Photodecarboxylation of Carboxylic Acids sensitized by Triplet Benzophenone and Duroquinone. A Flash Photolysis Electron Spin Resonance and Chemically Induced Dynamic Nuclear Polarization Nuclear Magnetic Resonance Investigation

By **P. R. Bowers, K. A. McLauchlan,*** and **R. C. Sealy,** Physical Chemistry Laboratory, South Parks Road, Oxford OX1 3QZ

E.s.r. and CIDNP n.m.r. spectroscopy have been used to provide direct evidence for the mediation of $R^1XCH_2^{\cdot}$ and other radicals in the decarboxylation of substituted carboxylic acids $R^1XCH_2CO_2H$ photosensitized by carbonyl compounds. In some systems there is evidence for scavenging of $R^1XCH_2^{\cdot}$ radicals by sensitizer, and it is suggested that the rates of these scavenging reactions are greatly enhanced by polar interactions between radical (acting as an electron donor) and carbonyl compound (an electron acceptor).

THERE have been several reports of the decarboxylation of substituted carboxylic acids, $R^1XCH_2CO_2H$, photosensitized by carbonyl compounds.[1-5] The mechanism of the process has been inferred largely from analysis of reaction products and the intermediates have received little direct attention.[1] We report here the e.s.r. and CIDNP n.m.r. investigation of the photo-reactions of benzophenone (BP) and duroquinone (DQ) with some of these acids ($X = S$ or O); the results are used to rationalize the products of both these and other reactions.

Two e.s.r. techniques have been used, the direct detection of transient radicals following flash photolysis in time-resolved experiments[6] and spin-trapping with a radical scavenger.[7] The latter revealed the mediation of certain radicals from which transient signals were not obtained, owing to either a low quantum yield for their formation, a short lifetime ($<10^{-4}$ s), or e.s.r. lines too broad for detection. Whilst e.s.r. allows identification of the radicals present it does not directly disclose the products of their reactions. These can be obtained directly and uniquely from n.m.r. observations of the reacting system: the products often display nuclear polarized (CIDNP) spectra in which the phases of the signals carry the mechanistic information.

In our experiments[8] the sample is illuminated along the axis of the n.m.r. tube *via* a light pipe that terminates sufficiently above the receiver coil of the spectrometer to avoid deterioration of the resolution. The reactants have to be in sufficiently low concentration for light to reach the coil region and conversions are also low so that the products are in exceptionally low concentration ($<10^{-4}$M) and cannot be extracted and isolated for identification. Indeed their equilibrium n.m.r. signals with the reaction stopped are normally too weak to observe. In principle the chemical shifts of the polarized peaks should allow their direct analysis but dilution can cause large shifts in peak positions from their literature values; although chemical shifts are defined at infinite dilution such measurements belong to a more exact age

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[1] E. J. Baum and R. O. C. Norman, *J. Chem. Soc.* (*B*), 1968, 227.

[2] R. S. Davidson and P. R. Steiner, *J. Chem. Soc.* (*C*), 1971, 1682.

[3] R. S. Davidson, K. Harrison, and P. R. Steiner, *J. Chem. Soc.* (*C*), 1971, 3480.

[4] R. S. Davidson and P. R. Steiner, *J.C.S. Perkin II*, 1972, 1357.

[5] M. Weinstein, K. A. Muszkat, and J. Dobkin, *J.C.S. Chem. Comm.*, 1975, 68.

[6] P. W. Atkins, K. A. McLauchlan, and A. F. Simpson, *J. Phys.* (*E*), 1970, **3**, 547.

[7] E. G. Janzen, *Accounts Chem. Res.*, 1971, **4**, 31; M. J. Perkins, ' Essays in Free-Radical Chemistry,' Chemical Society Special Publication No. 24, The Chemical Society, London, 1970.

[8] P. W. Atkins, J. M. Frimston, P. G. Frith, R. C. Gurd, and K. A. McLauchlan, *J.C.S. Faraday II*, 1973, 1542.

of n.m.r. experimentation. Where the products are known the observed peaks can be assigned and it is shown below that 'infinite' dilution shifts differ by 0.25—0.50 p.p.m. in changing the solvent from tetrachloromethane and carbon disulphide to benzene. When duroquinone is used adducts are formed with the sensitizer and yield CIDNP peaks; some of these products change between solvents. In the absence of samples of the pure adducts, which have not been synthesized, these peaks cannot be assigned with certainty. We have listed these notwithstanding, in the hope that future work will allow their identification; because of the large solvent shifts coincidences in peak positions in different solvents may only be apparent.

