*-**9** by $Me_3N\rightarrow\dot{B}HBu$ were measured separately relative to $MeOCH_2CH_2Cl$ at temperatures between 160 and 260 K; of course, both isomers afford the same dioxanyl radical. For comparison, the rates of chlorine-atom abstraction by $Me_3N\rightarrow\dot{B}HBu$ from *cis*- and *trans*-**10** were also determined, this time relative to 1-chlorobutane; the results are given in Table 3. The two β-oxygen substituents present in **9** again exert a marked accelerating effect on chlorine-atom abstraction by $Me_3N\rightarrow\dot{B}HBu$, however, for both **9** and **10**, it is the *cis*-isomer that is 2–3 times more reactive than the *trans*. This could be partly a ground-state effect, because the *cis*-isomers are less stable than the *trans*, or it could be the result of steric or torsional strain effects in the transition state, but clearly the antiperiplanar C–O bond in *trans*-**9** is not significantly more activating than the synclinal C–O bond in the *cis*-isomer. This result militates strongly against an anomeric delocalisation of negative charge as the origin of the β-oxygen substituent effect and points to a σ-inductive or electrostatic field effect as the cause of the observed reactivity trends.



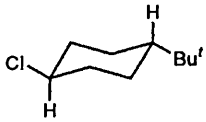
cis-**9**



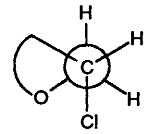
trans-**9**



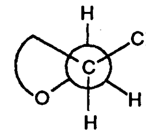
cis-**10**



trans-**10**



11a (*cis*)



11b (*trans*)

At this point it is appropriate to draw attention to the differences between the effects on radical reactions of α-and β-oxygen substituents at a carbon centre. The α-alkoxy group in a molecule of the type $ROCH_2X$ exerts an enthalpic effect on the

---

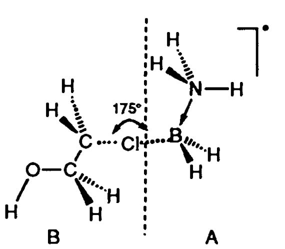
† Reactions of $Et_3N\rightarrow\dot{B}H_2$ were studied only in oxirane because $Et_3N\rightarrow BH_3$ is not very soluble in cyclopropane at low temperatures.

‡ The value of $\Delta G_{c\rightarrow t}$ for 5-chloro-2-isopropyl-1,3-dioxane has been determined in a similar way to be −3.9 kJ mol^{-1} in chloroform at 298 K, although it is solvent dependent (ref. 27).

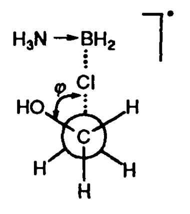
abstraction of the atom X, because the derived radical $R\ddot{O}\text{–}\dot{C}H_2 \longleftrightarrow R\overset{+}{\dot{O}}\text{–}\overset{-}{\ddot{C}}H_2$ is stabilised by delocalisation of the unpaired electron onto oxygen. The α-oxygen substituent will also exert a polar effect and will facilitate abstraction of $X^{\bullet}$ by electrophilic radicals ($E^{\bullet}$), because of a stabilising charge transfer interaction in the transition state, as represented by inclusion of the structure $[ROCH_2^{+}\ X^{\bullet}\ \bar{:}E]$ in a valence bond description. The polar effect of an α-oxygen substituent is thus the converse of that of an α-trialkylsilyl group which favours abstraction of $X^{\bullet}$ by a nucleophilic radical (see above). The importance of such polar effects is illustrated by the relative rates of chlorine-atom abstraction by the nucleophilic $Me_3N{\rightarrow}\dot{B}HBu$ from $MeOCH_2Cl$ and Me_3SiCH_2Cl, compared with the relative rates of hydrogen-atom abstraction by the electrophilic $Bu^tO^{\bullet}$ from Me_2O and Me_4Si, as determined by EPR spectroscopy in the usual way.[16,19,23] Thus at 200 K in cyclopropane, Me_3SiCH_2Cl is 9.3 times *more* reactive than $MeOCH_2Cl$ towards $Me_3N{\rightarrow}\dot{B}HBu$, while Me_4Si is 37.7 times *less* reactive than Me_2O towards $Bu^tO^{\bullet}$ at the same temperature in tetramethylsilane solvent.†

Molecular Orbital Calculations.—*Ab initio* molecular orbital calculations were carried out for the reactants and transition states for a number of model chlorine-atom transfer reactions in order to probe the relative importance of anomeric, σ-inductive and electrostatic field effects. Except where stated otherwise, computations employed the standard 3-21G* basis set as implemented in the GAUSSIAN 92 package of programs.[29]

(*i*) *The Ammonia–Boryl Radical with 2-Chloroethanol.*—Geometry optimisation within C_s symmetry resulted in the transition state structure **12** for which selected properties are given in Table 4. Structure **12** showed a single imaginary normal vibrational mode ($\tilde{\nu}_i = -640.5\ \text{cm}^{-1}$), which characterises a transition state, associated with transfer of the chlorine atom between carbon and boron; the C ··· Cl ··· B moiety is close to linear. The calculation was repeated with the dihedral angle OCCCl (φ in structure **13**) fixed at 60° and at 90° (structures **14a** and **14b**, respectively; see Table 4), with all other geometrical parameters held at the optimised values for **12**. The results are given in Table 4, along with the charge separations between the fragments A and B derived from Mulliken population analysis.



12



13

It is evident that there is significant transfer of electronic charge (0.195e) from the amine–boryl fragment A to the 2-chloroethanol fragment B in the C_s structure **12**, in accord with the nucleophilic character of $H_3N{\rightarrow}\dot{B}H_2$ and as represented by inclusion of structures **8c** and **8d** (M = $H_3N{\rightarrow}BH_2$) in a valence bond description of the transition state. In the terminology of perturbational molecular orbital theory, we have a dominant interaction involving electron transfer from the SOMO of $H_3N{\rightarrow}\dot{B}H_2$ into the C–Cl σ* orbital of the 2-chloroethanol. In structure **12** the C–O bond is aligned antiperiplanar to the rupturing C–Cl bond, the optimum conformation for anomeric delocalisation of the developing negative charge into the C–O σ* orbital. However, when φ was constrained to be 60° and even when the C–O bond was held orthogonal to the C–Cl bond (φ = 90°), there was an insignificant reduction in the extent of charge transfer from fragment A to fragment B. This implies that anomeric delocalisation is unimportant in facilitating charge transfer from A to B and in stabilising the transition state for chlorine-atom abstraction, in accord with the experimental results for **9**.

