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Spin Trapping of Benzoyloxycyclohexadienyl Radicals by 2,3,5,6-Tetramethylnitrosobenzene (Nitrosodurene) in the Decomposition of Dibenzoyl Peroxide in Benzene

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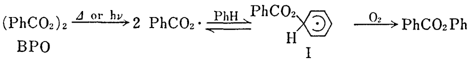
The aroyloxycyclohexadienyl radicals (VIII), the key intermediates in the homolytic aromatic aroyloxylation, were detected and identified in the decomposition of dibenzoyl peroxide, bis(4-methylbenzoyl) peroxide, and bis(4-methoxybenzoyl) peroxide in benzene-d_6 as spin adducts of nitrosodurene.

Irradiation of dibenzoyl peroxide (BPO) in benzene causes a benzoyloxylation of the solvent benzene to give substantial yields of phenyl benzoate at room temperature, if molecular oxygen is present. Such a benzoyloxylation takes place also in the thermal decomposition of BPO in benzene, where the yield of phenyl benzoate increases with lowering of the reaction temperature.[1] The genesis of phenyl benzoate has been accounted for in terms of the reversible addition of benzoxyl radicals to benzene followed by the oxidation of the resulting benzoyloxycyclohexadienyl radicals (I) by molecular oxygen (Scheme 1).[1]

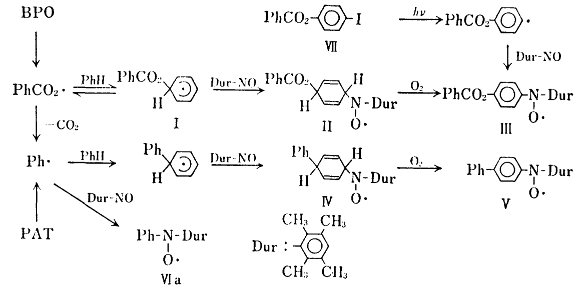


Scheme 1.

In the decomposition of bis(pentafluorobenzoyl) peroxide in the presence of benzene in hexachloro-1,3-butadiene CIDNP effects are detected in the proton NMR spectra of benzene and other products. The observed polarizations have been explained by assuming a singlet radical pair of a pentafluorobenzoyloxycyclohexadienyl radical and a pentafluorobenzoxyl radical.[2] Recently, the direct observation of the radical adduct of benzoxyl radicals to 1,3,5-tris(trimethylsiloxy)benzene was attained by ESR spectroscopy.[3] However, no definitive spectroscopic evidence indicating the formation of I has hitherto been reported in the decomposition of BPO in benzene. We showed previously that the decomposition of arylazotriphenylmethanes in the presence of 2,3,5,6-tetramethylnitrosobenzene (nitrosodurene) in benzene affords arylcyclohexadienyl 2,3,5,6-tetramethylphenyl nitroxides (arylcyclohexadienyl duryl nitroxides). Thus, success has been achieved in trapping arylcyclohexadienyl radicals, produced by the addition of aryl radicals to benzene, by nitrosodurene.[4] We therefore decided to employ this spin trapping technique for the detection of I.

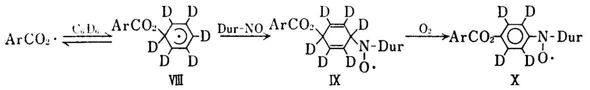
Results and Discussion

Heating dibenzoyl peroxide (BPO) at 80 °C in benzene containing nitrosodurene under an atmosphere of argon gave an ESR spectrum consisting of three complex sets (a_N=9.5 gauss) ascribable to duryl phenyl nitroxides (VIa).[4,5] Apparently these radicals (VIa) are produced by the fast decarboxylation of benzoxyl radicals followed by trapping of the resulting phenyl radicals by nitrosodurene. When the decomposition was carried out at 40 °C in benzene, VIa could not be detected at all; instead an ESR signal (three triplets, a_N=9.7 and $a_{ortho\text{-}H}$=2.7 gauss) consistent with 4-benzoyloxyphenyl duryl nitroxide (III)[6] was observed. The structural assignment is mainly based on the value of the nitrogen hyperfine splitting constant (a_N) and the partially resolved splitting due to the two *ortho*-hydrogens. The possible assignment to 4-biphenylyl duryl nitroxide (V), which might be formed by the oxidation of a spin adduct of phenylcyclohexadienyl radicals (IV), can be eliminated, since no signals due to 4-biphenylyl duryl nitroxide (V) were detected in the decomposition of phenylazotriphenylmethane (PAT) in the presence of nitrosodurene at 40 °C in benzene; the phenyl radicals arising from PAT are trapped by nitrosodurene to yield VIa before they add to benzene. Further verification for the structural assignment of III was obtained in the trapping experiment by the photolysis of 4-iodophenyl benzoate (VII) in carbon tetrachloride (Scheme 2). The ESR spectrum obtained agrees well with that observed above.



Scheme 2.

To gain more insight into the formation of III, BPO was decomposed in benzene-d_6 at 40 °C in the presence of nitrosodurene. The ESR spectrum showed three triplets (a_N=13.4 and $a_{\beta\text{-}D}$=1.5 gauss), which diminished in intensity on exposure to oxygen, while a new signal composed of a broad triplet (a_N=9.6 gauss) increased. The latter signal is attributed to the deuterated 4-benzoyloxyphenyl duryl nitroxide (Xa) by comparison of the a_N value with that of III. The magnitude of the nitrogen and β-hydrogen (deuterium) hyperfine splitting constants (hfsc) in the former signal is close to that of hfsc's of arylcyclohexadienyl duryl nitroxides among the newly prepared nitroxides.[4] These findings as well as the observations that the former signal was replaced by that of Xa lead us to assign the former signal to the deuterated benzoyloxycyclohexadienyl duryl nitroxide (IXa) (Scheme 3).



