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The Thermal Decomposition of Cyanodiphenylmethyl *t*-Butyl Peroxide: An Example of C–O Bond Scission

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Synopsis. The thermal decomposition of cyanodiphenylmethyl *t*-butyl peroxide was investigated. The peroxide is abnormally stable and decomposes slowly at 130—135 °C, and the main reaction product is tetraphenylsuccinonitrile. A main reaction path including the C–O bond scission, in contrast to the case of triphenylmethyl *t*-butyl peroxide, is proposed.

It has been reported that cyanodiphenylmethyl *t*-butyl peroxide(I)1) is unaffected by treatment with two molar equivalents of phenylmagnesium bromide.2) The stability of the α-cyano group and that of the O–O bond of I attracted our attention. This peroxide resembles triphenylmethyl *t*-butyl preoxide(II) in its molecular structure as well as its stability towards the Grignard reagent. Upon thermal decomposition in cumene, II yields 1-phenoxy-1,1,2-triphenyl-2-methylpropane (60%) as a result of the rearrangement of the triphenylmethoxyl radical, followed by recombination with the cumyl radical.3) The preferential migration of the *p*-nitrophenyl group in *p*-nitrophenyldiphenylmethoxyl radical has also been reported.3,4) These facts led the present authors to study the thermal decomposition of I.

Peroxide I was also unaffected by treatment with iodide ions in both the absence5) and presence6) of ferric ions at room temperature.2) Treatment in boiling acetic acid7) liberated iodine, but the thiosulfate-titer went up to extraordinarily high values (250—500 mol%) and fluctuated seriously. Thus, no iodometric search for the decomposition course of I was not made in this work.

When peroxide I was decomposed in some alkylbenzenes (toluene, ethylbenzene, *p*-xylene, mesitylene, and cumene) at their boiling temperatures, acetone and *t*-butyl alcohol were produced. The manner of the variation in the molar ratio of the two products (Table 1) is consistent with the reactivities of these aromatics towards the hydrogen abstraction by the *t*-butoxyl radical.8)

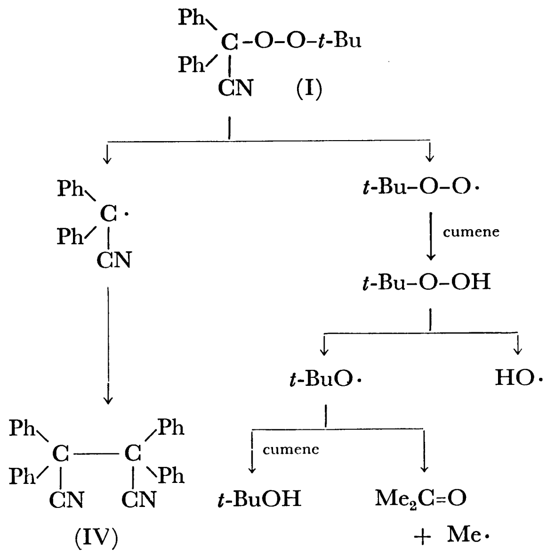
After a solution of I(1.0 M) in cumene had been heated at 130—135 °C for 5 h, the yields of acetone and *t*-butyl alcohol were 5 and 16% respectively. From the viscous oily mixture obtained after the complete evaporation of cumene under reduced pressure, a large amount of unreacted I (53%) and a small amount of dicumyl(III) were detected by NMR spectroscopy on the basis of the *t*-butyl- and methyl-proton signals. Tetraphenylsuccinonitrile(IV), the main reaction product, was separated from the unreacted I by the elution of the mixture with petroleum ether–benzene through a silica-gel column. A small amount of benzophenone (V, 7%), accompanied by a trace of benzhydrol (VI), was detected by GLC. The yields of III and IV were estimated to be 9 and 31% respectively from the integrated NMR spectrum of the mixture (See Experimental Section).

