Spin Trapping by Tetraphenylcyclopentadienone and 2,3-Diarylindenones. New Long-lived Radicals and Their Relevance to Benzyne Promotion From Benzenediazonium Acetate

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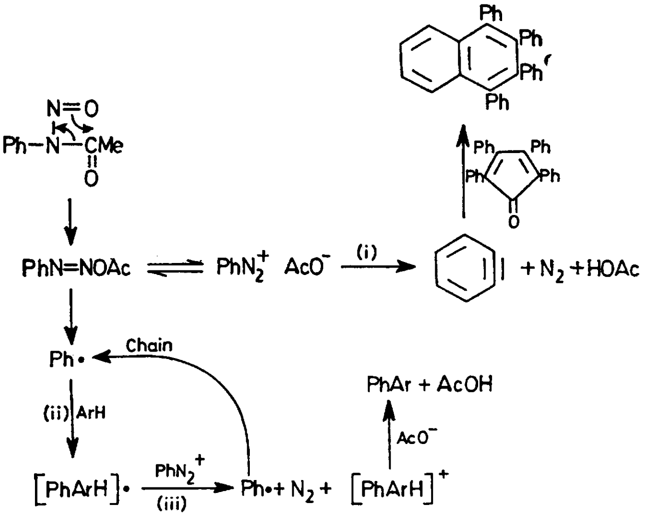
Summary Benzenediazonium acetate, formed from *N*-nitrosoacetanilide *in situ*, in benzene in the presence of tetraphenylcyclopentadienone or 2,3-diarylindenones give e.s.r. signals corresponding to new long-lived radicals (**2**) and (**3**) formed by trapping of phenyl radicals by the dienones, thus providing evidence relating to the mechanism of benzyne promotion in these reactions.

TETRAPHENYLCYCLOPENTADIENONE (tetracyclone) and 2,3-diphenylindenone (**1**; $Ar^1 = Ar^2 = Ph$) are effective promoters of the conversion of benzenediazonium acetate into benzyne.[1] It has been suggested that they act by trapping a phenyl radical vital in the competing radical chain phenylation (ii) and (iii) (Scheme), thereby promoting the benzyne-forming reaction (i).[1]

We now present evidence for such spin trapping based on e.s.r. spectroscopic detection of new long-lived radicals such as (**2**) and (**3**).

Thus benzenediazonium acetate, formed *in situ* from *N*-nitrosoacetanilide (NNA), in benzene in the presence of tetracyclone at room temperature gave an intense 17-line signal spread over 1·45 mT which persisted for several days and was markedly different from the known[2] 39-line signal spread over 0·5 mT of the tetracyclone radical anion (**4**), which in theory could have been formed by electron



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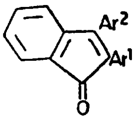
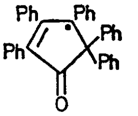
transfer and thus have been responsible for benzyne promotion. Lack of resolution precluded a precise assignment of structure, but superficially our signal was in accord with that expected from radical (**2**). Far better resolved, and therefore diagnostically more significant, signals were obtained from reaction of NNA with 2,3-diarylindenones (**1**). Thus the signal from 2,3-diphenylindenone (**1**; $Ar^1 = Ar^2 = Ph$) (Figure, a) corresponds to the radical (**3**; $Ar^1 = Ph$; $X = H$) in that it shows the expected coupling of the unpaired electron with 9 protons, 5 in the 3-phenyl ring, and 4 in the fused ring. Convincing support for this assignment is given by simulation (Figure, b).

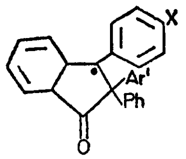
The following observations are also in accord with this interpretation and strengthen the suggestion that the observed long-lived radicals are formed by attack of aryl radicals at position 2 of 2,3-diarylindenones to give (**3**) rather than at other positions in (**1**).