(*ii*) *The Ammonia–Boryl Radical with* 1-*Chloropropane and with* 1-*Chloro*-3-*fluoropropane.*—Similar calculations were carried out for the C_s transition states **15** and **16**; the optimised structures each showed a single imaginary vibrational mode and selected properties are given in Table 5. The extent of charge transfer to the 1-chloropropane residue in the transition state **15** (0.188e) is very similar to that to the 2-chloroethanol residue in **12**, and even the presence of the very electronegative fluorine atom in **16** results in only a small increase (to 0.198e) in the amount of electron transfer to the alkyl halide moiety. When the dihedral angle FCCCl was fixed at 60° and at 90° (structures **17a** and **17b**, respectively; see Table 5), only very small changes occurred in the charge distribution between the A and B fragments. Hence, it appears that the extent of charge transfer depends mainly on the electronegativities of the atoms

Table 3 Relative rate constants at 200 K and Arrhenius activation parameters for halogen-atom abstraction from the cyclic chlorides **9** and **10** by $Me_3N{\rightarrow}\dot{B}HBu$ in cyclopropane

Chloride	k_{rel}[a]	A_{rel}[b]	E_{rel}[c]	k_{cis}/k_{trans}
cis-**9**	48.9	0.42	7.9	2.0
trans-**9**	24.3	0.13	8.7	
cis-**10**	1.0	3.3	−2.0	3.1
trans-**10**	0.32	7.0	−5.1	

[a] k_{rel} = *k*(chloride)/*k*(BuCl). [b] A_{rel} = *A*(chloride)/*A*(BuCl). [c] E_{rel} = E_a(BuCl) − E_a(chloride).

Table 4 Results of 3-21G* calculations for structures **12** and **14**

Structure	*E*/hartree[a] (E_{rel}/kJ mol^{-1})	Bond lengths and angles (Å or °)						μ/D	Fragment charges	
		B–Cl	C–Cl	N–B	C–O	CClB[b]	φ[c]		A	B
12	−691.562 252 (0)	2.574	2.031	1.664	1.449	175.2	180	4.493	+0.195	−0.195
14a	−691.557 324 (+12.9)	2.574	2.031	1.664	1.449	175.2	60	5.004	+0.190	−0.190
14b	−691.557 440 (+12.6)	2.574	2.031	1.664	1.449	175.2	90	4.866	+0.194	−0.194

[a] $\langle S^2 \rangle$ *ca.* 0.84. [b] Dihedral angle CCClB = 180°. [c] Dihedral angle OCCCl defined in structure **13**.

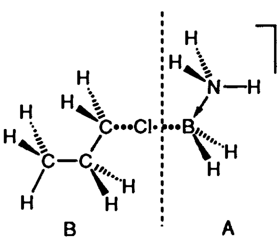
---

† Relative reactivities are quoted on a per molecule basis: there are actually twice as many equivalent abstractable hydrogen atoms in Me_4Si as in Me_2O. In addition to the polar effect of the α-oxygen substituent, it is possible that the adjacent oxygen atom may lead to some strengthening of the C–Cl bond in $MeOCH_2Cl$ as a result of ionic resonance involving $MeOCH_2^{+}\ \bar{:}Cl$ (a ground-state effect).

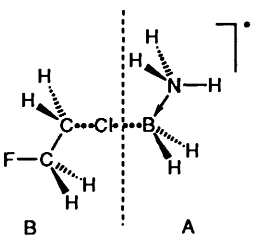
Table 5 Results of 3-21G* calculations for structures **15**–**17**

		Bond lengths and angles (Å or °)						Fragment charges	
Structure	E/hartree[a]	B–Cl	C–Cl	N–B	CClB	XCCCl[b]	μ/D	A	B
15[c]	−655.953 000	2.582	2.043	1.665	175.3	180	5.861	+0.188	−0.188
16[d]	−715.448 318	2.592	2.007	1.663	175.5	180	6.847	+0.198	−0.198
17a	−715.444 568	2.592	2.007	1.663	175.5	60	7.149	+0.190	−0.190
17b	−715.443 325	2.592	2.007	1.663	175.5	90	7.037	+0.191	−0.191

[a] $\langle S^2 \rangle$ *ca.* 0.84. [b] X = C or F. [c] Single imaginary vibrational mode, $\tilde{\nu}_i = -642.7$ cm^{-1}. [d] Single imaginary vibrational mode, $\tilde{\nu}_i = -632.7$ cm^{-1}.



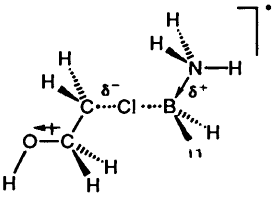
15



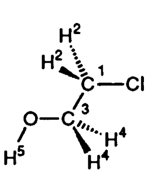
16

undergoing covalency change, *i.e.*, carbon, chlorine and boron. These results lead to the conclusion that the increased rate of chlorine-atom abstraction by nucleophilic radicals in the presence of β-oxygen substituents is the consequence of an electrostatic field effect which stabilises the transition state. The β-C–O bond dipole could interact through space with the dipolar C • • • Cl • • • M group in the transition state to stabilise the latter and thereby facilitate halogen abstraction. This electrostatic dipole–dipole interaction is illustrated in structure **18** and would not lead to significant transfer of negative charge from the CCl group to the β-oxygen atom.

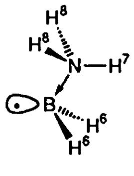
In Table 6 the Mulliken charge distributions for the geometry-optimised C_s conformations of 2-chloroethanol **19** and the ammonia-boryl radical† **20** are compared with the charge distribution in the transition state **12**. Upon going from the reactants to the transition state, electronic charge transfer takes place mainly (0.183e) from the BH_2 group in the amine–boryl radical to the CH_2Cl group (0.159e) of the 2-chloroethanol, although the negative charge on C-1 actually decreases slightly on going to the transition state. There is a negligible increase in the negative charge on the OH group on moving to the transition state, in accord with the proposal that the β-oxygen substituent increases the rate of chlorine-atom transfer to nucleophilic radicals mainly by an electrostatic field effect, rather than a classical σ-inductive effect or an anomeric effect.



18

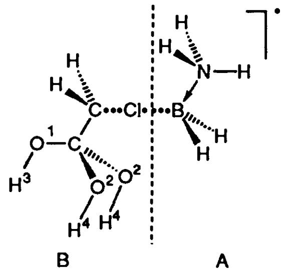


19



20

(*iii*) *The Ammonia–Boryl Radical with* 1-*Chloro*-2,2,2-*trihydroxyethane*.—Calculations for this model reaction provide evidence in support of some anomeric delocalisation of negative charge in the transition state for chlorine-atom abstraction from $(MeO)_3CCH_2Cl$ by amine–boryl radicals. The geometry of the transition state **21** was optimised within C_s symmetry and the properties of the resulting structure are compared with those of **12** in Table 7 (the conformation of the three OH groups in **21** is not likely[11] to be the most stable).



21

The extent of charge transfer from A to B is increased by *ca.* 11% in **21** as compared with **12**. Although it appears that the interaction between the C • • • Cl • • • M group and the C–O bonds is still primarily dipole–dipole in nature, there are also indications of an angularly dependent delocalisation of negative charge onto oxygen (*i.e.*, an anomeric effect) now that three electronegative substituents are present on C_β. Thus, the negative charge on the OH group which is *anti* to the C • • • Cl bond is 7% larger than that on the OH groups *gauche* to it. The antiperiplanar C–O bond is also longer by 0.02 Å than the synclinal C–O bonds, consistent with greater electron donation from the CH_2 • • • Cl group into the antiperiplanar σ* C–O orbital than into a synclinal σ* C–O orbital.

