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INTERMEDIACY OF CYCLOHEXADIENYL RADICALS WITH AN AROYLOXY GROUP ON THE METHYL-SUBSTITUTED IPSO CARBON ATOM IN PHOTOLYSES OF BIS(2-THIOPHENECARBONYL) AND DIBENZOYL PEROXIDES IN 1,3,5-TRIMETHYLBENZENE

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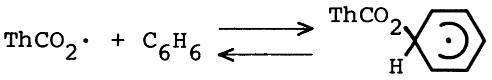
Investigation of the products arising from photolyses of bis(2-thiophenecarbonyl) and dibenzoyl peroxides in 1,3,5-trimethylbenzene provided clear evidence for participation of cyclohexadienyl radicals with the aroyloxy group on the methyl-substituted ipso carbon atom in formation of 2,3',4,5',6-pentamethyldiphenylmethane through recombination with 3,5-dimethylphenylmethyl radicals.

Although much attention has been focused on free-radical ipso substitution, the reactions are limited to aromatic compounds bearing substituents possessing a good leaving nature as a free radical.1) In photolysis of bis(2-thiophenecarbonyl) peroxide (TPO) in benzene, we recently reported a noticeable formation of biphenyl through dimerization of 2-thiophenecarbonyloxycyclohexadienyl radicals followed by elimination of 2-thiophenecarboxylic acid ($ThCO_2H$) (Eqs. 1 and 2); stability of 2-thiophenecarbonyloxyl radicals ($ThCO_2\cdot$) and thus a high concentration of 2-thiophenecarbonyloxycyclohexadienyl radicals play important roles in the formation of biphenyl.2) In the course of investigation on the nature of aroyloxyl radicals, we have found formation of a quite unusual product in the conventional mechanisms for free-radical reactions. As described below, its formation provides evidence for involvement of ipso intermediates formed by addition of aroyloxyl radicals on the methyl-substituted ipso positions and assisting formation of solvent-derived products without elimination of methyl substituents.



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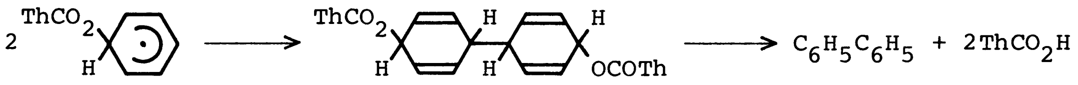

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Irradiation of TPO (0.03 mol/dm^3) in 1,3,5-trimethylbenzene at 20°C afforded thiophenecarboxylate esters, 2,4,6-trimethylphenyl 2-thiophenecarboxylate (**1**, 0.20 mol/mol peroxide) and 3,5-dimethylphenylmethyl 2-thiophenecarboxylate (**2**, 0.07 mol), dimers from the solvent, 1,2-bis(3,5-dimethylphenyl)ethane (**3**, 0.17 mol) and

