Acylarylnitrosamines. Part X.[1] An Electron Spin Resonance Spectroscopic Investigation of the Reactions of Aryl Radicals with Tetraphenylcyclopentadienone and 2,3-Diarylindenones: Detection of 1-Oxo-2,2,3-Triphenylindenyl and Related Radicals and their Relevance to Dienone-promoted Formation of Benzyne from Benzenediazonium Acetate

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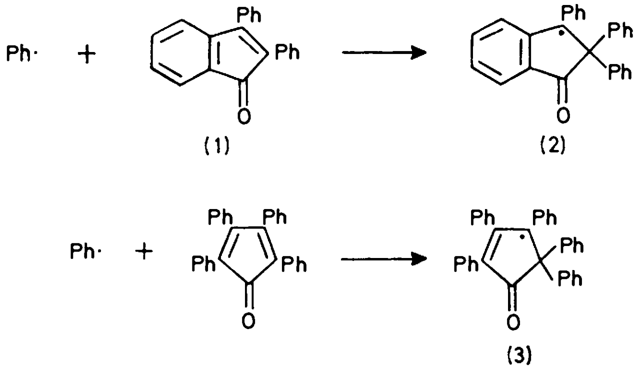
Decomposition of benzenediazonium acetate, formed *in situ* in benzene from *N*-nitrosoacetanilide (NNA), in the presence of tetraphenylcyclopentadienone (tetracyclone) gives e.s.r. signals corresponding to new long lived radicals (4) formed by addition of a phenyl radical to position 2 of tetracyclone. Similar reactions of NNA with 2,3-diphenylindenone gave long lived signals corresponding to the 1-oxo-2,2,3-triphenylindenyl radical (5), an assignment supported by computer simulation. The use of dibenzoyl peroxide or pentyl nitrite–aniline as alternative sources of phenyl radicals also led to the formation of radical (5). The assignments of structures (4) and (5) were supported by analysis of the related signals obtained from reactions of NNA with 2-phenyl-3-(*p*-t-butylphenyl)- and 3-phenyl-2-(*p*-t-butylphenyl)-indenone, and by reactions of *p*-t-butyl-NNA with 2,3-diphenylindenone and with 2-phenyl-3-(*p*-t-butylphenyl)indenone. Related studies with 2-methyl-3,4,5-triphenyl-, 2,5-diethyl-3,4-diphenyl-, and 3,4-diphenyl-2,5-di-*p*-tolylcyclo-pentadienones were also carried out. These results with those described in the preceding paper lend support to the suggestion that benzyne promotion from NNA by tetracyclone and 2,3-diphenylindenone is explicable on the basis of inhibition of the competing NNA-derived radical chain phenylation of the solvent.

IN Part IX[1] we showed that a series of unsaturated compounds, including 2,3-diphenylindenone (1), promoted the formation of benzyne from benzenediazonium acetate, formed *in situ* from *N*-nitrosoacetanilide (NNA), at the expense of the competing radical chain phenylation of benzene. It was suggested that this could be due to the formation of long lived radicals such as (2) by addition of phenyl radicals to 2,3-diphenylindenone. This process itself could lead to suppression of the chain phenylation, with the added possibility that the radical (2) could act as a chain inhibitor. This led to the proposal that similar addition of phenyl radicals to tetraphenylcyclopentadienone (tetracyclone) to give long lived radicals (3) could be the cause of the marked benzyne promoting effect of tetracyclone.[1]

We now describe the results of an e.s.r. spectroscopic investigation which clearly point to the presence of radicals such as (2) and (3) in these reactions.



