Direction of Ring-opening of *cis*- and *trans*-2-Methylcyclopropylcarbinyl Radicals

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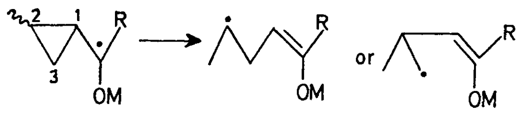
Summary The ring-opening of *cis*- and *trans*-2-methylcyclopropylalkyl radicals to give secondary and primary alkyl radicals respectively is not dependent on the presense of an OH or $OSnR_3$ substituent at the reaction centre, and any interpretation of this effect in terms of the polar nature of these groups is insufficient.

We have shown that the hydroxy- and stannyloxy-substituted radicals (I, M = H or Bu_3Sn) undergo selective ring-opening at low temperatures such that *cis*-(I) gives the secondary alkyl radical (II) but *trans*-(I) gives the primary alkyl radical (III).[1]



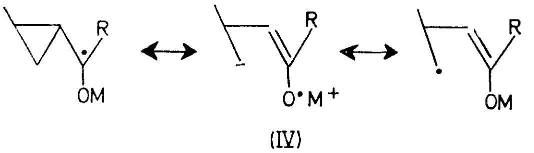
(I) (II) (III)

Table. Products of ring-opening of cyclopropylalkyl radicals (VI)

Cyclopropyl reactant (V)	Radical reagent[a]	Radical (VI)	Radicals observed (VII)	(VIII)	T/°C	[(VII)]:[(VIII)]
(Va)	$Bu^tO\cdot$	(VIa)	(VIIa)	(VIIIa)	−75	[(VII)] < [(VIII)][b]
(Vb)	$Et_3Si\cdot$	(VIa)	(VIIa)	(VIIIa)	−70 −125	20:80 17:83
(Vc)	$Bu^tO\cdot$	(VIb)	(VIIa)	(VIIIa)	−65	[(VII)] > [(VIII)][b]
(Va)	$Et_3Si\cdot$	(VIb)	(VIIa)	(VIIIa)	−65 to −115	80:20
(Ve)	$Me_3SiO\cdot$	(VIc)	(VIIb)[c]	(VIIb)	−130 −20	85:15 66:34
(Ve)	$(EtO)_2\dot{P}O$	(VId)	(VIIc)[d]	(VIIIc)	−90 −38	74:26 68:22

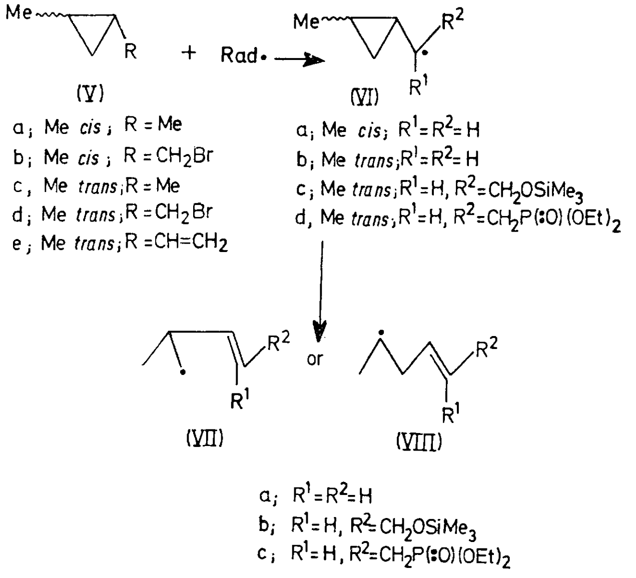
[a] From the photolysis of (i) di-t-butyl peroxide, (ii) di-t-butyl peroxide and triethylsilane, (iii) bis(trimethylsilyl) peroxide (ref. 4), or (iv) di-t-butyl peroxide and tetraethyl pyrophosphite (ref.5) as appropriate. [b] These spectra were relatively weak, and the spectrum of the radical in lower concentration was below the noise level. [c] At low temperature the Me_3SiO group will tend to lie in the nodal plane of the p-orbital carrying the unpaired electron. [d] At low temperature the $(EtO)_2PO$ group will tend to eclipse the singly occupied p-orbital.

It might be suggested that this remarkable selective formation of the less stable primary alkyl radical† from the *trans* derivative could result from the contribution of a polar structure (IV) to the transition state of the reaction, which confers some carbanionic character on the incipient alkyl radical.[3]



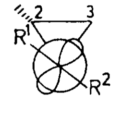
(IV)

We now report the results of experiments (see Table) carried out to test the reality of this polar effect. The cyclopropyl compounds (Va—e) shown in the Table were caused to react with a variety of photolytically generated radicals to give the cyclopropylalkyl radicals (VI), and the radicals (VII) or (VIII), formed by ring opening, were monitored over a range of temperature by e.s.r. spectroscopy.

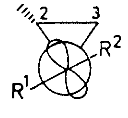


It is apparent from the results in the Table that the regioselectivity of these ring-opening reactions is independent of the presence of a polar OH or $OSnR_3$ substituent at the radical centre in (VI): *trans*-(VI) radicals still give predominantly the primary alkyl radicals (VII), and *cis*-(VI) radicals the secondary alkyl radicals (VIII). If $R^1 = R^2 = H$, consistent results were obtained when the radical (VI) was derived from the appropriate hydrocarbon or bromide, although the spectra from the former system were relatively weak. The selectivity was progressively less complete in the 'staggered' radical (VI; $R^1 = H$, $R^2 = CH_2OSiMe_3$),[6] and in the 'eclipsed' radical [VI; $R^1 = H$; $R^2 = (EtO)_2PO$],[7] but the *trans*-reactants still gave predominantly the primary alkyl radical.

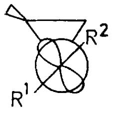
The polar effect illustrated in structure (IV) cannot be invoked to account for this selectivity in the compounds discussed here, and some more general explanation is needed. This might be based on the fact that the methyl substituent interacts with the polarisable electrons of the cyclopropyl ring to render the C^1–C^3 bond electronically non-equivalent with the C^1–C^2 (and C^2–C^3) bond.



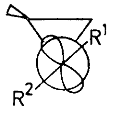
(IX)



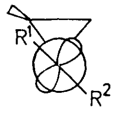
(X)



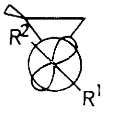
(XI)



(XII)



(XIII)



(XIV)

Interaction between the singly occupied p-orbital and the C^1–C^3 bond orbital might then cause the conformer (IX) to

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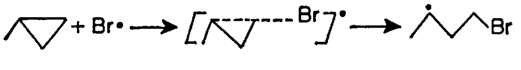
† As an example of more conventional behaviour, methylcyclopropane reacts with bromine atoms with ring opening to give only the secondary alkyl radical (ref. 2).



be more highly populated than (X), leading to preferential cleavage of the C^1–C^3 bond.

In *trans*-(VI), the effect described above may dominate, but in *cis*-(VI) it might be overridden by the opposing effect of the relative stabilities of the conformations (XI) and (XII), which are the precursors of the secondary radical, over those of the more congested conformations (XIII) and (XIV) which lead to the primary radicals.

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