TABLE 1

Radicals from decarboxylation of $RXCH_2CO_2H$

Sensitizer	Acid	Conditions [a]	Radical(s) [d]	Hyperfine splittings (mT)	g	References
BP	$PhSCH_2CO_2H$	(i)	$Ph_2\dot{C}OH$	a (2 H) 0.36; a (4 H) 0.32; a (H) 0.24; a (2 H) 0.13	2.003 0	*h*
		(ii)	$PhSCH_2^{\cdot}$	a (2 H) 1.65 [f]	2.004 2 [g]	*i*
			$Bu^tNHO^{\cdot}$	a (N) 1.41; a (H) 1.25	2 006 2	*j*
			$Bu^tN(O^{\bullet})CH_2SPh$	a (N) 1.39; a (2 H) 0.60	2.006 5	*j*
			$Bu^tN(O^{\cdot})SPh$	a (N) 1.67	2.006 7	*j*
BP	$Bu^tSCH_2CO_2H$	(i)	$Ph_2\dot{C}OH$	a (2 H) 0.36; a (4 H) 0.32; a (H) 0.24; a (2 H) 0.13	2.003 0	*h*
		(ii)	$Bu^tSCH_2^{\bullet}$	a (2 H) 1.61	2.004 9	*k*
			$Bu^tNHO^{\bullet}$	a (N) 1.41; a (H) 1.27	2.006 2	*j*
			$Bu^tN(O^{\cdot})CH_2SBu^t$	a (N) 1.44; a (2 H) 0.60	2.006 5	
			$Bu^tN(O^{\cdot})SBu^t$	a (N) 1.59	2.006 7	
BP	$PhOCH_2CO_2H$	(ii) [b]	$Bu^tNHO^{\cdot}$	a (N) 1.41; a (H) 1.27	2.006 2	*j*
			$Bu^tN(O^{\bullet})CH_2OPh$	a (N) 1.33; a (2 H) 0.46	2.006 4	
DQ	$PhSCH_2CO_2H$	(i) [c]	$DQH^{\bullet}$	a (6 H) 0.49; a (6 H) 0.08	2.004 3	*l*
		(ii)	$PhSCH_2^{\bullet}$	a (2 H) 1.65 [f]	2.004 2 [g]	*i*
			$Bu^tN(O^{\bullet})CH_2SPh$	a (N) 1.39; a (2 H) 0.59	2.006 5	*j*
			$Bu^tN(O^{\bullet})SPh$	a (N) 1.67	2.006 7	*j*
DQ	$Bu^tSCH_2CO_2H$	(i) [c]	$DQH^{\cdot}$	a (6 H) 0.49; a (6 H) 0.08	2.004 3	*l*
		(ii)	$Bu^tSCH_2^{\bullet}$ [e]	a (2 H) 1.61	2.004 9	*k*
			$Bu^tN(O^{\bullet})CH_2SBu^t$	a (N) 1.44; a (2 H) 0.60	2.006 5	
			$Bu^tN(O^{\cdot})SBu^t$	a (N) 1.59	2.006 7	
DQ	$PhOCH_2CO_2H$	(i) [c]	$DQH^{\bullet}$	a (6 H) 0.49; a (6 H) 0.08	2.004 3	
		(ii)	$Bu^tN(O^{\bullet})CH_2OPh$ [e]	a (N) 1.33; a (2 H) 0.46	2.006 4	

[a] (i) Experiments were carried out in the absence of trap, (ii) experiments in the presence of 10^{-2}M-Bu^tNO. [b] No signals were obtained in the absence of trap. [c] Bu^tOH solution; only weak signals were obtained in benzene. [d] Weak signals from $Bu^t_2NO^{\bullet}$ were also obtained in several of the trapping experiments. [e] Very weak signals. [f] ±0.02 mT. [g] ±0.000 2. [h] Ref. 17. [i] A. Hudson and H. A. Hussain, *J. Chem. Soc. (B)*, 1969, 793. [j] Ref. 12. [k] B. C. Gilbert, J. P. Larkin, and R. O. C. Norman, *J.C.S. Perkin II*, 1973, 272. [l] T. E. Gough and M. C. R. Symons, *Trans. Faraday Soc.*, 1966, **62**, 269.

Despite these difficulties the major reaction pathways have been established from the peaks that can be assigned. The identities of the adducts are speculative since the only information we have is the chemical shifts in highly dilute solution of the protons (not necessarily all) which show polarized spectra.

EXPERIMENTAL

The e.s.r.[6] and n.m.r.[8] spectrometers used in the transient and CIDNP experiments have been described previously; all spectra were obtained at ambient temperature (293 and 308 K respectively). Solvents and other chemicals were the purest available commercially and were used without further purification. The e.s.r. experiments employed solutions which were generally 0.1M (BP) or 0.05M (DQ) in sensitizer and 0.1—1M in acid; the solvent was benzene except where indicated. The radical trap 2-methyl-2-nitrosopropane, Bu^tNO, was used in 0.01M concentration. All the spectra were obtained using 100 kHz modulation and were calibrated against a proton magnetometer, with appropriate correction for the difference in magnetic field at the sample and the magnetometer probe. Unless otherwise stated, hyperfine splittings were measured to ±0.01 mT, g values to ±0.000 1.