(*iv*) *Abstraction of Chlorine from* 2-*Chloroethanol by Ammonia–Methylboryl, Silyl and Ethyl Radicals*.—It has been pointed out that vertical radical ionisation energies (E_i), which are in good agreement with experiment, can be calculated 'indirectly' (*i.e.*, not making use of Koopman's theorem) as the difference in energies of $R^\bullet$ and R^+ at the geometry of $R^\bullet$.[31] Ionisation energies calculated in this way at the MP3(full)/6-31G**//U(R)HF/6-31G** level[32] are given in Table 8; the result for the electrophilic $H_2\dot{N}\rightarrow BH_3$ is included for comparison. Both amine–boryl radicals have extremely low ionisation energies, implying high nucleophilicity, and the smaller value of E_i calculated for $H_3N\rightarrow\dot{B}HMe$ as compared with that for $H_3N\rightarrow\dot{B}H_2$ suggests that the former radical should be somewhat more nucleophilic.

Calculations were carried out for the transition state **22** making simplifying assumptions about its geometry. The $HOCH_2CH_2ClBNH_3$ moiety was constrained to have local C_s symmetry and local C_{3v} symmetry was imposed on the CH_3 group; properties of the resulting 'transition state' (which will not, because of the constraints, be a true saddle point on the potential energy surface) are given in Table 9. The degree of charge transfer from the amine–boryl moiety A to the 2-chloroethanol residue B in **22**, is, however, only marginally greater than that in **12**.

Calculations were also carried out within C_s symmetry for the

---

† We have previously reported calculations at the 6-31G** level for this radical.[21,30]

Table 6 Charge distributions in 2-chloroethanol **19**, the ammonia–boryl radical **20** and the transition state **12**

			Atomic charges[a]											
Structure	*E*/hartree	μ/D	Cl	C-1	H-2	C-3	H-4	O	H-5	B	H-6	N	H-7	H-8
19[b,c]	−610.045 685	2.453	−0.109	−0.490	+0.278	−0.084	+0.212	−0.682	+0.386	—	—	—	—	—
20[c]	−81.533 413	5.909	—	—	—	—	—	—	—	−0.092	−0.087	−0.865	+0.374	+0.378
12	−691.562 252	4.493	−0.225	−0.455	+0.239	−0.094	+0.205	−0.682	+0.374	+0.035	−0.059	−0.881	+0.375	+0.392
			(−0.116)	(+0.035)	(−0.039)	(−0.010)	(−0.007)	(0.000)	(−0.012)	(+0.127)	(+0.028)	(−0.016)	(+0.001)	(+0.014)

[a] Changes in atomic charge on going from the reactants to the transition state are shown in parentheses for **12**. [b] r_{CCl} = 1.810 Å. [c] All vibrational frequencies are positive.

Table 7 Results of 3-21G* calculations for structures **12** and **21**

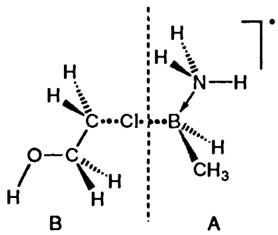
			Fragment charges		Bond lengths/Å		Atomic charges[a]			
Structure	E/hartree	μ/D	A	B	C–O¹	C–O²	O¹	H³	O²	H⁴
21[b]	−840.453 432	2.361	+0.216	−0.216	1.425	1.406	−0.690 (−0.330)	+0.360	−0.682 (−0.315)	+0.367
12	−691.562 252	4.493	+0.195	−0.195	1.449	—	−0.682 (−0.308)	+0.374	—	—

[a] Charge on the whole OH group in parentheses. [b] r_{BCl} = 2.507, r_{CCl} = 2.008 Å, ∠CClB = 175.2°; $\langle S^2 \rangle$ = 0.84.

Table 8 Calculated v al ionisation energies at the MP3(full)/6-31G**//U(R)HF/6-31G** level

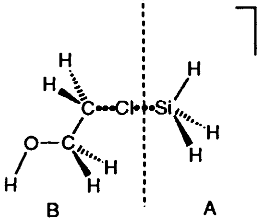
Radical	E_i/eV[a]
$H_3N\rightarrow\dot{B}H_2$[b]	5.86
$H_3N\rightarrow\dot{B}HMe$[c]	5.47
$H_2\dot{N}\rightarrow BH_3$[b]	10.44
$H_3C\text{–}\dot{C}H_2$[b]	8.35 (8.51)[d]
$H_3Si^{\bullet}$[e]	8.58 (8.74)[f]
$Me_3Si^{\bullet}$	6.81[g] (6.5)[h]

[a] Experimental values in parentheses. [b] Geometry taken from ref. 30. [c] Geometry taken from ref. 17. [d] Ref. 33. [e] r_{SiH} = 1.476 Å, <HSiH = 111.0°. [f] Ref. 34. [g] MP4/6-31G*//6-31G* result from ref. 31. [h] Ref. 35.

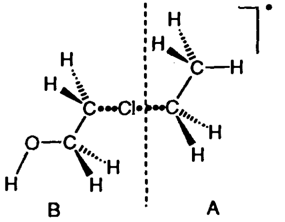


22

transition states **23** and **24** for abstraction of chlorine by silyl and by ethyl radicals, respectively. As judged from the ionisation energies (Table 8), the silyl radical is expected to be less nucleophilic than the amine–boryl radicals and the degree of charge transfer in the transition state **23** is indeed significantly less than that in **12** or **22**. However, the ionisation energy of $Me_3Si^{\bullet}$ is appreciably smaller than that of $H_3Si^{\bullet}$ and thus trialkylsilyl radicals would be expected to be more nucleophilic than their unsubstituted parent. The ethyl radical is the isoelectronic organic analogue of the ammonia–boryl radical; it has an appreciably larger ionisation energy than the latter and, as judged by experiment,[17,19,21,36] is much less nucleophilic. In agreement with this, the extent of electronic charge transfer in the transition state **24** is much less than in **12**.



23



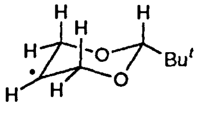
24

Comparison of the data in Tables 1 and 2 shows that the relative reactivities of the various chlorides towards halogen-atom abstraction by amine–boryl radicals are not very different in cyclopropane and in oxirane, even though the computed transition states have relatively large dipole moments in accord with the valence bond representation **8**. However, the amine–boryl radicals themselves are very polar species and, even though the relative permittivity (dielectric constant) of oxirane (13.9) is significantly larger than that of cyclopropane (*ca.* 2),[37] the reactants and the transition state could well be stabilised to similar extents in each solvent.[38] The mean of the calculated dipole moments of C_s 2-chloroethanol **19** and $H_3N\rightarrow\dot{B}H_2$ **20** (4.2 D) is very close to the calculated dipole moment for the transition state **12** (4.5 D).

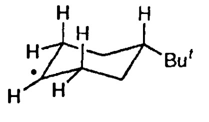
EPR Spectra.—The EPR parameters for the radicals **25**–**30** discussed in this work are collected in Table 10 and several points of interest arise from the data. All radicals were generated by UV irradiation of cyclopropane solutions containing DTBP, $Me_3N\rightarrow BH_2Bu$ and the corresponding alkyl chloride; the spectra of **26**, **27** and **29** are shown in Figs. 1–3.