SCHEME 1

Reaction of Acylarylnitrosamines with Tetracyclone and Related Compounds.—(i) *NNA with tetracyclone.* E.s.r. examination of the reaction of NNA with tetracyclone in benzene at room temperature revealed an intense signal (Figure 1) which could be detected over a period of several days. While incomplete resolution prevents precise analysis, the 17-line pattern and its extent (1.46 mT) are consistent with a large splitting (*ca.* 0.19 mT) due to six approximately equivalent protons and a smaller splitting (*ca.* 0.08 mT) due to four protons. For reasons to be discussed later the signal is assigned to radical (4) formed by addition of a phenyl radical to the 2-position of tetracyclone. Delocalisation of the unpaired electron through the phenyl rings at positions 3 and 5 of the cyclopentadienone ring gives rise to large splittings from the *ortho*- and *para*-protons and smaller

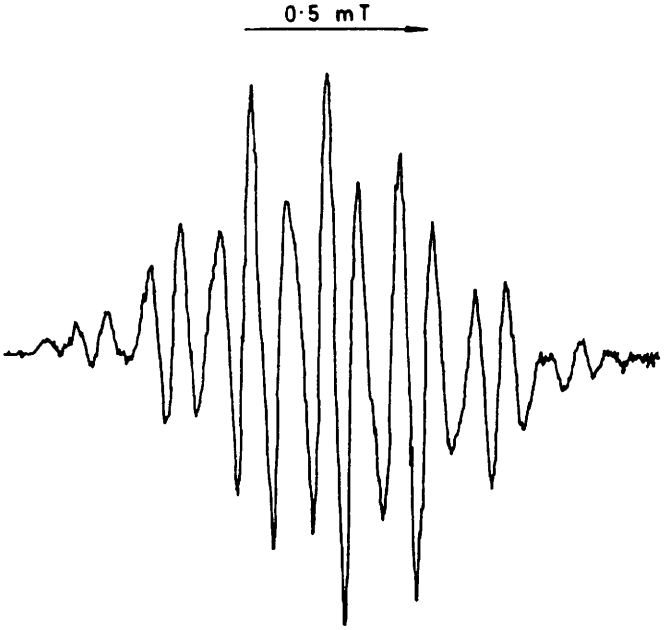


FIGURE 1 E.s.r. spectrum of the reaction of NNA with tetracyclone

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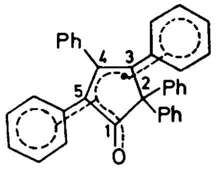
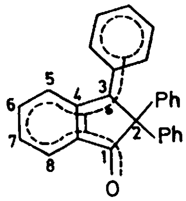
[1] Part IX, J. I. G. Cadogan, C. D. Murray, and J. T. Sharp, preceding paper.

splittings at the *meta*-position. Unresolved coupling to the protons of the phenyl ring at the 4-position and the non-equivalence of the 3- and 5-phenyl rings may be the cause of the large linewidth (0.032 mT) and the incomplete resolution.



(4)

(ii) *NNA with 2,3-diphenylindenone.* In contrast to the foregoing tetracyclone case, the signal (Figure 2a) obtained from the reaction of NNA with 2,3-diphenylindenone is well resolved, being spread over 2.21 mT with a linewidth of 0.019 mT. The spectrum was analysed with the aid of computer simulation (Figure 2b) and found to show coupling of the unpaired electron to nine protons, as required by a radical with structure (5) in which there is delocalisation through the 3-phenyl and fused rings, but not to the aryl ring derived from NNA nor to that attached to the 2-position of the indenone. The values of the hyperfine coupling constants and their assignments to the nine protons are listed in Table 1. The allocation of a slightly larger value for the *para*-proton compared to those at the *ortho*-positions is consistent with similar observations for phenyl-substituted carbon-centred radicals such as benzyl[2] and triphenylmethyl.[3]



(5)

In order to test the hypothesis that aryl radical addition does occur at the 2-position, to give radicals with structure (5), rather than elsewhere in the molecule, reactions of NNA with diarylindenones containing a *p*-t-butyl group in either the 2- or 3-aryl group were studied. The replacement of a proton by a t-butyl group has been found to result in effective removal of the splitting due to that proton, the very small coupling to the t-butyl protons being manifested in an increased linewidth,[4] and this effect would be expected on phenyl radical addition to position 2 in 2-phenyl-3-(*p*-t-butylphenyl)indenone to give the radical (6; $R^1 = Bu^t$, $R^2 = H$), but not in the case of addition to position 3 or in the case of addition to position 2 in 3-phenyl-2-(*p*-t-butylphenyl)indenone. By the same token substitution of a *p*-t-butyl group in the phenyl radical in the above cases should have negligible effects on the spectra.