In the n.m.r. experiments, solutions in tetrachloromethane, carbon disulphide, and benzene were 0.08M in acid and 0.02M in sensitizer. Benzophenone and duroquinone are themselves photoactive and their solutions exhibit CIDNP even in the absence of added quencher;[9] a 4 : 1 concentration ratio appeared to suppress this behaviour. Irradiation was with the unfiltered light from a 500 W mercury high-pressure source, of which *ca.* 3×10^{-3} W reached the sample in the carbonyl absorption region.[9] Peak positions were measured relative to tetramethylsilane added after the reactions were stopped.

The intensities of CIDNP peaks vary with time[10] and some are detectable above the noise level for a comparatively short time (of the order of tens of seconds) which depends on both the spin-lattice relaxation times of the nuclei and the radical reaction rates. To observe all the CIDNP peaks it was necessary to sweep each spectrum a little at a time, as short a period after commencing irradiation as possible; the peaks listed in Table 2 are composites of several different experimental runs. In well defined systems the time behaviour can be analysed to give kinetic data[9,11] but the present systems are too complex.

RESULTS AND DISCUSSION

The e.s.r. data are summarised in Table 1. Both transient and spin-trapping experiments were performed on each system. The abbreviation $DQH^{\bullet}$ is used for the

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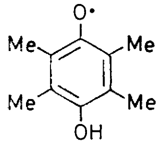
[9] P. G. Frith and K. A. McLauchlan, to be published.

[10] P. G. Frith and K. A. McLauchlan, 'Chem. Soc. Special Periodical Reports, N.m.r.,' 1974, **3**, 368.

[11] P. G. Frith and K. A. McLauchlan, *J.C.S. Faraday II*, 1976, 87.

protonated (neutral) durosemiquinone radical (1). Many spectra exhibited electron spin polarization and this behaviour is described below.



(1)

The majority of the spectra obtained have been reported previously and radicals were identified from literature data. Others (spectra from adducts of $Bu^tS^{\cdot}$, $Bu^tSCH_2^{\cdot}$, and $PhOCH_2^{\cdot}$ with Bu^tNO) were assigned as follows.

TABLE 2

CIDNP signals observed in decarboxylation reactions

Sensitizer	Acid	Shift (δ) Benzene	Shift (δ) CCl_4	Shift (δ) CS_2	Phase	Assignment
BP	$PhSCH_2CO_2H$	2.00	2.45		E	$PhSCH_3$
BP	$Bu^tSCH_2CO_2H$	3.13	3.57		E	$PhSCH_2CO_2H$
		1.68	1.91		E	Bu^tSCH_3
		2.85	3.13		E	$Bu^tSCH_2CO_2H$
DQ	$PhSCH_2CO_2H$	3.20			E	$Bu^tSCH(CO_2H)CPh_2OH$
		1.29	1.63	1.66	E	CH_3 in adducts
		1.40	1.87	1.90	E	
		1.72	2.00	2.00	E	CH_3 in DQ
		1.87	2.13	2.12	A	CH_3 in DQH_2
			2.28		E	
		2.03	2.45	2.48	A	$PhSCH_3$
				2.86	E	
		2.84	3.13		E	
			3.40	3.32	E	
		3.13	3.57	3.57	E	$PhSCH_2CO_2H$
		3.62			E	
DQ	$Bu^tSCH_2CO_2H$		5.32		A	HO in DQH_2
			1.90	1.93	E	CH_3 in adducts and/or Bu^tSCH_3
			2.00	2.00	E	CH_3 in DQ
			2.12		A	CH_3 in DQH_2
			2.15		E	
			2.27		E	
DQ	$PhOCH_2CO_2H$	2.37		2.85	E	
		1.35			E	CH_3 in adducts
		1.64			E	
		1.70			E	CH_3 in DQ
		1.95			A	CH_3 in DQH_2
		2.78			E	

The spectrum with *g* 2.006 7, *a*(N) 1.59 mT obtained from systems employing $Bu^tSCH_2CO_2H$ as quencher may be identified as an adduct of a thiyl radical from its high *g* value. Of the two possibilities [$Bu^tN(O^{\cdot})SBu^t$ and $Bu^tN(O^{\cdot})SCH_2CO_2H$] only the $Bu^tSCH_2^{\cdot}$ adduct is expected to have a nitrogen splitting of the magnitude found. (Increased alkyl substitution in alkylthiyl radicals tends to lower the nitrogen coupling in the nitroxide [12]). The spectra from adducts of $Bu^tSCH_2^{\cdot}$ and $PhOCH_2^{\cdot}$ (from $Bu^tSCH_2CO_2H$ and $PhOCH_2CO_2H$ respectively) were assigned from their splitting patterns and *g* values. Consistent with the latter assignment, substitution of anisole (from which $PhOCH_2^{\cdot}$ is expected to be formed directly) for $PhOCH_2CO_2H$ gave an identical spectrum.

