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REACTIVITY PATTERN OF ARYL RADICALS TOWARD BENZENE AND NITROSODURENE. TRAPPING OF CYCLOHEXADIENYL RADICALS BY NITROSODURENE

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Thermal decompositions of arylazotriphenylmethanes in benzene solution in the presence of nitrosodurene afforded either arylcyclohexadienyl duryl nitroxides or aryl duryl nitroxides depending upon whether the substituents on aryl radicals were electron withdrawing or electron donating. These results reflect the different reactivities of aryl radicals toward benzene nucleus.

Reactivities of aryl radicals toward aromatic molecules were studied for homolytic arylation reactions[1,2] and the results were summarized in terms of partial rate factors. These factors evaluate the relative rates for arylation reaction of a definite aryl radical toward various aromatic nuclei, but the relative reactivities of various aryl radicals toward a certain aromatic molecule have remained obscure. We have investigated reactions of aryl radicals by spin trapping technique and found outstanding capabilities of nitrosodurene* (ND) in trapping arylcyclohexadienyl radicals and thus in sorting aryl radicals in groups by their reactivities toward benzene nucleus.

Heating of trichlorophenylazotriphenylmethane (Cl_3-PAT) with ND in benzene solution under an argon atmosphere gave an esr spectrum composed of triplet of doublets (A, a_N13.4 G, $a_{\beta\text{-H}}$ 8.5 G). Prolonged heating, bubbling with oxygen and even standing at room temperatures caused the change of the shape of spectrum from triplet of doublets to triplet of multiplets (B, a_N 9.2 G, $a_{o\text{-H}}$ 2.6 G, $a_{m\text{-H}}$ 0.9 G). Irradiation of 2,4,6-trichloroiodobenzene in benzene solution containing ND yielded the same spectrum of the type B. Evidences for inclusion of a benzene molecule during the formation of the nitroxides A and B were brought about by the thermolysis of 2',4',6'-trichlorobiphenyl-4-yl-azotriphenylmethane in carbon tetrachloride - ND showing the same spectrum as B, and by thermal decomposition of Cl_3-PAT in benzene-d_6 - ND affording a spectrum of triplet of triplets (C, a_N 13.4 G, $a_{\beta\text{-D}}$ 1.6 G). The latter spectrum transformed slowly into a broad triplet of a_N 9.3 G (D). Duryl trichlorophenyl nitroxide (E) was formed by the reaction of Cl_3-PAT with ND in carbon tetrachloride solution and gave a spectrum of broad triplet (a_N 8.9 G). These results support the structure, arylcyclohexadienyl duryl nitroxide, for the nitroxides of the type A and C, and suggest that Cl_3-phenyl radicals add faster to benzene nucleus giving arylcyclohexadienyl radicals than to ND yielding Cl_3-phenyl duryl nitroxide. The nitroxides of the type A and C changed into substituted biphenylyl duryl nitroxides of the type B and D, and the finding that the conversion from C to D is slower than that from A to B indicates a presence of hydrogen kinetic isotope effect. (Scheme 1)

Substituted phenylazotriphenylmethanes such as 2,4,6-Br_3-PAT, F_5-PAT, 4-NO_2-PAT, 2-Cl-PAT, 4-Cl-PAT, 2-Br-PAT and 4-Br-PAT, all produced nitroxides of the type A, B, C, and D, and each nitroxide exhibited esr spectrum similar in shape to that found in the case of Cl_3-PAT.(Group I)

Heating of 4-CH_3-PAT in benzene and also in benzene-d_6 solution in the presence of ND afforded a nitroxide of the type E alone, and the esr spectrum was composed of triplet of multiplets (a_N 9.6 G, $a_{o\text{-}H}$ 2.8 G, $a_{m\text{-}H}$ 0.9 G, $a_{p\text{-}CH_3}$ 2.7 G). This result suggests that 4-CH_3-phenyl radicals add faster to ND to yield 4-CH_3-phenyl duryl nitroxide than to benzene nucleus to give 4-CH_3-phenyl-