For alkyl radicals which contain a $H_\beta C_\beta \dot{C}_\alpha$ fragment, the major mechanism for interaction between the unpaired electron and H_β is hyperconjugation. The value of $a(H_\beta)$ is given by the semiempirical Heller–McConnell (H–M) eqn. (8),[39] in which θ is the dihedral angle between the $H_\beta CC$ plane and the axis of the formally singly occupied C_α–$2p_\pi$ orbital, $\rho^{\pi}_{C\alpha}$ is the π unpaired electron population on C_α, and A and B are constants. Estimates of A vary, although there is agreement that it is very small in relation to B.

$MeOCH_2\dot{C}H_2$ **25** $(MeO)_2CH\dot{C}H_2$ **26** $(MeO)_3C\dot{C}H_2$ **27** $Me_3Si\dot{C}H_2$ **28**



29



30

$$a(H_\beta) = (A + B\cos^2\theta)\rho^{\pi}_{C\alpha} \quad (8)$$

Cramer[40] has reported that Fermi contact integrals (FIs) obtained from *ab initio* molecular orbital calculations using the UMP2 density matrix give hyperfine coupling constants which, after a small scaling factor is applied, are in good agreement with experiment. We have carried out such calculations for the ethyl radical with the H_3CC and CCH_2 fragments constrained to have local C_{3v} and C_{2v} symmetry, respectively. This approach is more appropriate than full geometry optimisation, because of the assumptions implicit in the H–M equation. Within these constraints, the structure (see **31a** and **31b**) was optimised with $\theta = 0°$ at the UHF/6-31G** level to give the geometrical parameters shown in **31a** (bond lengths in Å). With these bond lengths and angles fixed, single point calculations were carried out at the UMP2(full)/6-311G** level[40] for values of θ varying in 5° steps between 0 and 90°. Fig. 4 shows a plot of the FI for H* [which is proportional to a(H*)] against $\cos^2\theta$. The effectively perfect straight line (correlation coefficient, $R^2 = 0.9999$) passes almost through the origin, indicating that A is very close to zero.[41] The calculated total unpaired electron

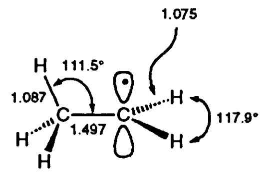
Table 9 Results of 3-21G* calculations for structures **12** and **22**–**24**

			Bond lengths and angles (Å or °)			Fragment charges	
Structure	*E*/hartree	μ/D	M–Cl	C–Cl	CClM	A	B
12	−691.562 252	4.493	2.574	2.031	175.2	+0.195	−0.195
22	−730.394 952	4.208	2.610	2.015	175.5	+0.200	−0.200
23	−899.184 308	1.802	2.611	2.077	180.3	+0.156	−0.156
24	−688.169 439	2.079	2.220	2.223	179.8	+0.093	−0.093

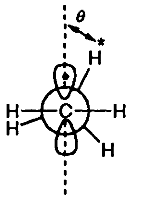
Table 10 EPR parameters for radicals in cyclopropane at 200 K

Radical	*g*-factor[a]	Hyperfine splittings/G[b]	[d*a*(H_β)/d*T*]/ mG K^{-1}[c]
$MeOCH_2\dot{C}H_2$[c] **25**	2.0026	21.95 (2 H_α), 32.59 (2 H_β)[d]	−35.6
$(MeO)_2CH\dot{C}H_2$ **26**	2.0026	22.68 (2 H_α), 25.67 (1 H_β), 0.18 (3 H_δ)[e]	−27.4
$(MeO)_3C\dot{C}H_2$ **27**	2.0025	22.95 (2 H_α), 0.20 (3 H_δ),[e] 32.3 ($^{13}C_\alpha$), 13.6 ($^{13}C_\beta$), 2.6 ($^{13}C_\delta$)[e,f]	—
$Me_3Si\dot{C}H_2$ **28**	2.0024	20.92 (2 H_α), 0.42 (9 H_α), 15.5 (^{29}Si),[e] 5.5 ($^{13}C_\gamma$)[e]	—
29	2.0025	21.48 (1 H_α), 41.74 (2 H_β^{ax}), 16.98 (2 H_β^{eq})	−24.8,[g] +24.8[h]
30[i]	2.0027[j]	21.17 (1 H_α), 41.91 (2 H_β^{ax}), 6.28 (2 H_β^{eq}), 0.66 (2 H_γ^{ax}), 1.08 (2 H_γ^{eq})	−15.9,[g] +5.1[h]

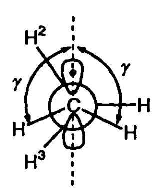
[a] Corrected for second-order effects. [b] Nuclei indicated in parentheses. [c] In the region *ca.* 150–250 K. [d] The splitting of 0.41 G from three equivalent protons at 137 K reported in ref. 49 is clearly an error (see Fig. 2 in ref. 49). [e] At 160 K. [f] Total satellite intensity *ca.* 1% of main peak. At 269 K, $\langle a(^{13}C)\rangle$ = 1.8 G and the total satellite intensity is *ca.* 3% of the main peak. [g] For the larger splitting. [h] For the smaller splitting. [i] Data from ref. 51. [j] At 145 K.



31a



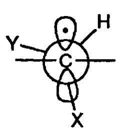
31b



31c

population on C_α is essentially independent of θ and, from experimental data, the value of $\rho^\pi_{C_\alpha}$ for the ethyl radical has been estimated to be 0.92 by Fessenden and Schuler.[42] The FIs corresponding to $\theta = 0$ and 90° are $+2.75 \times 10^{-2}$ and -7×10^{-6} atomic units (au), respectively, and the theoretical factor to convert these into proton splittings is 1595 G au^{-1}.[43] Taking $\rho^\pi_{C_\alpha}$ to be 0.92 gives the H–M constants *A* and *B* to be −0.01 and +47.7 G, respectively. The experimental[44] temperature-independent value of *a*($3H_\beta$) for ethyl is 26.9 G, corresponding to free rotation about the C_α–C_β bond ($\langle\cos^2\theta\rangle = 0.5$). When these theoretical values are scaled (×1.227) to give the experimental result, we obtained *A* = −0.01 and *B* = +58.5 G. The corresponding values of *A* and *B* computed at the UMP2(full)/6-31G** level are +0.19 and +58.1 G, respectively.†

To investigate the effect on *a*(H_β) of deviation from planarity at C_α, the geometry of the 'staggered' conformation **31c** was first optimised within C_s symmetry (*i.e.*, the angle between the α-C–H bonds and the line through C_α and perpendicular to the H^1CC plane, $\gamma = 90°$). With all other parameters fixed at the optimised values, single point UMP2(full)/6-311G** calculations were carried out for values of γ between 91 and 110°. For $\gamma = 90°$, the computed (FI × 1595 × 1.227 G) value of *a*(H^1) is −0.02 G, and this changes only very slightly for small deviations from planarity (−0.03, −0.05, −0.09 and −0.14 G for γ = 95, 100, 105 and 110°, respectively). The corresponding computed values (all positive) of *a*(H^2) are 41.0, 39.6, 37.7, 35.5 and 33.0 G, and of *a*(H^3) are 41.0, 41.8, 42.0, 41.7 and 41.2 G for γ = 90, 95, 100, 105 and 110°, respectively. We conclude that even when the radical centre is somewhat nonplanar, the H–M equation should still provide a good basis for the semi-quantitative discussion of the conformations of alkyl radicals.