(iii) *NNA with 2-phenyl-3-*(p*-t-butylphenyl)indenone.* The observed signal (Figure 3a) shows a reduction in the number of hyperfine components compared to that found for the unsubstituted analogue, while there is a corresponding reduction in the overall extent of the signal from 2.21 to 1.88 mT, in accord with the removal of the splitting (0.32 ± 0.01 mT) due to the *para*-proton of the 3-phenyl ring. At the same time the assignment

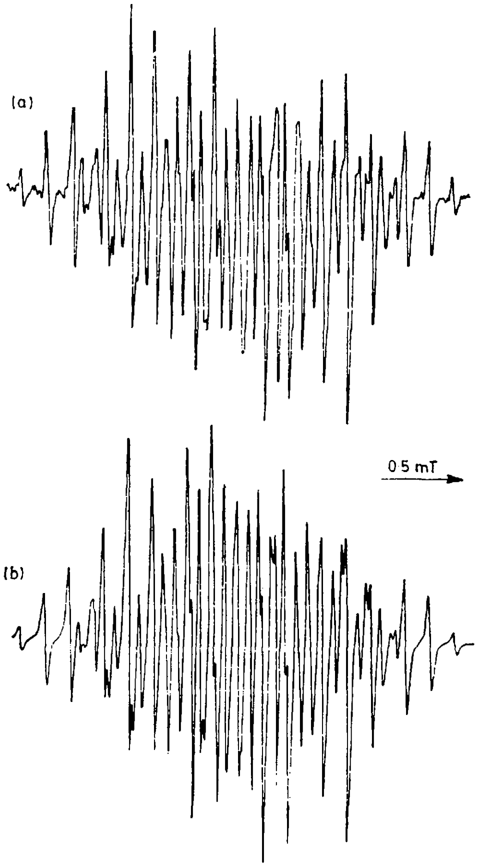
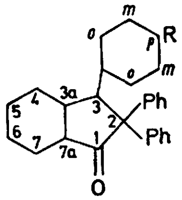


FIGURE 2 a, Experimental and b, simulated e.s.r. spectra of the reaction of NNA with 2,3-diphenylindenone

TABLE 1

Hyperfine coupling constants (mT) for radicals derived from 2,3-diphenylindenone *



Proton	R=H	R=Bu^t
ortho (2 H)	0.30	0.30
meta (2 H)	0.125	0.125
para	0.32	
Bu^t (9 H)		0.01
4	0.43 or 0.36	0.43 or 0.36
5	0.125	0.125
6	0.36 or 0.43	0.36 or 0.43
7	0.125	0.125

* *a* ± 0.01 mT.

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[2] A. Carrington and I. C. P. Smith, *Mol. Phys.*, 1965, **9**, 137.

[3] D. B. Chesnut and G. J. Sloan, *J. Chem. Phys.*, 1960, **33**, 637.

of this splitting is confirmed. Further, as predicted, there is an increase in the linewidth from 0.019 to 0.045 mT due to unresolved coupling to the nine equivalent protons of the t-butyl group.

Computer simulation (Figure 3b) using the same hyperfine coupling constants found for radical (5), but replacing the splitting of 0.32 mT (1 H) with one of 0.01 mT (9 H) reproduces the essential features of the observed spectrum. The radical is therefore assigned the structure (6; $R^1 = Bu^t$; $R^2 = H$).