Scheme I

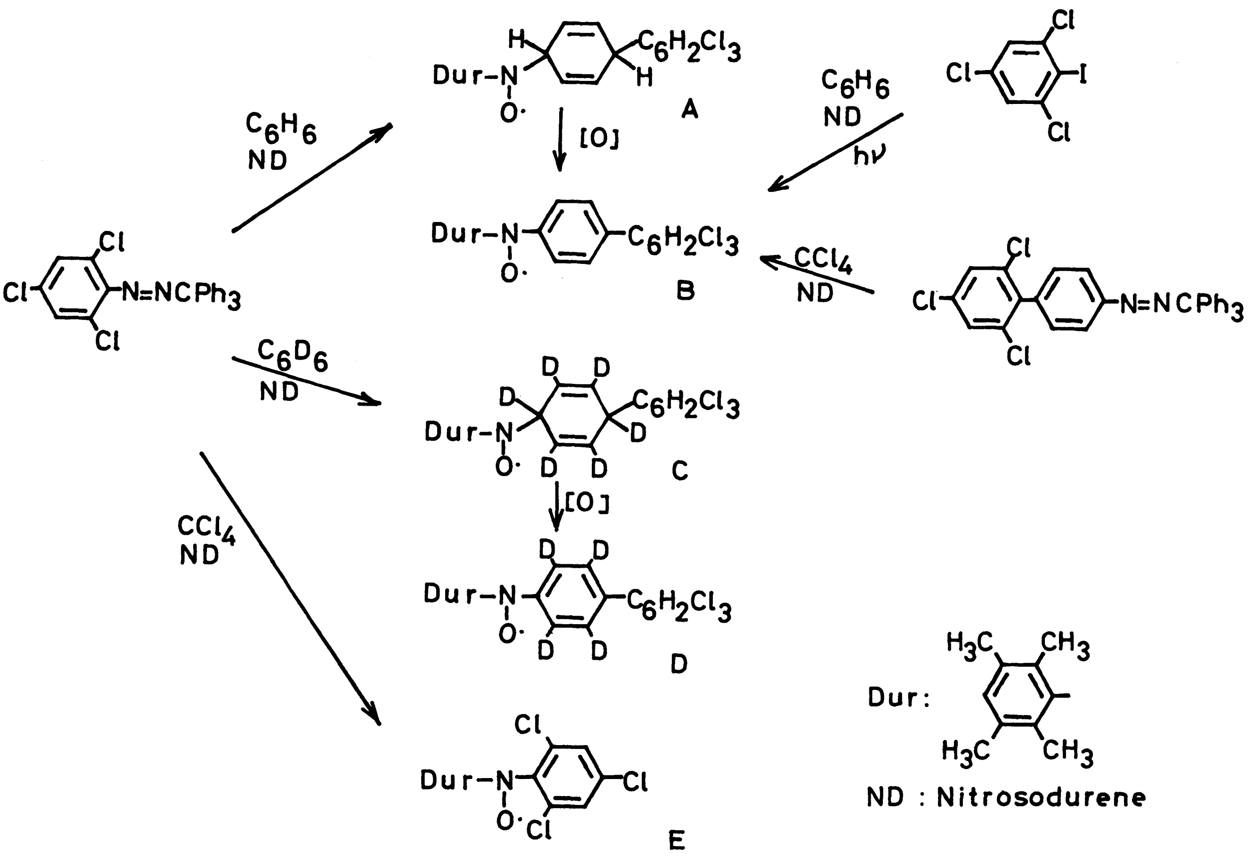

Fig. 1. ESR-Spectra of nitroxides formed by the reaction of Cl_3-PAT with ND

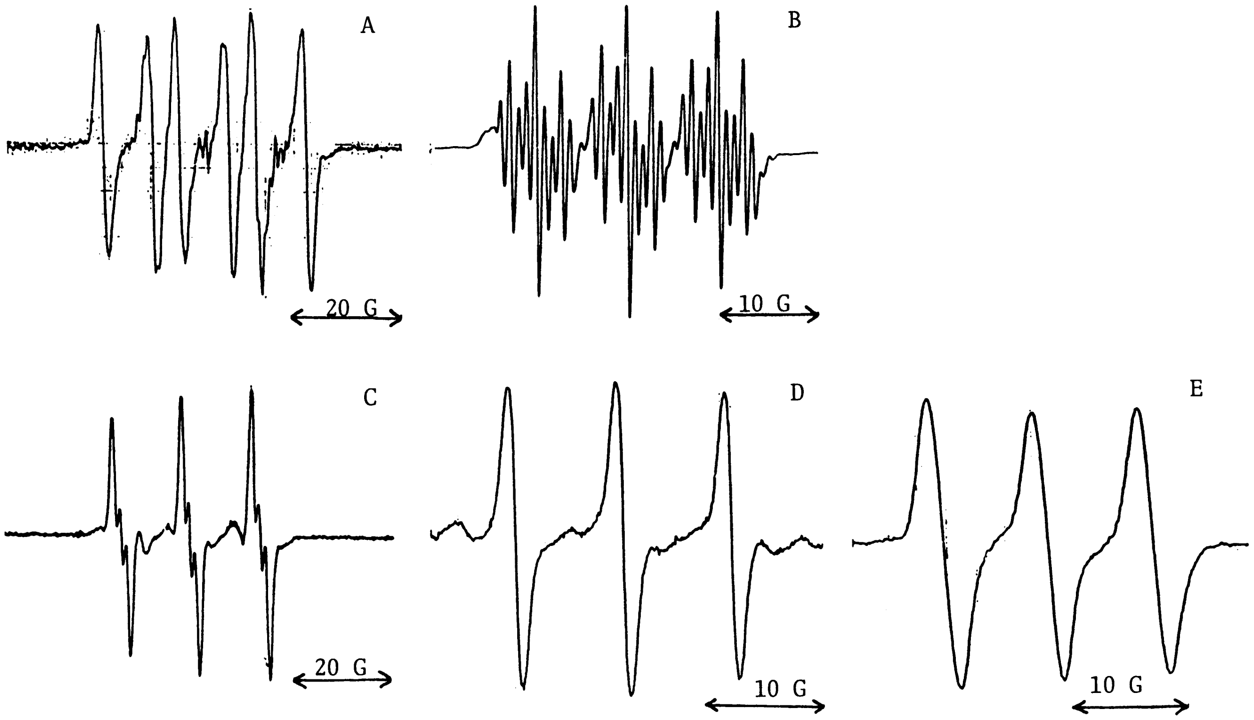

Table 1. Hyperfine-splitting constants of duryl nitroxides (G)

Substituents on phenyl radical						Nitroxide					
	Type A		Type B			Type C		Type D	Type E		
	a_N	$a_{\beta\text{-H}}$	a_N	$a_{o\text{-H}}$	$a_{m\text{-H}}$	a_N	$a_{\beta\text{-D}}$	a_N	a_N	$a_{o\text{-H}}$	$a_{m\text{-H}}$
2,4,6-Cl_3-	13.4	8.5	9.2	2.6	0.9	13.4	1.6	9.4$^{a)}$	8.9$^{a)}$		
2,4,6-Br_3-	13.4	8.7	9.2	2.6	0.9	13.1	1.6	9.3$^{a)}$	8.9$^{a)}$		
2,3,4,5,6-F_5-	13.2	9.3	9.1	2.6	0.9	13.4	1.7	9.1$^{a)}$	9.2$^{b)}$		
4-NO_2-	c)		9.3	2.7	0.7	13.6	2.0	9.2$^{a)}$	8.4$^{b)}$		
4-Cl-	c)		9.3	2.6	0.9	13.5	2.1	9.5$^{a)}$	9.3	2.7$^{b)}$	
4-Br-	c)		9.4	2.6	0.9	13.7	1.9	9.4$^{a)}$	9.3	2.7	1.0
4-CH_3S-	c)		9.4	2.4	0.9			9.4$^{a)}$	9.1	2.6	0.9
H	c')		d)			d)		d)	9.5	2.7	0.9
4-CH_3-	d)		d)			d)		d)	9.6	2.8	0.9 (CH_3 2.7)
2,4,6-$(CH_3)_3$-	d)		d)			d)		d)	9.6$^{b)}$		
4-CH_3O-	d)		d)			d)		d)	9.9	2.7	0.4 (CH_3 0.4)

a) Broad spectrum

b) With fine structures.

c) The spectra are made up by the superposition of signals arising from nitroxides of the type A and B; c') Superposition of A and E.

d) Nitroxides are not formed.

cyclohexadienyl radicals. Arylazotriphenylmethanes such as 2-CH_3-PAT, 2,4,6-$(CH_3)_3$-PAT, 2-CH_3O-PAT and 4-CH_3O-PAT produced nitroxides of the type E alone (Group II).