32

---

† These essentially-zero values for *A* compare with the value of *ca.* −1 G calculated for this constant by Ellinger *et al.*[45]

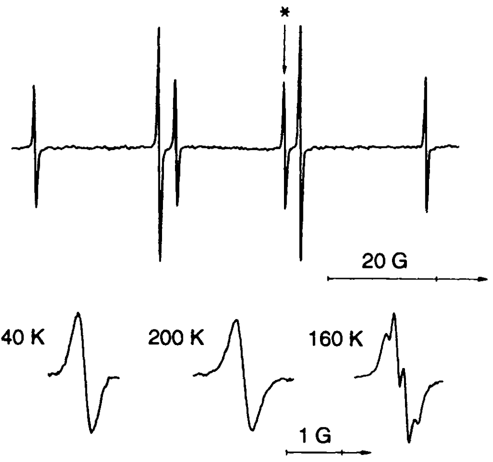


Fig. 1 EPR spectrum of the 2,2-dimethoxyethyl radical **26** in cyclopropane at 200 K; expansions of the line indicated with an asterisk are shown inset at three temperatures

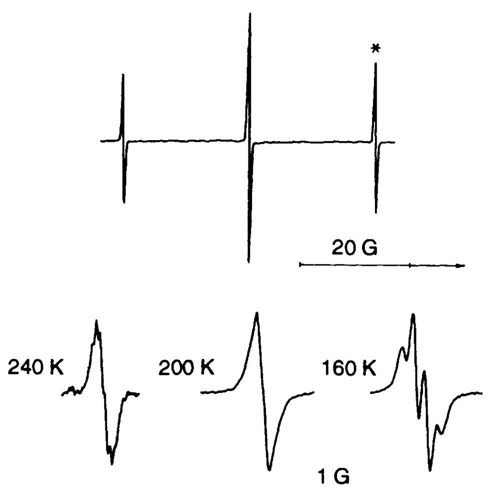


Fig. 2 EPR spectrum of the 2,2,2-trimethoxyethyl radical **27** in cyclopropane at 200 K; expansions of the line indicated with an asterisk are shown inset at three temperatures

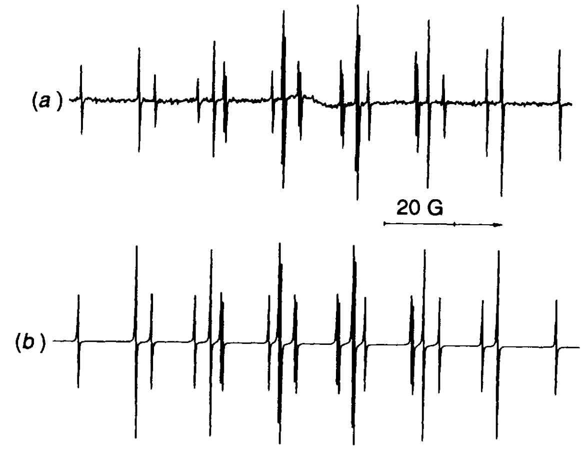


Fig. 3 (*a*) EPR spectrum of the dioxanyl radical **29** in cyclopropane at 200 K; (*b*) computer simulation, including second-order effects, using the parameters given in Table 10

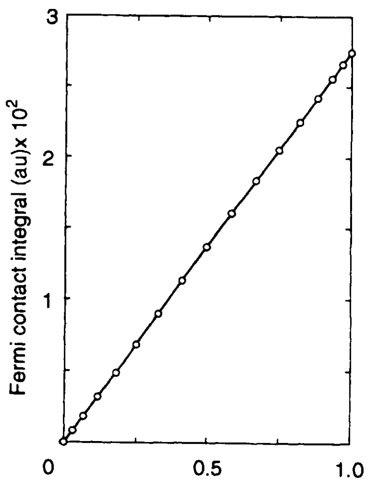
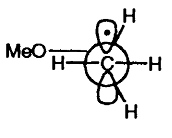


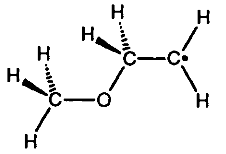
Fig. 4 Plot of $\cos^2 \theta$ against the FI for H* in **31b**, obtained from UMP2(full)/6-311G** calculations

For substituted alkyl radicals of the type **32** the value of B is sensitive to the nature of the groups X and Y, and B decreases as the electronegativities of these groups increase.[46–48] As was pointed out by Symons,[46] this is because of the poorer energetic match between the C_α–$2p_\pi$ orbital and the doubly occupied C–H_β σ orbital, together with the smaller contribution from the H_β–1s orbital to the latter, as the electronegativities of X and Y increase. Guerra[48] has suggested a modified form of the H–M equation which takes account of the change in B with the nature of the β-substituents.

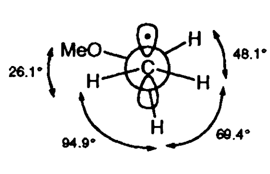
Chen and Kochi[49] have proposed that the 2-methoxyethyl radical **25** prefers the staggered conformation **33a**, based on the large value of $a(2H_\beta)$ below 250 K and its negative temperature dependence. The two β-protons were magnetically equivalent down to 143 K and we have confirmed that the spectrum of **25** shows no selective broadening of the $M(2H_\beta) = 0$ lines down to 126 K in cyclopropane–ethene solvent (3:1 v/v).† Of course, this precise conformation with a planar radical centre is unlikely to be at a minimum on the potential energy surface,[48b] because the α-C–H and β-C–O bonds are eclipsed. When the geometry of the C_s conformation **33b** was optimised at the UHF/6-31G** level, the resulting structure ($E = -192.482\,292$ hartree, $\tilde{\nu}_i = -166.4$ cm^{-1}) was indeed a transition state. However, when the symmetry constraint was removed, the resulting minimum energy C_1 structure **34** ($E = -192.482\,438$ hartree) was more stable by only 0.38 kJ mol^{-1}. Thus, **33** is actually the transition state for inversion at the slightly pyramidal radical centre in **34**, but we conclude that **33** is an adequate representation of the time-averaged structure of the quasi-planar 2-methoxyethyl radical. The preference for this conformation indicates that C–H hyperconjugation is more stabilising than C–O hyperconjugation, presumably because the C–H σ orbital is higher in energy than the C–O σ orbital.[46] Because of the high electronegativity of oxygen, it is probable that the H–M



33a



33b



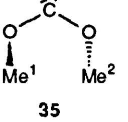
34

---

† The radical was generated by UV photolysis of DTBP in the presence of $MeOCH_2CH_2Br$ and Me_3SiH.[18a]

constant B for **25** will be smaller than that for the ethyl radical. It seems very likely that a basically similar conformational situation holds for the related 2-hydroxyethyl radical, as proposed previously,[50] despite suggestions to the contrary in the more recent literature.[3,48b]

The value of B is expected to be still smaller for the 2,2-dimethoxyethyl radical **26**, in accord with the magnitude and negative temperature dependence of $a(1H_\beta)$, which at 200 K is already less than $a(3H_\beta)$ for the ethyl radical (26.9 G). This negative temperature dependence shows that $\langle\cos^2\theta\rangle$ for the single β-proton is >0.5 at 200 K and implies that C–H hyperconjugation is still slightly preferred over C–O hyperconjugation. However, the value of $a(1H_\beta)$ indicates that there is no large conformational preference about the C_α–C_β bond and, therefore, that the non-equivalence of the methoxy groups observed at low temperature is probably a result of restriction of rotation about the MeO–C_β bonds in a conformation of the type **35**. The preference for this conformation could result because of anomeric interactions between the geminal methoxy groups, as proposed for 1,1-dimethoxymethane which adopts a similar conformation.[11] It seems likely that the proton splitting resolvable at 160 K arises from Me-1 which is *gauche* to the C_α–C_β bond. As the temperature is increased from 160 K, exchange between Me-1 and Me-2 takes place on the EPR timescale, but at high temperatures the linewidth precludes observation of the predicted averaged septet splitting (see Fig. 1).



