Production of Specific Radicals for Electron Spin Resonance Studies

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Summary Photolysis of mixtures of t-butyl peroxide, triethylsilane, and an organic bromide RBr, in the cavity of an e.s.r. spectrometer affords a convenient specific source of the radical R·.

PHOTOLYSIS of t-butyl peroxide at low temperatures produces t-butoxy-radicals which react with solvents (Z–H) containing abstractable hydrogen, to give the corresponding radical Z·.[1,2] For solvents containing hydrogen atoms in more than one environment, this method gives either a mixture of radicals, or the most stable possible radical: in either case there is a restriction on the types of radical which can be detected.

We find that specific organic radicals can be obtained from the corresponding organic bromide by the following convenient procedure. The bromide (RBr), mixed with t-butyl peroxide and a trialkylsilane, for example triethylsilane, is photolysed in the cavity of an e.s.r. spectrometer at about −40°. The e.s.r. spectra obtained show that normally the only radical present in significant amount is the radical R·, presumably produced by the following sequence of reactions:

$$\mathrm{Bu^tO{-}OBu^t} \xrightarrow{h\nu} \mathrm{2\,Bu^tO\cdot} \qquad (1)$$

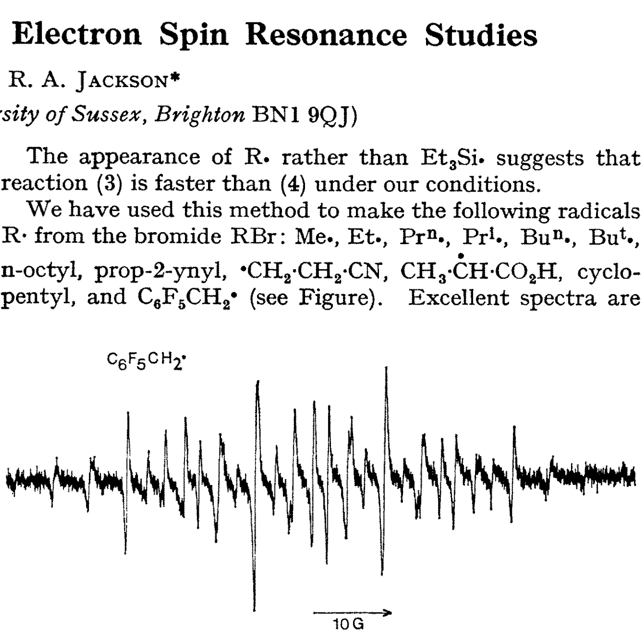
$$\mathrm{Bu^tO\cdot + Et_3SiH \rightarrow Bu^tOH + Et_3Si\cdot} \qquad (2)$$

$$\mathrm{Et_3Si\cdot + RBr \rightarrow Et_3SiBr + R\cdot} \qquad (3)$$

$$[\mathrm{R\cdot + Et_3SiH \rightarrow RH + Et_3Si\cdot} \qquad (4)]$$

The appearance of R· rather than $Et_3Si\cdot$ suggests that reaction (3) is faster than (4) under our conditions.

We have used this method to make the following radicals R· from the bromide RBr: Me·, Et·, $Pr^n\cdot$, $Pr^i\cdot$, $Bu^n\cdot$, $Bu^t\cdot$, n-octyl, prop-2-ynyl, $\cdot CH_2\cdot CH_2\cdot CN$, $CH_3\cdot\dot{C}H\cdot CO_2H$, cyclopentyl, and $C_6F_5CH_2\cdot$ (see Figure). Excellent spectra are observed; for example, the second order splittings in t-butyl are fully resolved. Organic chlorides appear less efficient as sources, though we have observed the spectra of $Bu^s\cdot$, $Bu^t\cdot$, allyl, benzyl, $CH_3\dot{C}HCO_2H$, $\cdot CCl_2CO_2H$, and $CH_3CCl_2\cdot$ from the corresponding chlorides. Data for new or little studied radicals are collected in the Table. Coupling constants for well known radicals agree with literature values·



FIGURE

On the whole, our method gives better results than the direct abstraction of hydrogen from the hydrocarbon, even when the latter process would preferentially give a particular radical. This seems to be particularly true when electron-withdrawing groups are present: for example we obtain a better spectrum of $C_6F_5{\cdot}CH_2\bullet$ from $C_6F_5{\cdot}CH_2Br$ than by direct hydrogen abstraction from $C_6F_5{\cdot}CH_3$. The magnitude of the ^{19}F hyperfine interactions in fluorinated benzyl radicals will be discussed elsewhere.[3]

TABLE

Coupling constants for new or relatively little studied radicals

Radical	α-H	β-H	γ-H	Other
Octyl	22·1	28·3	0·7	
$\bullet CH_2{\cdot}C{\equiv}CH$[a]	19·0	—	12·6	
$\bullet CH_2{\cdot}CH_2CN$	23·0	28·4	—	
$\bullet CCl_2{\cdot}CH_3$	—	19·9	—	Cl 4·2
$\bullet CH_2{\cdot}C_6F_5$	16·8	—	—	*o*-F 9·5; *m*-F 4·9 *p*-F 17·1
$\cdot CMe_2{\cdot}O{\cdot}SiEt_3$	—	20·3	—	
$CF_3{\cdot}\dot{C}(OH){\cdot}O{\cdot}SiEt_3$	—	3·7	—	F 19·3

[a] See also ref. 2.

For the production of particular radicals of the type $\bullet CR^1_2{\cdot}OSiR^2_3$ the method may be modified by the addition of R^1_2CO to the reaction mixture instead of RBr (silanes other than Et_3SiH may also be used): the trialkylsilyl radical produced by reaction (2) appears to add specifically to the oxygen of the C=O bond to produce the radical $\bullet CR^1_2{\cdot}O{\cdot}SiR^2_3$. (Evidence for the intermediacy of radicals of this type when silyl radicals add to ketones has also been provided by product studies[4]). It is interesting that when trifluoroacetic acid is used instead of a ketone, addition of a silyl radical to the carbonyl group takes place, to give $CF_3{\cdot}\dot{C}(OH)OSiEt_3$, whereas trichloroacetic acid undergoes abstraction of a chlorine atom to give $\bullet CCl_2{\cdot}CO_2H$. The $CF_3{\cdot}\dot{C}(OH)OSiEt_3$ radical shows a temperature-dependent line-width alternation in the quarter from the ^{19}F atoms; the central lines are considerably broadened at −40°, probably because of the restricted rotation of the trifluoromethyl group.

Other methods recently suggested for the production of specific organic radicals in static systems† include the displacement of an organic radical from a triorganoborane[5] (5), and the photolysis of acyl peroxides[6] (6).

$$Bu^tO\bullet + R_3B \rightarrow Bu^tOBR_2 + R\bullet \tag{5}$$

$$(RCOO)_2 \xrightarrow{h\nu} 2R\bullet + 2CO_2 \tag{6}$$

We believe that our method may be more generally useful: organic bromides are usually more accessible and easier to handle than organoboron compounds or acyl peroxides.

(*Received, September 17th,* 1969; *Com.* 1403.)

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† For possible sources of specific radicals in flow systems, see ref. 7.

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