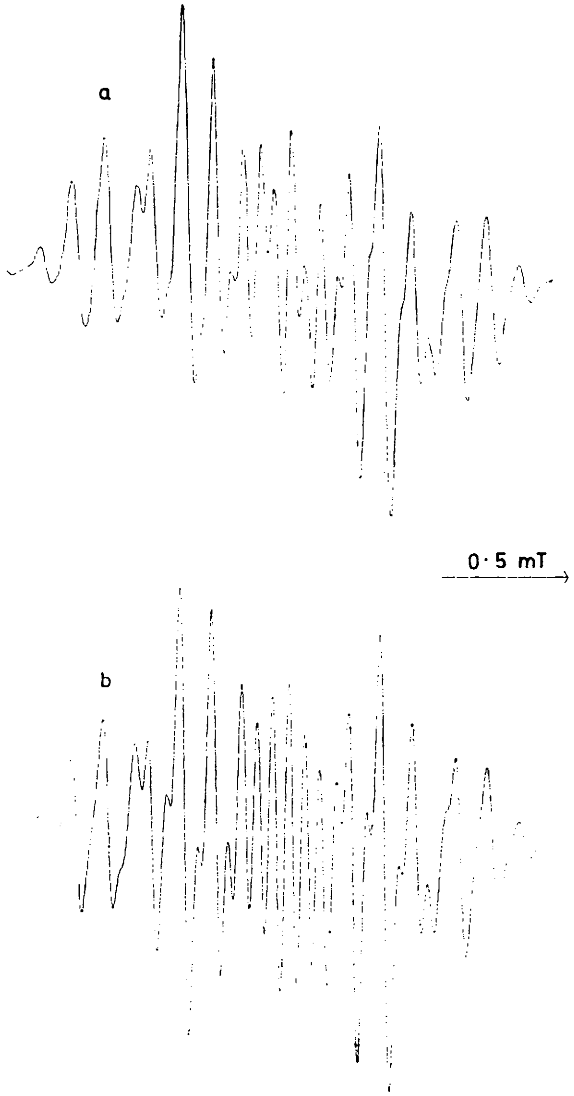
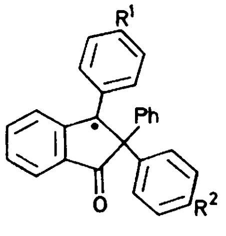


FIGURE 3 a, Experimental and b, simulated e.s.r. spectra of the reaction of NNA with 2-phenyl-3-(*p*-t-butylphenyl) indenone

(iv) *NNA with* 3-*phenyl*-2-(p-*t-butylphenyl*)*indenone.* In this case the spectrum is indistinguishable from that (Figure 2a) found for the unsubstituted analogue, indicating that, as expected, negligible unpaired electron density reaches the substituents attached to the 2-position of the radical, and confirming that the location of aryl radical attack is at the 2- rather than the 3-position of the diarylindenone to give the radical (6; $R^1 = H$, $R^2 = Bu^t$).

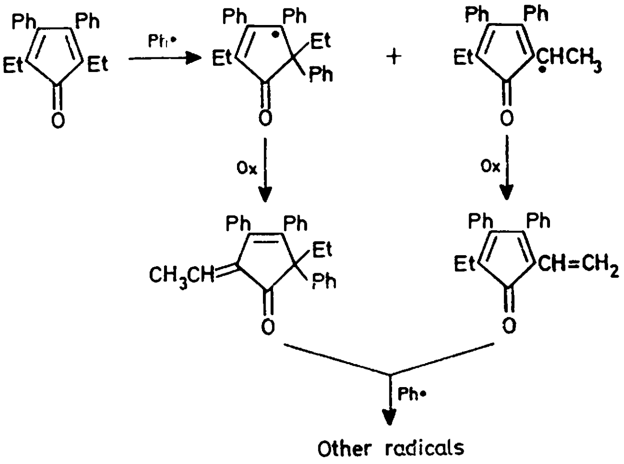


(6)

(v) p-*t-Butyl-NNA with* 2,3-*diphenylindenone and* 2-*phenyl*-3-(p-*t-butylphenyl*)*indenone.* The observed spectra were indistinguishable from those found for NNA itself with these substrates, as required for radicals (6; $R^1 = H$, $R^2 = Bu^t$) and (6; $R^1 = R^2 = Bu^t$), showing that the unpaired electron density distribution is independent of the *para*-substituent of the aryl ring derived from the acylarylnitrosamine in accord with expectation.

(vi) *NNA with* 2,5-*diethyl*-3,4-*diphenylcyclopentadienone* (*Table* 2). An intense, long lived signal was detected during this reaction. Not only did the large linewidth (0.044 mT) and limited resolution prevent detailed analysis, but the overall shape changed with time. While the signal remained symmetrical throughout, the intensities of the middle hyperfine components increased with time, indicating two radical species with similar *g* values present in varying concentrations. These results may be explained by the presence of the readily abstractable α-methylene protons of the ethyl groups, providing alternative pathways for the consumption of aryl radicals (Scheme 2), thus leading to further, unidentified long-lived radicals.