35

For the 2,2,2-trimethoxyethyl radical **27** rotation about the C_α–C_β is probably not significantly hindered, but exchange between instantaneously non-equivalent methoxy groups takes place on the EPR timescale as a result of rotation about the MeO–C bonds. Thus, at 160 K one methoxy group gives rise to a three-proton splitting of 0.20 G and one methoxy (probably the same) group gives rise to the ^{13}C splitting of 2.6 G, while at high temperatures exchange occurs rapidly with the other two groups which give near-zero proton splittings and smaller ^{13}C splittings (that are not resolved at 160 K). At 240 K an averaged splitting of 0.07 G from nine protons is detected (Fig. 2) and, at 269 K, an averaged natural-abundance ^{13}C splitting of 1.8 G is observed.

At first sight, the β-proton splittings for the dioxanyl radical **29** are unexpected in relation to those[51] for the cyclohexyl radical **30**. Thus, while $a(2H_\beta^{ax})$ is similar for these radicals, $a(2H_\beta^{eq})$ is much larger for **29** than for **30**. The α-proton coupling constants are very similar for the two radicals and the configurations at C_α should also be similar, *i.e.*, somewhat pyramidal with H_α equatorial, but easily planarised.[51] As discussed before, the H–M constant B for **29** should be smaller than that for **30**, because of the presence of the two β-oxygen atoms in the former. We propose that the chair conformation of the dioxane ring in **29** differs from that in **30** such that the axial and equatorial C–H bonds in the former radical subtend appreciably smaller dihedral angles (θ_{ax} and θ_{eq}) with the axis of the SOMO on C_α. However, the corresponding increase in $\cos^2\theta_{ax}$ on going from **30** to **29** is offset by the smaller value of B for the latter, to make $a(2H_\beta^{ax})$ fortuitously similar for the two radicals. Because $d\cos^2\theta/d\theta$ is strongly dependent on the value of θ, the corresponding increase in $\cos^2\theta_{eq}$ on going from **30** to **29** could be much greater and, even though B is smaller for **29**, could result in a relatively large value of $a(2H_\beta^{eq})$ as observed. This argument receives support from UHF/4-31G* calculations for the C_s chair conformations of the 1,3-dioxan-5-yl and cyclohexyl[51] radicals, both constrained to be planar at C_α, which indicate that the conformation of the former ring system differs from that of the latter in the manner envisaged. The computed values of θ_{ax} and θ_{eq} are 2.6 and 63.0° for 1,3-dioxan-5-yl and 15.4 and 78.5° for cyclohexyl, respectively.

Conclusions

β-Alkoxy groups increase the rate of halogen-atom abstraction from alkyl chlorides by nucleophilic amine–boryl and triethylsilyl radicals, especially by the former. This substituent effect arises because the β-RO group stabilises the transition state for chlorine-atom transfer and thereby lowers the activation energy. Negative charge builds up on the alkyl halide residue in the transition state and the dipolar $C\cdots Cl\cdots M$ grouping is stabilised mainly by a through-space electrostatic interaction with the permanent C–O bond dipole. Anomeric delocalisation of negative charge from the reaction centre into the β-C–O σ* orbital appears to be very small, unless other electronegative substituents are present at C_β, when it may play a part in stabilising the transition state. Any thermodynamic radical stabilising effect of a β-RO group is probably very small, unless a π donor substituent is also present at C_α when a synergistic stabilising interaction[7,9,15] (a captodative effect) may possibly be important.

If the β-oxygen substituent effect on radical reactions is a polar effect which operates in the transition state, then it would be expected that it is sometimes rate-enhancing and sometimes rate-decreasing, depending on the charge distribution in the transition state as compared with that in the reactants. Very recent reports,[52] which appeared during the preparation of this manuscript and after publication of our preliminary communication,[10] indicate that a β-alkoxy group does indeed *retard* hydrogen-atom abstraction by *electrophilic tert*-butoxyl radicals from C–H bonds in cyclic and acyclic ethers, and this result was ascribed to a destabilising polar effect in the transition state.

It is noteworthy that heterolytic nucleophilic substitution at saturated carbon by neutral nucleophiles is retarded by β-alkoxy groups. Richardson[53] has attributed this substituent effect to unfavourable electrostatic interactions between the β-C–O dipole and the dipoles associated with the bonds from C_α to the entering and leaving groups in the transition state.

Experimental

EPR spectra were recorded during continuous UV irradiation of samples positioned in a standard variable temperature insert in the microwave cavity of a Varian E-109 or a Bruker ESP-300 spectrometer operating at 9.1–9.4 GHz, as described previously.[16,51] Samples were prepared using a vacuum line and were sealed in evacuated Suprasil quartz tubes (2 or 3 mm i.d., 0.5 mm wall, depending on the dielectric properties of the contents). The temperature of the sample during photolysis was determined, using the method described previously,[16] by careful measurement of the value of $a(H_\beta)$ for the isobutyl radical in cyclopropane. The heating effect at full light intensity varied between 5 and 7 K depending on conditions.

Relative radical concentrations were determined by double integration of appropriate lines in each spectrum and/or by computer simulation of the composite spectrum. The EPR spectra of some radicals exhibited CIDEP effects such that corresponding hyperfine lines to low- and high-field of the spectrum centre were of unequal intensity (E/A polarisation).[22]

In these circumstances, relative radical concentrations were determined by taking the average intensity of corresponding low- and high-field lines. Computer simulations of spectra were obtained using a modified version of ESRSPEC2,[54] extended to handle composite spectra from up to four radicals with different centres, second-order shifts for coupling to single nuclei with $I > \frac{1}{2}$, and lineshapes continuously variable between 100% Gaussian and 100% Lorentzian.