Unsubstituted PAT gave a mixture of phenyl duryl nitroxide and phenylcyclohexadienyl duryl nitroxide. Thus phenyl radical is intermediate in reactivity between two groups of aryl radicals derived from PATs mentioned above.

These observations indicate the trend that aryl radicals carrying electron withdrawing substituents add faster to benzene than to ND. In contrast with this aryl radicals with electron donating substituents behave in a reverse manner. This means that ND acts as electron acceptor and catches alkyl radicals efficiently, which are inherently electron donating, and ND becomes selective in reaction toward radicals, which are not electron donating. The reaction of 4-CH_3S-phenyl radicals is worthy of note: they yield 4-CH_3S-phenylcyclohexadienyl duryl nitroxides. In view of our assumption that aryl radicals carrying electron withdrawing substituents add faster to benzene than to ND, the 4-CH_3S-substituent seems likely to be more or less electron withdrawing.**
Highly remarkable is that cyclohexadienyl radicals are trapped by ND, although this is not the case for α-phenyl-N-t-butylnitrone.[3)]

References

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* Nitrosodurene was introduced as spin trapping agent by R. Konaka and his colaborators, J. C. S. Perkin II, (1973) 1252.

** As the substituent constants for 4-CH_3S group, σ-value of 0.00, and σ^+-value of -0.16 are inferred by S. L. Murov in " Handbook of Photochem. " M. Dekker Inc., N.Y. (1973), p. 205.

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