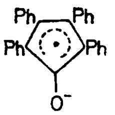
(1)



(2)



(3)



(4)

(*a*) The signal produced on decomposition of NNA in the presence of 3-*p*-t-butylphenyl-2-phenylindenone (**1**; $Ar^1 = Ph$; $Ar^2 = p\text{-}Bu^tC_6H_4$) corresponds to (**3**; $Ar^1 = Ph$; $X = Bu^t$) in that it shows coupling to 8 protons, *i.e.* the coupling involving the 4-proton in (**3**; $Ar^1 = Ph$; $X = H$) has been removed. Further, as expected, unresolved coupling involving the t-butyl protons is manifested in increased line width. Again, this analysis is supported by computer simulation. (*b*) Reaction of phenyl radicals produced from other sources, *via* pentyl nitrite and aniline or benzoyl peroxide, with 2,3-diphenylindenone gives the same radical (**3**; $Ar^1 = Ph$; $X = H$). (*c*) *p*-t-Butylphenyl radicals, from *p*-t-butyl-NNA, in the presence of 2,3-diphenylindenone gave a signal identical with those obtained in (*b*) above showing, as expected, that the signal corresponding to (**3**; $Ar^1 = p\text{-}Bu^tC_6H_4$; $X = H$) is independent of the nature of a *p*-substituent in an aryl group non-conjugated with the radical centre. (*d*) Similarly, NNA with 2-t-butylphenyl-3-phenylindenone gave the same signal as in (*c*) above and 3-*p*-t-butylphenyl-2-phenylindenone gave the same signal with NNA and *p*-t-butyl-NNA.

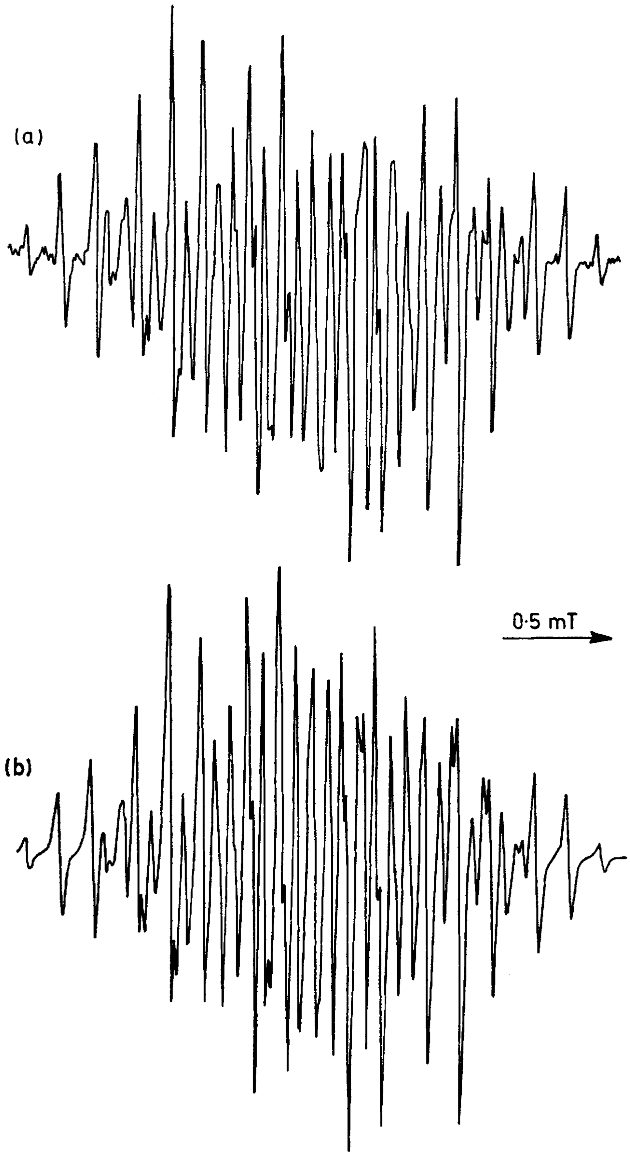


FIGURE. 2,3-Diphenylindenone and NNA. (a) Observed signal: g 2·0027, linewidth 0·019 mT; (b) simulated signal assuming a_H 0·428 (1H), 0·360 (1H), 0·322 (1H), 0·299 (2H), 0·125 mT (4H) and linewidth 0·019 mT.

Besides their mechanistic implications these results are of interest because they suggest that 2,3-diphenylindenone may have potential as a readily available radical inhibitor.

(*Received*, 12*th May* 1975; *Com.* 547.)

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[2] N. K. Ray, P. T. Narasimhan, and R. K. Gupta, *Indian J. Pure Appl. Phys.*, 1969, **7**, 175; W. Broser, H. Kurreck, P. Siegle, and J. Reusch, *Z. Naturforsch. B*, 1969, **24**, 685.