Materials.—NMR spectra were recorded using a Varian VXR-400 instrument (400 MHz for ^{1}H). The solvent was $CDCl_3$ and chemical shifts are reported relative to Me_4Si; *J*-values are quoted in Hz. Di-*tert*-butyl peroxide (98%, Aldrich) was passed down a column of basic alumina (activity 1) and distilled (b.p. 46–47 °C/76 Torr); cyclopropane (Union Carbide) and oxirane (Fluka) were used as received. Triethylamine–borane (Aldrich) was distilled and stored under argon. Trimethylamine–butylborane[55] and dipentanoyl peroxide[56] were prepared by published methods. 1-Chloro-2,2,2-trimethoxyethane (b.p. 35 °C/1.6 Torr) was prepared from chloroacetonitrile and methanol following the method of McElvain and Nelson.[57] Reagents other than those described below were obtained commercially and purified if necessary before use.

cis-1-*tert*-Butyl-4-chlorocyclohexane was prepared from 4-*tert*-butylcyclohexanol (Aldrich, 80% *trans* + 20% *cis*) by treatment with triphenylphosphine in refluxing carbon tetrachloride, as described by Beckwith and Westwood.[58] The fraction with b.p. 38–40 °C/0.5 Torr (mainly the *cis*-isomer) was further purified by preparative GLC[28] [3.7 m × 1 cm column packed with 30% polyfluorinated silicone oil (QF1) on Chromosorb W; oven temperature 100 °C, N_2 carrier gas] to give the pure *cis*-isomer, which was estimated by ^{1}H NMR spectroscopy to contain < 0.2% of the *trans*-isomer. δ_H 0.88 (s, 9 H), 1.55 (m, 4 H), 1.58 (m, 1 H), 1.73 (m, 2 H), 2.06 (m, 2 H) and 4.49 (quintet, 1 H, $\langle J \rangle$ 2.95, C*H*Cl); δ_C 21.0, 27.5, 32.6, 34.6, 47.7 and 60.1.

The *trans*-isomer (containing < 0.2% *cis*) was prepared in the same way from *cis*-4-*tert*-butylcyclohexanol, itself prepared in *ca.* 99% isomeric purity by reduction of 4-*tert*-butylcyclohexanone with LiB(CHMeCHMe$_2$)$_3$H (LS-Selectride,® Aldrich) in tetrahydrofuran (THF).[59] δ_H 0.86 (s, 9 H), 1.08 (m, 3 H), 1.59 (m, 2 H), 1.82 (m, 2 H), 2.22 (m, 2 H) and 3.80 (tt, 1 H, *J* 11.79 and 4.27, C*H*Cl); δ_C 27.5, 27.6, 32.3, 37.8, 46.7 and 60.5.

cis- *and* trans-2-tert-*Butyl*-5-*chloro*-1,3-*dioxanes*.—The isomeric mixture was prepared by a route similar to that described for related compounds by Abraham *et al.*[27] Diethyl chloromalonate (Aldrich) was reduced with AlH_3 in THF to give crude 2-chloropropane-1,3-diol.[27] The crude diol (10.0 g, 90 mmol if pure), trimethylacetaldehyde (8.0 g, 93 mmol) and toluene-*p*-sulfonic acid (*ca.* 20 mg) in dichloromethane (100 cm^3) were heated under reflux for 24 h using a Dean and Stark water separator. A further portion of trimethylacetaldehyde (2 cm^3) was added after 6 h and again after 12 h. The solvent was removed under reduced pressure and the residual oil was distilled to give the dioxanes (4.9 g, b.p. 30–38 °C/0.5 Torr). The isomers were separated by preparative HPLC on Lichrosorb silica gel (95% hexane–5% ethyl acetate eluent).

cis-2-tert-*Butyl*-5-*chloro*-1,3-*dioxane*.—Isomeric purity ⩾99.8%, m.p. 35.1–36.0 °C (Found: C, 53.8; H, 8.5; Cl, 19.9. $C_8H_{15}ClO_2$ requires: C, 53.8; H, 8.5; Cl, 19.8%); δ_H 0.96 (s, 9 H), 3.88 (quintet, 1 H, $\langle J \rangle$ 1.78, C*H*Cl), 4.06 and 4.13 (AB system of multiplets, 4 H, *J* 12.69, CH_2O) and 4.14 (s, 1 H, Bu^{t}C*H*); δ_C 24.5, 35.1, 53.3, 71.4 and 108.0.

trans-2-tert-*Butyl*-5-*chloro*-1,3-*dioxane*.—Isomeric purity ⩾99.8%; m.p. 33.5–35.5 °C (Found: C, 53.7; H, 8.5; Cl, 19.9. $C_8H_{15}ClO_2$ requires: C, 53.8; H, 8.5; Cl, 19.8%); δ_H 0.89 (s, 9 H), 3.54 (t, 2 H, $\langle J \rangle$ 11.0, CHH^{ax}), 3.97 (tt, *J* 10.76 and 4.74, C*H*Cl), 4.10 (s, 1 H, Bu^{t}C*H*) and 4.25 (dd, 2 H, *J* 11.17 and 4.74, CHH^{eq}); δ_C 24.7, 34.7, 48.2, 71.9 and 107.8.

Equilibration of the cis- and trans-*Isomers*.—An isomerically pure sample of the dioxane (*ca.* 0.5 mol dm^{-3}) in $CDCl_3$ containing Amberlyst-15 sulfonic acid resin (*ca.* 30 mg) was left to stand in an NMR tube immersed in a thermostatted water bath at 20 °C, with occasional shaking, and the approach to equilibrium was monitored by ^{1}H NMR spectroscopy. The equilibrium mixture (84.2% *trans*, 15.8% *cis*) was obtained after 240 h, starting from either the pure *cis*- or the pure *trans*-isomer.

Acknowledgements

We are very grateful to Dr. R. A. J. Janssen (Eindhoven University of Technology) for his help with the calculation of hyperfine coupling constants using the *ab initio* UMP2 density matrix.

References

1 *Substituent Effects in Radical Chemistry*, eds. H. G. Viehe, Z. Janousek and R. Merényi, Reidel, Dordrecht, 1986.

2 D. H. R. Barton, W. Hartwig and W. B. Motherwell, *J. Chem. Soc., Chem. Commun.*, 1982, 447.

3 C. Sosa and H. B. Schlegel, *J. Am. Chem. Soc.*, 1987, **109**, 7007.

4 J. E. Leffler, *An Introduction to Free Radicals*, Wiley-Interscience, New York, 1993, p. 176.

5 J. L. Holmes, F. P. Lossing and P. M. Mayer, *J. Am. Chem. Soc.*, 1991, **113**, 9723.

6 B. P. Roberts and A. J. Steel, *J. Chem. Soc., Perkin Trans. 2*, 1994, 2155.

7 A. L. J. Beckwith and S. Brumby, *J. Chem. Soc., Perkin Trans. 2*, 1987, 1801.

8 J. Dupuis, B. Giese, D. Rüegge, H. Fischer, H.-G. Korth and R. Sustmann, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 896.

9 H.-G. Korth, R. Sustmann, J. Dupuis and B. Giese, *J. Chem. Soc., Perkin Trans. 2*, 1986, 1453.

10 B. P. Roberts and A. J. Steel, *Tetrahedron Lett.*, 1993, **34**, 5167.

11 A. J. Kirby, *The Anomeric Effect and Related Stereoelectronic Effects at Oxygen*, Springer-Verlag, Berlin, 1983.

12 A. E. Reed, C. Schade, P. v. R. Schleyer, P. V. Kamath and J. Chandrasekhar, *J. Chem. Soc., Chem. Commun.*, 1988, 67.

13 C. J. Kramer, *J. Org. Chem.*, 1992, **57**, 7034.

14 K. Bowden and E. J. Grubbs, *Prog. Phys. Org. Chem.*, 1993, **19**, 183.

15 A. J. Dobbs, B. C. Gilbert and R. O. C. Norman, *J. Chem. Soc., Perkin Trans. 2*, 1972, 786; B. C. Gilbert, M. Trenwith and A. J. Dobbs, *J. Chem. Soc., Perkin Trans. 2*, 1974, 1772.