With the exception of the benzophenone–phenoxyacetic acid case all the systems investigated by e.s.r. exhibited CIDNP in their n.m.r. spectra. The peaks observed and their phases, either emission (E) or absorption (A), are listed in Table 2.

The Primary Photochemical Process.—Reaction with acid is known to proceed *via* the lowest excited triplet state of the carbonyl compound [4] and probably involves exciplex formation, one decay mode of which is decarboxylation [reaction (1)].

$$R_2CO^* + R^1XCH_2CO_2H \longrightarrow \overline{R_2\dot{C}O^- \, R\overset{\cdot +}{X}CH_2CO_2H} \longrightarrow R_2\dot{C}OH + R^1XCH^{\cdot}_2 + CO_2 \quad (1)$$

If this reaction is sufficiently fast so that the rate of chemical deactivation competes with the triplet relaxation rate (${}^3T_1{}^{-1}$), the two radicals are expected to exhibit their e.s.r. spectra in initial emission.[13,*] Using DQ as photosensitizer, with *ca.* 0.1M-$PhSCH_2CO_2H$, $DQH^{\cdot}$ and $PhSCH_2^{\cdot}$ were detected initially in emission. For DQ* in Bu^tOH solution ${}^3T_1$ has been measured as *ca.* 10^{-8} s [14] and this implies an overall rate constant for reaction (1) of *ca.* 10^9 dm^3 mol^{-1} s^{-1}, which compares well with the literature value for chloranil of 2.2×10^9 dm^3 mol^{-1} s^{-1} in benzene.[4]

Much higher concentrations of acid (1M in cyclopentanol) were required to observe emission when BP was used as sensitizer; assuming a value for its ${}^3T_1$ similar to that for duroquinone this implies a reaction rate constant of *ca.* 10^8 dm mol^{-1} s^{-1}, again in good agreement with the literature.[4]

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[*] In the present experiments a further condition for the detection of emission is that the radical T_1 values are not markedly shorter than the time constant of the 100 kHz detection system.

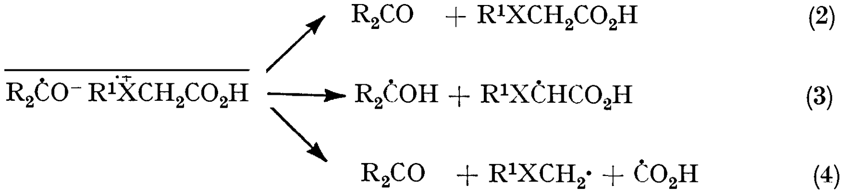
[12] I. H. Leaver and G. C. Ramsay, *Tetrahedron*, 1969, **25**, 5669.

[13] *E.g.* A. J. Dobbs, *Mol. Phys.*, 1975, **30**, 1073.

[14] P. W. Atkins, A. J. Dobbs, and K. A. McLauchlan, *Chem. Phys. Letters*, 1975, **29**, 616.

These observations show, as usual in our photolytic experiments with aromatic ketones, that the triplet mechanism of electron polarization dominates the subsequent radical-pair one and little or no influence of the latter is observed in the e.s.r. spectra although it is the origin of the nuclear polarized transitions in the n.m.r. spectra of the products.

Radical Intermediates.—In addition to the decarboxylation the exciplex has been postulated to decay in several other modes [2-5] [reactions (2)—(4)]. The e.s.r. evidence strongly suggests that in the majority, if not all, of the systems investigated the major radical products are $R_2\dot{C}OH$ and $R^1XCH_2^{\bullet}$.



$$\overline{R_2\dot{C}O^- R^1\overset{+}{\dot{X}}CH_2CO_2H} \longrightarrow \begin{cases} R_2CO + R^1XCH_2CO_2H & (2) \\ R_2\dot{C}OH + R^1X\dot{C}HCO_2H & (3) \\ R_2CO + R^1XCH_2^{\bullet} + \dot{C}O_2H & (4) \end{cases}$$

This does not rule out contributions from reactions (3) and (4) and indeed reaction (3) must be invoked to rationalize the CIDNP behaviour. The benzophenone photosensitized reactions are discussed first.