(vii) *NNA with* 2-*methyl*-3,4,5-*triphenylcyclopentadienone and* 3,4-*diphenyl*-2,5-*di*-(p-*tolyl*)*cyclopentadienone* (*Table* 2). The intense signals detected during the reaction of NNA with these dienones were incompletely resolved. This together with the broad linewidth prevented complete analysis. Nevertheless, as with the

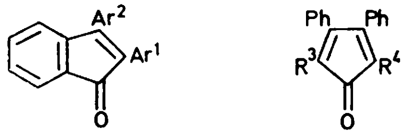


SCHEME 2

other substituted cyclopentadienones, the spectra are superficially compatible with radicals analogous to (4).

TABLE 2

E.s.r. spectra observed during reactions of aryl radicals with indenones (A) and tetracyclones (B)



(A) (B)

Ar source	(A) Ar^1	(A) Ar^2	(B) R^3	(B) R^4	Radical [a] produced	Signal [b] extent (mT)	g [c]	Linewidth [d] (mT)	Figure
NNA	Ph	Ph			(5)	2.21	2.0027	0.019	2a
NNA	p-Bu^{t}C$_6$H$_4$	Ph			(6; R^1 = H, R^2 = Bu^t)	2.24	2.0026	0.023	
NNA	Ph	p-Bu^{t}C$_6$H$_4$			(6; R^1 = Bu^t, R^2 = H)	1.88	2.0027	0.048	3a
p-Bu^{t}NNA	Ph	Ph			(6; R^1 = H, R^2 = Bu^t)	2.21	2.0027	0.024	
p-Bu^{t}NNA	Ph	p-Bu^{t}C$_6$H$_4$			(6; R^1 = R^2 = Bu^t)	1.89	2.0027	0.045	
PhNH$_2$–RONO [e]	Ph	Ph			(5)	2.23	2.0027	0.024	
(PhCO$_2$)$_2$ [e]	Ph	Ph			(5)	2.28	2.0027	0.043	
NNA			Ph	Ph	(4)	1.45	2.0032	0.032	1
NNA [f]			Et	Et		2.25	2.0031	0.044	
NNA			Me	Ph			2.0031	0.043	
NNA			p-MeC$_6$H$_4$	p-MeC$_6$H$_4$ p-MeC$_6$H$_4$			2.0032		

[a] See text. [b] ±0.02 mT. [c] ±0.0001. [d] ±0.001 mT. [e] Other unidentified signals were also obtained. [f] Signal shape varied with time (see text).

Reaction of Aniline and Pentyl Nitrite with 2,3-*Diphenylindenone*.—To obtain further proof of the assignment (5) of the e.s.r. signal (Figure 2a) derived from 2,3-diphenylindenone by reaction with phenyl radicals from NNA, the use of aniline and pentyl nitrite as an alternative source of phenyl radicals [5] was studied. In accord with the above interpretations reaction at 50—70° gave an intense well resolved signal indistinguishable from that (Figure 2a) found for NNA. The exceptionally long life-time of these radicals was indicated by the endurance of the signal with high intensity far in excess of a month at room temperature.

Reaction of Dibenzoyl Peroxide with 2,3-*Diphenylindenone*.—The e.s.r. signal observed during the thermolysis (60°) of dibenzoyl peroxide in the presence of 2,3-diphenylindenone was unsymmetrical indicating the presence of more than one long-lived radical species with differing g values. In spite of this complication the presence of radical (5) was evident from the spectrum.

Conclusions.—The detection of radicals such as (4) and (5) is in accord with the mechanism outlined in Part IX [1] which explains the benzyne-promoting effect of tetracyclone. This is subject to the general caveat that the observation of e.s.r. signals is not necessarily mechanistically important in quantitative terms. Nevertheless, we suggest that this evidence, taken with other observations reported in previous Parts, significantly reduces the mechanistic obscurity surrounding this complex reaction.