Table 1. Variation of the molar ratio of *t*-butyl alcohol and acetone with aromatics

Aromatics	[*t*-BuOH]/[Acetone]
Mesitylene	0.1
Cumene	3.1
Fluorene (ArH/I=1.0)a)	1.1
(ArH/I=2.0)	1.6

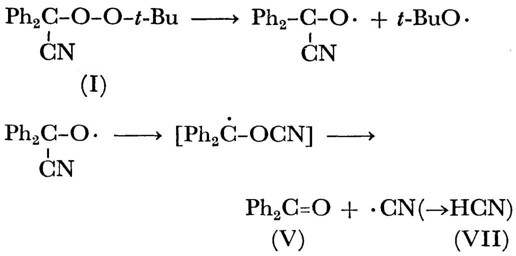
a) Peroxide I and fluorene (0.004 mol), dissolved in chlorobenzene (50 ml), were heated in an oil bath maintained at 180—185 °C.

The results of the product analysis imply that I is remarkably stable and that it decomposes in a novel manner. The stability of I is evident in comparison with II; it was reconfirmed that the latter decomposed completely after 5 h under the same reaction conditions.3) The substantially high yield of IV (67%) suggests that the main reaction path begins with the cleavage of the C–O bond (Scheme 1).



Scheme 1.

The yield of V did not exceed 7 mol% in any of the aromatics used. Hydrogen cyanide (VII) was detected by the use of a piece of test paper impregnated with an aqueous solution of cupric acetate–benzidine acetate.9) The formation of V, VI, and VII suggests a concurrent minor reaction path beginning with the ordinary O–O bond scission, as is shown in the following:



$$\mathrm{Ph_2\underset{\displaystyle CN}{\underset{|}{C}}\text{-}O\text{-}O\text{-}}t\text{-Bu} \longrightarrow \mathrm{Ph_2\text{-}\underset{\displaystyle CN}{\underset{|}{C}}\text{-}O\cdot} + t\text{-BuO}\cdot$$

(I)

$$\mathrm{Ph_2\underset{\displaystyle CN}{\underset{|}{C}}\text{-}O\cdot} \longrightarrow [\mathrm{Ph_2\dot{C}\text{-}OCN}] \longrightarrow$$

$$\underset{\text{(V)}}{\mathrm{Ph_2C{=}O}} + \underset{\text{(VII)}}{\cdot\mathrm{CN}(\rightarrow \mathrm{HCN})}$$

Though no direct evidence was obtained, the migration of the cyano group in the cyanodiphenylmethoxyl radical should be taken into account.[3,4]

Another example of the C–O bond scission of organic peroxide has been found in the thermal decomposition of *N*-cyclohexyl-1-*t*-butylperoxycyclohexylamine, which afforded the corresponding imine by the loss of *t*-butyl hydroperoxide,[10] but this manner of decomposition is probably due to the existence of the neighboring NH group. Though the reason for the unexpected stability of peroxide I remains obscure, its C–O bond scission can be ascribed to the stabilization of the cyanodiphenylmethyl radical by the spin-delocalization[11]; this is consistent with the absence of diphenylacetonitrile, which shows the low hydrogen-abstracting ability of the radical.

Experimental

Materials. The peroxide I was prepared by the treatment of diphenylacetonitrile with *t*-butyl hydroperoxide; mp 52 °C.[1] The peroxide II was prepared by the reported method.[3] Dicumyl(III) was prepared by the thermal decomposition of di-*t*-butyl peroxide in cumene.[12] Tetraphenylsuccinonitrile(IV) was prepared from diphenylacetonitrile.[1]

Procedures. Thermal decomposition was carried out using 1.0 M solution of I under a N_2 atmosphere. After the oil bath had been removed, a few mililiters of the aromatic solvent of the reaction mixture were distilled into an ice-cooled receiver and the ratio of the contents of acetone and *t*-butyl alcohol in the distillate was then determined by means of GLC.

In order to obtain a mixture of high-boiling products for the NMR measurement, the cumene was completely removed by the repeated dissolution of the oily mixture into CCl_4 and by evaporation under reduced pressure; the resulting pale yellow viscous oil was free from cumene (checked by GLC) and could be analyzed by the integration of the NMR spectrum. The contents of I and III were estimated on the basis of the intensities of the *t*-butyl- and methyl-proton signals; the intensities corresponding to the phenyl-protons of I and III were substracted from the overall intensity in the same region. The result gave the sum of the contents of IV and V, the latter of which had been determined by the use of GLC.

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