In the transient work, (phenylthio)acetic acid yielded the two radicals $Ph_2\dot{C}OH$ and $PhSCH_2^{\bullet}$ (the three broad lines of the latter were easily picked out by saturating out the $Ph_2\dot{C}OH$ lines at high microwave power). $Ph_2\dot{C}OH$ decayed with second-order kinetics ($\tau_{\frac{1}{2}}$ *ca.* 0.6 ms) and although the significantly faster decay of $PhCSH_2^{\bullet}$ was distorted by the response time of the spectrometer it was not affected significantly by changes in the concentrations of reactants; it appears that both radicals undergo combination reactions. The absence of the spectrum of $PhS\dot{C}HCO_2H$ probably reflects its formation in low quantum yield rather than its having a very short lifetime.

Experiments with the radical scavenger Bu^tNO also established that $Ph_2\dot{C}OH$ and $PhSCH_2^{\bullet}$ last sufficiently long to react with the trap: the radicals $Bu^tNHO^{\bullet}$ (from $Ph_2\dot{C}OH$ and Bu^tNO[12]) and $Bu^tN(O^{\bullet})CH_2SPh$ were detected. Rather surprisingly a spectrum identical with that reported [12] for $Bu^tN(O^{\bullet})SPh$ was also observed. This suggests the presence of $PhS^{\bullet}$ radicals which are probably formed [reaction (5)] *via* a small amount of alkyl radical scavenging by traces of thiophenol present as an impurity in the acid.

$$PhSCH_2^{\bullet} + PhSH \longrightarrow PhSCH_3 + PhS^{\bullet} \qquad (5)$$

This spectrum was also obtained (although at much lower intensity), together with that of $Bu^t{}_2NO^{\bullet}$, when no benzophenone was present. This originates from the photocleavage [7] of Bu^tNO to yield t-butyl radicals which are scavenged by both the nitroso-compound and thiophenol. Further evidence for the presence of thiol comes from the product studies of Davidson and Steiner,[2] who found traces of thiophenol in a chloranil–$PhSCH_2CO_2H$ reaction mixture.

Very similar results were obtained with $Bu^tSCH_2CO_2H$, with trapping experiments again revealing the presence of thiyl radicals, presumably from thiol present.

Using $PhOCH_2CO_2H$ no transient radicals were detected, no doubt owing to the low quantum yield for decarboxylation,[4] but the expected radicals [$Bu^tNHO^{\bullet}$ and $Bu^tN(O^{\bullet})CH_2OPh$] were detected in the presence of the nitroso-compound.

When duroquinone was the photosensitizer, generally similar results were obtained although much stronger transient signals were observed in t-butyl alcohol solution than in benzene. With $PhSCH_2CO_2H$ the $DQH^{\bullet}$ and $PhSCH_2^{\bullet}$ radicals were observed and the latter again had the shorter lifetime (<0.5 ms, *cf.* 2.0 ms), unaffected by changes in the concentrations of the reactants (in the concentration ranges 0.01—0.1M in DQ and 0.1—0.5M in $PhSCH_2CO_2H$). In benzene solutions addition of Bu^tNO gave the spectra of the $PhSCH_2^{\bullet}$ and $PhS^{\bullet}$ adducts ($DQH^{\bullet}$, like other aryloxyl radicals,[12] is apparently not scavenged by the nitroso-compound under these conditions). Similar results were obtained with $Bu^tSCH_2CO_2H$, except that the transient spectrum of $Bu^tSCH_2^{\bullet}$ was weak.

Reaction with phenoxyacetic acid gave a strong transient spectrum of $DQH^{\bullet}$ but $PhOCH_2^{\bullet}$ could not be detected; we conclude that it has too short a lifetime, probably disappearing in a pseudo-first-order reaction with ground-state duroquinone, which is a moderate scavenger for methyl radicals.[15] The trapping experiments displayed only traces of a $PhOCH_2^{\bullet}$ adduct, consistent with this view. The difference in behaviour of the $PhOCH_2^{\bullet}$ and $PhSCH_2^{\bullet}$ radicals is discussed below. Some other weak transitions, which may have originated in an adduct radical, were detected in the transient spectrum but the complexity of the composite spectrum precluded their assignment.

Products and CIDNP Interpretation.—In this section knowledge of Kaptein's rules [16] for CIDNP is assumed and the mechanistic deductions made from the CIDNP observations are consistent with the phases of the signals listed in Table 2; a description of the application of the rules is omitted for conciseness.