EXPERIMENTAL

Reagents.—*N*-Nitrosoacetanilide and p-t-butyl-*N*-nitrosoacetanilide were prepared as described previously.[1,6] Substituted cyclopentadienones and 2,3-diphenylindenone were as described in Part IX.[1] 2-*Phenyl*-3-(p-*t-butylphenyl*)*indenone* was prepared following the procedure for 2,3-diphenylindenone [7] by reaction of p-t-butylphenylmagnesium bromide with 3-benzylidenephthalide followed by treatment of the resulting Grignard complex with sulphuric acid. The product crystallised from ethanol as orange crystals, m.p. 145—147° (Found: C, 89.0; H, 6.4%; *m/e*, 338. $C_{25}H_{22}O$ requires C, 88.7; H, 6.55%; *M*, 338), τ ($CDCl_3$) 2.4—3.0 (13 ArH) and 8.69 (9 H, CMe$_3$). 3-*Phenyl*-2-(p-*t-butylphenyl*)*indenone*, dark red crystals from ethanol, m.p. 138°, was prepared similarly (Found: C, 88.6; H, 6.6%; *m/e*, 338).

This preparation involved the prior formation of 3-(4-*t-butylbenzylidene*)*phthalide* by reaction of p-t-butylphenylacetic acid (5 g) and phthalic anhydride (3.3 g) with fused sodium acetate (0.1 g) at 230° for 3 h. Standard work-up gave the product (60%) as crystals from ethanol, m.p. 108—109° (Found: C, 82.6; H, 6.4. $C_{19}H_{18}O_2$ requires C, 82.7; H, 6.4%).

E.s.r. Spectroscopy.—*Instrumentation*. Spectra were recorded on a Decca X1 spectrometer, in conjunction with a Newport Instruments 8 in magnet and Hilger and Watts Microspin magnet controls, using 100 kHz modulation and an X-band klystron at room temperature, unless otherwise

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[4] G. Binsch, E. Merz, and C. Rüchardt, *Chem. Ber.*, 1967, **100**, 247; J. I. G. Cadogan, R. M. Paton, and C. Thomson, *J. Chem. Soc.* (*B*), 1971, 583.

[5] J. I. G. Cadogan, *J. Chem. Soc.*, 1962, 4257.

[6] D. L. Brydon, J. I. G. Cadogan, J. Cook, M. J. Harger, and J. T. Sharp, *J. Chem. Soc.* (*B*), 1971, 1996.

[7] C. F. H. Allen, J. W. Gates, and J. A. Van Allan, *Org. Synth.*, 1947, **27**, 30.

stated, whereupon the temperature was controlled by means of a Decca variable-temperature cavity insert.

Simulations of e.s.r. spectra were carried out using an IBM 370/158 computer with a Calcomp 564 plotter. The programme was a modified version of Programme QCPE 83 obtained from Quantum Chemistry Program Exchange, Indiana University.

Determination of splitting constants, g *values and linewidths.* Measurements were made by comparison with a saturated sodium carbonate solution of Fremy's salt (potassium nitrosodisulphonate) for which $a_N = 1.3091 \pm 0.0004$ mT [8] and $g = 2.005\,50 \pm 0.000\,05$.[9]

Procedure. A measured volume (*ca.* 3 ml) of a solution of the dienone in benzene was added to a known weight of the aryl radical precursor. The mixture was transferred to a sample tube and degassed on a vacuum line by a process of repeated cycles of freezing, evacuation, and thawing. The time taken between the mixing of solids and solvent and the recording of the first spectrum was from 5 to 15 min, and the reaction was followed for up to 3 h. For signals generated above room temperature one atmosphere of nitrogen was admitted to the sample tube after degassing to minimise bubbling.

NNA Reactions were examined at room temperature using equimolar quantities of NNA and addendum at initial concentrations of *ca.* 0.1M.

For aniline–pentyl nitrite as the radical source, temperatures of 50—70° were used and concentrations of *ca.* 0.6M.

Reactions involving dibenzoyl peroxide were studied at 60° using equimolar concentrations of *ca.* 0.1M.

The e.s.r. results are summarised in Table 2.

[5/1463 *Received*, 24*th July*, 1975]

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[8] R. J. Faber and G. K. Fraenkel, *J. Chem. Phys.*, 1967, **47**, 2462.

[9] J. Q. Adams and J. R. Thomas, *J. Chem. Phys.*, 1964, **39**, 1904.