16 J. A. Baban and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1981, 161; V. Diart and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1992, 1761.

17 V. Paul, B. P. Roberts and C. R. Willis, *J. Chem. Soc., Perkin Trans. 2*, 1989, 1953.

18 (*a*) A. Hudson and R. A. Jackson, *Chem. Commun.*, 1969, 1323; (*b*) C. Chatgilialoglu, K. U. Ingold and J. C. Scaiano, *Organometallics*, 1982, **1**, 466.

19 P. Kaushal, P. L. H. Mok and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1990, 1663.

20 C. Chatgilialoglu, K. U. Ingold and J. C. Scaiano, *J. Am. Chem. Soc.*, 1982, **104**, 5123.

21 V. Paul and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1988, 1183.

22 J. K. S. Wan and A. J. Elliot, *Acc. Chem. Res.*, 1977, **10**, 161; P. J. Hore, C. G. Joslin and K. A. McLauchlan, *Chem. Soc. Rev.*, 1979, **8**, 29; M. Anpo, K. U. Ingold and J. K. S. Wan, *J. Chem. Phys.*, 1983, **87**, 1674.

23 A. G. Davies, D. Griller and B. P. Roberts, *J. Chem. Soc. B*, 1971, 1823; D. Griller and K. U. Ingold, *Acc. Chem. Res.*, 1980, **13**, 317; H. Fischer and H. Paul, *Acc. Chem. Res.*, 1987, **20**, 200.

24 (*a*) F. Minisci and A. Citterio, *Adv. Free Radical Chem.*, 1980, **6**, 65; (*b*) C. Walling, *Free Radicals in Solution*, Wiley, New York, 1957; (*c*)

G. A. Russell in *Free Radicals*, ed. J. K. Kochi, Wiley-Interscience, New York, 1973, vol. 1, pp. 293–311; (*d*) I. Fleming, *Frontier Orbitals and Organic Chemical Reactions*, Wiley-Interscience, London, 1976, ch. 5.

25 E. W. Colvin, *Silicon in Organic Synthesis*, Butterworth, London, 1981.

26 J. W. Wilt, F. G. Belmonte and P. A. Zieshe, *J. Am. Chem. Soc.*, 1983, **105**, 5665.

27 R. J. Abraham, H. D. Banks, E. L. Eliel, O. Hofer and M. K. Kaloustian, *J. Am. Chem. Soc.*, 1972, **94**, 1913.

28 E. L. Eliel and R. J. L. Martin, *J. Am. Chem. Soc.*, 1968, **90**, 689.

29 GAUSSIAN 92, Revision B; M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart and J. A. Pople, Gaussian Inc., Pittsburgh PA, 1992.

30 I. G. Green and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1986, 1597; J. N. Kirwan and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1989, 539.

31 D. Danovich, Y. Apeloig and S. Shaik, *J. Chem. Soc., Perkin Trans. 2*, 1993, 321.

32 W. J. Hehre, L. Radom, P. v. R. Schleyer and J. A. Pople, *Ab Initio Molecular Orbital Theory*, Wiley, New York, 1986.

33 F. A. Houle and J. L. Beauchamp, *J. Am. Chem. Soc.*, 1979, **101**, 4067.

34 J. M. Dyke, N. Jonathan, A. Morris, A. Ridha and M. J. Winter, *Chem. Phys.*, 1983, **81**, 481.

35 S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin and W. G. Mallard, *J. Phys. Chem. Ref. Data*, 1988, **17**, supplement No. 1.

36 J. A. Baban, V. P. J. Marti and B. P. Roberts, *J. Chem. Res. (S)*, 1985, 90.

37 *Handbook of Chemistry and Physics*, ed. D. R. Lide, 73rd edn., CRC Press, Boca Raton, 1992.

38 C. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, VCH, Weinheim, 1988.

39 C. Heller and H. M. McConnell, *J. Chem. Phys.*, 1960, **32**, 1535.

40 C. J. Cramer, *J. Am. Chem. Soc.*, 1991, **113**, 2439.

41 D. Griller and K. U. Ingold, *J. Am. Chem. Soc.*, 1974, **96**, 6203.

42 R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 1963, **39**, 2147.

43 R. A. J. Janssen and H. M. Buck, *J. Mol. Struct. (Theochem)*, 1984, **110**, 139; R. A. J. Janssen, G. Visser and H. M. Buck, *J. Am. Chem. Soc.*, 1984, **106**, 3429.

44 D. Griller, P. R. Marriott and K. F. Preston, *J. Chem. Phys.*, 1979, **71**, 3703.

45 Y. Ellinger, R. Subra, B. Levy, P. Millie and G. Berthier, *J. Chem. Phys.*, 1975, **62**, 10.

46 J. A. Brivati, K. D. J. Root, M. C. R. Symons and D. J. A. Tinling, *J. Chem. Soc. A*, 1969, 1942; A. R. Lyons and M. C. R. Symons, *J. Chem. Soc., Faraday Trans. 2*, 1972, **68**, 622.

47 I. G. Green, K. M. Johnson and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1989, 1963.

48 (*a*) M. Guerra, *Chem. Phys. Lett.*, 1987, **139**, 463; (*b*) M. Guerra, *J. Am. Chem. Soc.*, 1992, **114**, 2077.

49 K. S. Chen and J. K. Kochi, *J. Am. Chem. Soc.*, 1974, **96**, 1383.

50 P. J. Krusic and J. K. Kochi, *J. Am. Chem. Soc.*, 1971, **93**, 846; S. Brumby, *J. Phys. Chem.*, 1983, **87**, 1917.

51 B. P. Roberts and A. J. Steel, *J. Chem. Soc., Perkin Trans. 2*, 1992, 2025; corrigendum, 1993, 1003.

52 W. K. Busfield, I. D. Grice, I. D. Jenkins and M. J. Monteiro, *J. Chem. Soc., Perkin Trans. 2*, 1994, 1071; W. K. Busfield, I. D. Grice and I. D. Jenkins, *J. Chem. Soc., Perkin Trans. 2*, 1994, 1079; I. D. Jenkins, *J. Chem. Soc., Chem. Commun.*, 1994, 1227.

53 A. C. Richardson, *Carbohydr. Res.*, 1969, **10**, 395.

54 P. J. Krusic, *QCPE*, Program No. 210.

55 M. F. Hawthorne, *J. Am. Chem. Soc.*, 1961, **83**, 831.

56 J. K. Kochi and P. E. Mocadlo, *J. Org. Chem.*, 1965, **30**, 1134.

57 S. M. McElvain and J. W. Nelson, *J. Am. Chem. Soc.*, 1942, **64**, 1825; W. H. Moos, R. D. Gless and H. Rapoport, *J. Org. Chem.*, 1981, **46**, 5064.

58 A. L. J. Beckwith and S. W. Westwood, *Aust. J. Chem.*, 1983, **36**, 2123.

59 H. C. Brown, J. L. Hubbard and B. Singaram, *J. Org. Chem.*, 1979, **44**, 5004.

Paper 4/03635B
Received 15*th June* 1994
Accepted 15*th July* 1994