(i) *Benzophenone-sensitized reactions.* The e.s.r. observations confirm the deductions from product analysis [2] that the major products arise through combinations of the primary radicals $Ph_2\dot{C}OH$ and $R^1XCH_2^{\bullet}$; these include $Ph_2C(OH)C(OH)Ph_2$ and $PhSCH_3$ from $PhSCH_2CO_2H$, and $Ph_2C(OH)C(OH)Ph_2$, $PhOCH_3$, and $PhOCH_2$-

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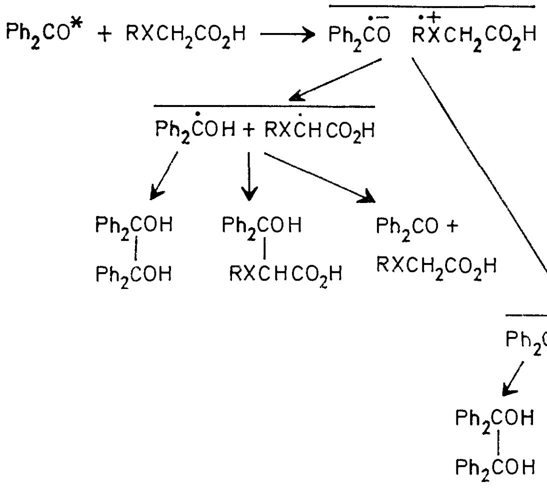
[15] A. Rembaum and M. Szwarc, *J. Amer. Chem. Soc.*, 1955, **77**, 4468.

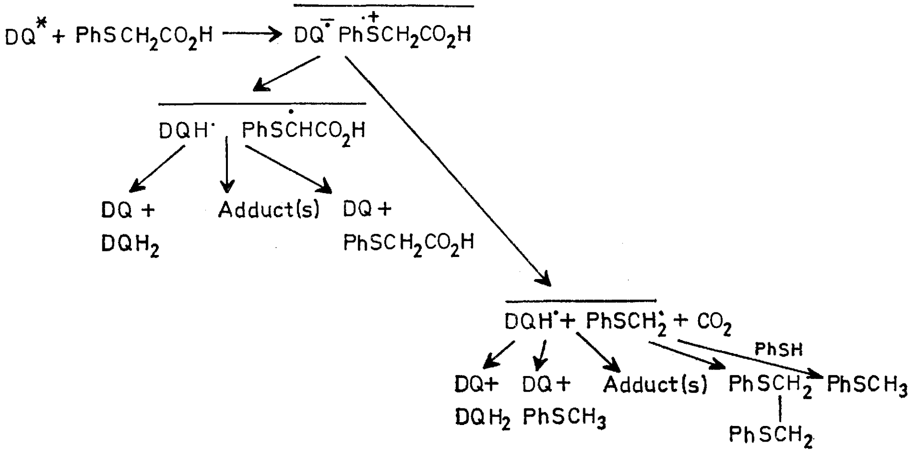
[16] R. Kaptein, *Chem. Comm.*, 1971, 732.

CH_2OPh from $PhOCH_2CO_2H$, which arise from dimerization and disproportionation reactions.

The CIDNP results on $PhSCH_2CO_2H$ and $Bu^tSCH_2CO_2H$ suggest however that $RS\dot{C}HCO_2H$ is also formed in the primary reaction (albeit in low concentration, as the e.s.r. data imply). The detection of $RSCH_2CO_2H$ with the methylene protons in emission seems best explained [5] by in-cage atom transfer between $Ph_2\dot{C}OH$ and $R^1S\dot{C}HCO_2H$ (the *g* values of these two radicals are 2.003 0 [17] and *ca.* 2.006 [18] respectively). A weak emission peak (δ 3.20) with $Bu^tSCH_2CO_2H$ may well be from the combination product. Observation of the $RSCH_3$ methyl peak in emission implies that, where the polarization process is concerned, the in-cage atom transfer between $Ph_2\dot{C}OH$ and $PhSCH_2^{\bullet}$ outweighs any absorptive contribution from scavenging with PhSH; however this cannot be placed on a quantitative basis. No polarization was observed from the $PhOCH_2CO_2H$ system, which is consistent with a low quantum yield for radical formation accentuated by a close similarity in radical *g* values which militates against large polarization factors.



Scheme 1



Scheme 2

The reactions of triplet benzophenone with the acids $R^1XCH_2CO_2H$ appear accommodated by Scheme 1.

(ii) *Duroquinone-sensitized reactions.* Above we have shown from the e.s.r. experiments that a different reaction mechanism pertains between $PhSCH_2CO_2H$ and $PhOCH_2CO_2H$ and this should be reflected in the reaction products. No product analyses have been performed on these systems but CIDNP data support this view of a difference in reaction pathway.