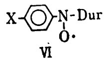
a : Ar$=C_6H_5$　　b : Ar$=$4-$CH_3C_6H_4$
c : Ar$=$4-$CH_3OC_6H_4$　　d : Ar$=$4-ClC_6H_4
e : Ar$=$4-$NO_2C_6H_4$

Scheme 3.

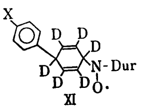
Contrary to the case in benzene-d_6, benzoyloxycyclohexadienyl duryl nitroxide (II) was not detected at all in the decomposition of BPO in benzene. Undoubtedly II is oxidized easily by traces of oxygen, while the oxidation of IXa proceeds slowly on account of the deuterium isotope effects.

The decomposition of bis(4-methylbenzoyl) peroxide (Me–BPO) in benzene-d_6 at 45 °C in the presence of nitrosodurene resulted in the formation of one stable paramagnetic species, the deuterated duryl 4-methylbenzoyloxycyclohexadienyl nitroxide (IXb, $a_N=13.3$ and $a_{\beta-D}=1.4$ gauss), which was then oxidized to a dehydrogenated nitroxide (Xb, $a_N=9.8$ gauss) on exposure to air. In the decomposition of Me–BPO at 50 °C, however, duryl 4-methylphenyl nitroxide (VIb)[4] was detected in addition to IXb. Bis(4-methoxybenzoyl) peroxide (MeO–BPO) gave a similar nitroxide (IXc, $a_N=13.1$ and $a_{\beta-D}=1.5$ gauss) at 45 °C and a mixture of IXc and its dehydrogenated nitroxide (Xc, $a_N=9.7$ gauss) at 50 °C, but none of a spin adduct of 4-methoxyphenyl radicals (VIc) was obtained. The air oxidation of IXc led to the formation of Xc. The alternative assignment of IXb and IXc to arylcyclohexadienyl duryl nitroxides (XIb and XIc, respectively) can be ruled out on the basis of the facts[4] that 4-methyl- and 4-methoxyphenylazotriphenylmethane (Me–PAT and MeO–PAT, respectively) do not yield any amounts of XIb and XIc, but afford the aryl duryl nitroxides, VIb and VIc, respectively. Thus, even if 4-methyl- and 4-methoxyphenyl radicals were generated in the decomposition of Me–BPO and MeO–BPO, respectively, the nitroxides, XIb and XIc, would not be formed at all.

When bis(4-chlorobenzoyl) and bis(4-nitrobenzoyl) peroxide (Cl–BPO and NO_2–BPO, respectively) were decomposed in the presence of nitrosodurene at 45 °C in benzene-d_6, the ESR signals ($a_N=13.3$ and $a_{\beta-D}=1.5$ gauss from Cl–BPO, and $a_N=13.4$ and $a_{\beta-D}=1.6$ gauss from NO_2–BPO) similar to those of IXb and IXc were observed and then replaced by other signals ($a_N=9.6$ gauss from both Cl–BPO and NO_2–BPO) by the air oxidation. The initially observed signals are similar in the shape and the magnitude of a_N to, but different in the magnitude of $a_{\beta-D}$ from, those of the spin adducts, XId ($a_N=13.5$ and $a_{\beta-D}=2.1$ gauss) and XIe ($a_N=13.6$ and $a_{\beta-D}=2.0$ gauss), formed from 4-chloro- and 4-nitrophenylazotriphenylmethane in benzene-d_6, respectively.[4] Although Cl–BPO and NO_2–BPO might produce XId and XIe through 4-chloro- and 4-nitrophenyl radicals, respectively, it can be assumed that the nitroxide radicals, IXd, Xd, IXe, and Xe, are also formed in the present cases by analogy with the behavior of the other peroxides.



VI



XI

a : X$=$H　　b : X$=CH_3$
c : X$=CH_3O$　　d : X$=$Cl
e : X$=NO_2$

Finally, it is interesting to note that the spin adduct of 4-methylphenyl radicals (VIb) was detected in the decomposition of Me–BPO at 50 °C, whereas none such was observed in the decomposition of MeO–BPO at the same temperature. This finding might reflect the higher activation energy required for the decarboxylation of 4-methoxybenzoxyl radicals than for that of 4-methylbenzoxyl radicals.[7]

Experimental

Nitrosodurene,[5] substituted dibenzoyl peroxides,[8] and 4-iodophenyl benzoate[9] were prepared according to the methods described in the literatures.

Decomposition of the peroxides was carried out as follows: a solution of nitrosodurene (5 mM) and a peroxide (10 mM) in benzene or benzene-d_6 was purged with argon for 2 min in an ESR tube prior to decomposition in order to remove dissolved oxygen and was heated at the specified temperature for 5 min. The ESR spectra were recorded on a JEOL JES-ME-1X spectrometer. Photolysis of 4-iodophenyl benzoate (VII) was carried out by irradiation of the solution (nitrosodurene, 5 mM and VII, 10 mM in carbon tetrachloride) in a Pyrex tube directly in the cavity by means of a 400 W high pressure mercury arc lamp.

References

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6) A 1,4-disubstituted structure was tentatively assigned to the spin adducts although 1,2- and/or 1,4-disubstituted isomers might be formed, which are undistinguishable by ESR spectrum.

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