With (phenylthio)acetic acid, the radical intermediates $DQH^{\bullet}$ and $PhSCH_2^{\bullet}$ seem mainly to combine to form products. The *g* values of these radicals are closely similar (they are the same within experimental error, although that of $DQH^{\bullet}$ may be slightly the higher) and little polarization is expected from $\overline{PhSCH_2^{\bullet}\ DQH^{\bullet}}$ radical pairs; the alternative radical pair $\overline{PhS\dot{C}HCO_2H\ DQH^{\bullet}}$ should provide the major polarizations in this system. Consistent with expectation, $PhSCH_3$ was produced in high yield in this system, its equilibrium n.m.r. spectrum being observable with the reaction stopped; also its polarization (absorption) was only weak. The suggestion [5] that it results from scavenging of $PhSCH_2^{\bullet}$ by the

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[17] R. S. Davidson and R. Wilson, *Mol. Photochem.*, 1974, **6**, 231; R. Wilson, *J. Chem. Soc.* (*B*), 1968, 84.

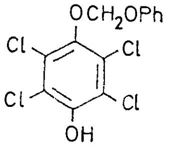
[18] Y. Kurita and W. Gordy, *J. Chem. Phys.*, 1961, **34**, 1285.

solvent is discounted on the grounds that benzene is a poor hydrogen donor and that the same product is obtained in deuteriobenzene solution with no apparent coupling to a deuteron. The methylene lines of $PhSCH_2CO_2H$ and the methyl ones of DQ were in emission, providing evidence for the involvement of the radical pair $\overline{PhS\dot{C}HCO_2H\ DQH^{\bullet}}$.

Other emission signals included two in the methyl region to high field of duroquinone, which are probably from groups in the products of radical addition to $DQH^{\bullet}$ at carbon. (Addition at oxygen would, and perhaps does, give methyl resonances in the durohydroquinone region.) At lower field (δ 2.28—3.62) other lines were obtained, with intensities that varied with solvent. These seem to originate from aliphatic protons bound to carbon centres in the adducts.

Fairly strong absorption signals were obtained from both the methyl and hydroxy-protons of durohydroquinone (DQH_2), which must therefore result from a scavenging reaction, possibly the disproportionation of two $DQH^{\bullet}$ radicals which react within the spin–lattice relaxation time after escaping from the primary cage.

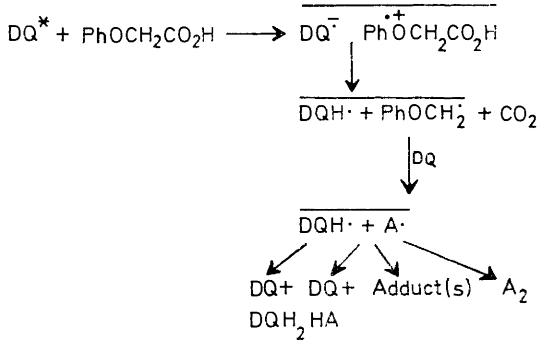
An overall reaction mechanism consistent with these observations is given in Scheme 2 which is very similar to that proposed in the benzophenone case. This scheme applies to the e.s.r. and CIDNP experiments but it may not be consistent with product analysis studies, where the relatively low initiation rates might favour chain reactions, for example between $PhSCH_2^{\bullet}$ radicals and DQ, and yield quite different products.



(2)

Phenoxyacetic acid, $PhOCH_2CO_2H$, shows a quite different behaviour. The lack of any n.m.r. signal from anisole is consistent with our previous conclusion that the $PhOCH_2^{\bullet}$ radical has a very short lifetime in the presence of duroquinone, and indeed low or zero yields of anisole have been reported[2] from several other quinone-initiated reactions. Also, no polarization was detected in the parent acid, and it seems that the major radical pair which leads to CIDNP behaviour may be that between $DQH^{\bullet}$ and an adduct (or adducts) of $PhOCH_2^{\bullet}$ with DQ, $A^{\bullet}$.

A pair of radicals is of course necessary and several previous CIDNP studies[19] have demonstrated the importance of such radical pair substitution effects in the presence of highly reactive primary radicals. Cage reaction can lead to a number of disproportionation and addition products and compound (2) has been isolated from the chloranil system. A number of quinonoid and benzenoid derivatives are possible whose methyl resonances would occur with chemical shifts in the DQ and DQH_2 regions. Those in the DQ region are in emission, whilst those in the DQH_2 one are in absorption. This is consistent with the existence of $\overline{DQH^{\bullet}\ A^{\bullet}}$ radical pairs provided that $g(DQH^{\bullet}) > g(A^{\bullet})$ (*cf.*[9] the polarizations found in the reaction leading to duroquinone dimer). The very high field resonances again presumably reflect some coupling to $DQH^{\bullet}$ of carbon. The reactions summarized in Scheme 3 account for the e.s.r. and CIDNP observations. Alternatively, polarized $DQH\cdot$ diffusing from the original cage might react to give polarized products without significant polarization resulting from a secondary pair; a small amount of reaction of triplet DQ with its ground state might also occur.



SCHEME 3

The possible overlap of resonances (see Table 2) made it difficult to ascertain whether significant amounts of Bu^tSCH_3 were produced in the n.m.r. experiments. It may be that $Bu^tSCH_2CO_2H$ displays behaviour intermediate between the extremes of Schemes 2 and 3.

The limitations of the CIDNP technique, that it may detect minor reaction pathways and that in its normal usage it cannot indicate the relative importance of different pathways, have been commented upon frequently. This work provides a further example, for the decarboxylation process is shown by the e.s.r. measurements to predominate in all cases; the necessity of making both transient e.s.r. and CIDNP observations is evident and a combination of these techniques allows a uniquely detailed insight into the reaction processes in solution.

Related Reaction Systems.—The general features of the systems investigated here are reproduced in many other systems that have been studied. At one extreme (*e.g.* BP–$PhSCH_2CO_2H$) high yields of dimers and substituted hydrocarbons are found, at the other (*e.g.* DQ–$PhOCH_2CO_2H$) yields of substituted hydrocarbon are low or zero and often cannot be increased even by adding a good hydrogen donor.

These latter reactions involve scavenging of $R^1XCH_2^{\bullet}$ radicals by the carbonyl compound in a reaction [probably addition, reaction (6), rather than electron transfer, reaction (7), in the weakly polar solvents employed]

$$R^1XCH_2^{\bullet} + R_2CO \longrightarrow \text{Adduct} \qquad (6)$$

$$R^1XCH_2^{\bullet} + R_2CO \longrightarrow R^1XCH_2^{+} + R_2\overset{\bullet-}{C}O \qquad (7)$$

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[19] R. Kaptein, F. W. Verhaus, and L. J. Oosterhoff, *Chem. Comm.*, 1971, 877; R. A. Cooper, R. G. Lawler, and H. R. Ward, *J. Amer. Chem. Soc.*, 1972, **94**, 552; J. A. den Hollander, *J.C.S. Chem. Comm.*, 1975, 352.

which, we suggest, depends markedly on the donor and acceptor properties of the species. [The rates of many other radical reactions (*e.g.*[20] the reduction of carbonyl compounds by hydroxyalkyl radicals) are known to depend strongly on polar factors of this kind.] The yields of substituted hydrocarbons from various sensitizers and quenchers are summarized in Table 3. Given similar rates of initiation and that R^1XCH_3 is formed predominantly through disproportionation of $R^1XCH_2^{\bullet}$ with $R_2\dot{C}OH$, then the yield of substituted hydrocarbon may be taken as a measure of the lifetime of the $R^1X\dot{C}H_2$ radical (since only the relatively long-lived radicals will participate in such radical–radical reactions), which in turn, since similar concentrations of carbonyl compounds were employed in these studies, should reflect the rate constants for reaction of $R^1XCH_2^{\bullet}$ with carbonyl compound.

TABLE 3

Yields of R^1XCH_3 from decarboxylation reactions

Radical [b] \ Sensitizer [a]	PhCOMe	Ph_2CO [d,e]	AQ [d]	DQ [a]	PQ [d]	Chloranil [d]
$PhSCH_2^{\bullet}$	High	High	High	High	High	Low
$RSCH_2^{\bullet}$	High	High	High	High	Zero	Zero
$PhOCH_2^{\bullet}$	High	High	High	Low	Zero	Zero
$PhNHCH_2$	High	High	Low		Zero	Zero

[a] AQ = anthraquinone, PQ = phenanthraquinone; sensitizers are listed in order of increasing redox potential. [b] In order of increasing donor character (see text). [c] Ref. 3. [d] Ref. 2. [e] This work.

From Table 3 we see that the lowest yields of substituted hydrocarbon and hence the fastest scavenging reactions are found in those systems in which radicals of high donor ability [as judged, for example, from the $(\sigma_p - \sigma_m)$ values [21] of the NHR, OR, and SR groups] are produced in the presence of carbonyl compounds of high redox potential; [22] the lack of effect of added thiol in several of these systems indicates that the addition reaction is sufficiently fast to preclude other routes for the removal of $R^1XCH_2^{\bullet}$. Conversely, the slowest reactions are those between radicals of low donor ability and carbonyl compounds of low redox potential.

The isolation of adducts [2,23] in some of the systems in which little R^1XCH_3 is produced is consistent with a mechanism such as that suggested for duroquinone in Scheme 3. Adducts are not found in systems involving $R^1NHCH_2^{\bullet}$ radicals, evidently [2] because the hydrogen-atom transfer reaction (8) is favoured.

$$R^1NHCH_2^{\bullet} + R_2CO \longrightarrow R^1N{=}CH_2 + R_2\dot{C}OH \qquad (8)$$

[5/1944 *Received, 6th October*, 1975]

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[22] F. J. L. Aparicio and W. A. Waters, *J. Chem. Soc.*, 1955, 4666.

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