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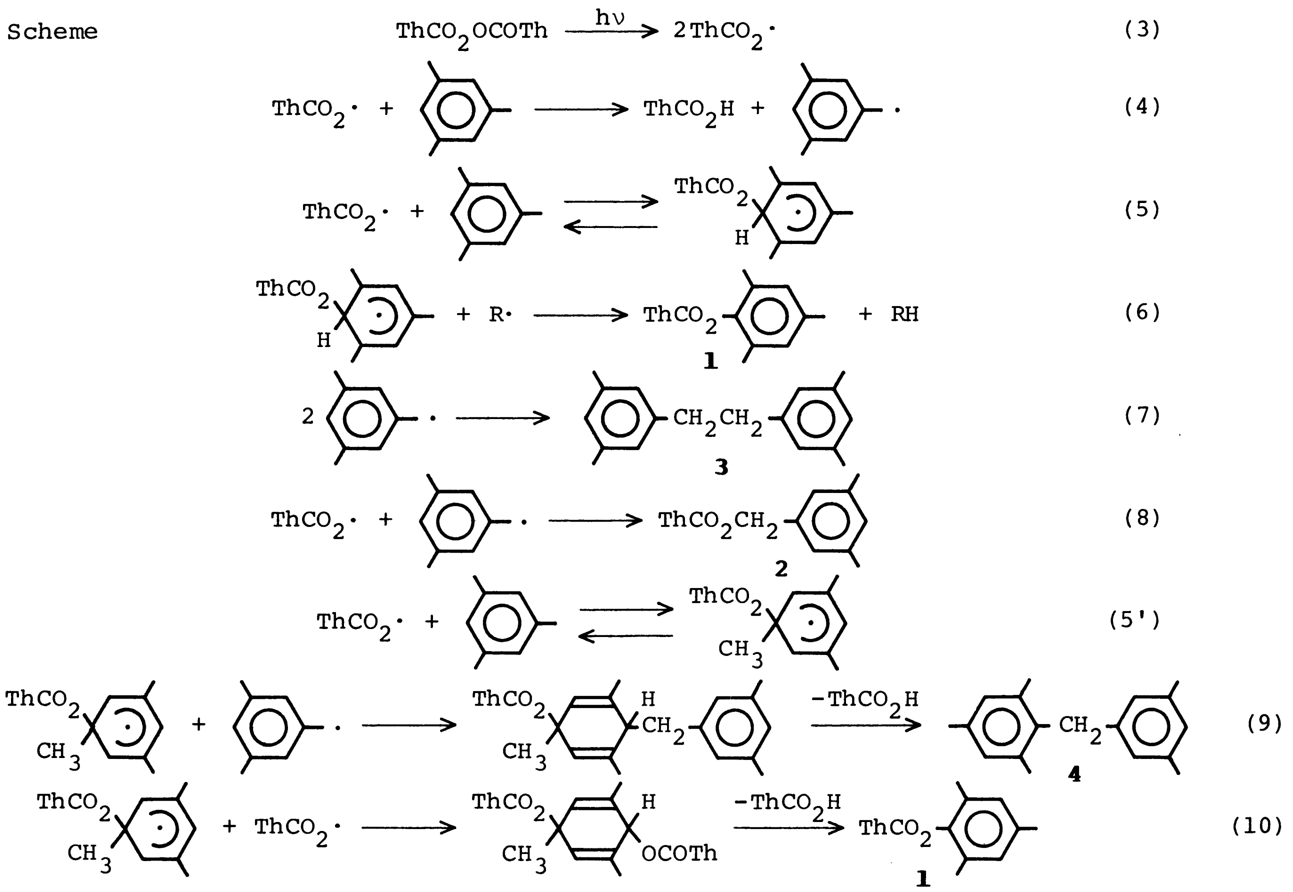
Scheme



2,3',4,5',6-pentamethyldiphenylmethane (**4**, 0.12 mol), and 2-thiophenecarboxylic acid (1.48 mol).[3] The formation of **1** and **3** can be understood by the usual radical processes (Eqs. 3-7).[2,4] The yield of **2** is rather high compared with the cases of other diaroyl peroxides like dibenzoyl peroxide (BPO). Taking account of the stability of 2-thiophenecarbonyloxyl radicals as characterized by their slow decarboxylation,[2,5] **2** is reasonably assumed to be formed through recombination of 2-thiophenecarbonyloxyl radicals with 3,5-dimethylphenylmethyl radicals (Eq. 8).

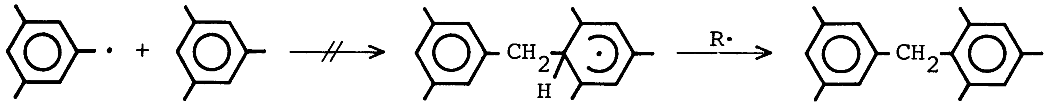
The formation of **4** is quite unusual since, as the following control experiments show, benzyl radicals in general do not facilely add to aromatic rings. Therefore, it is reasonably proposed that **4** is formed through recombination of 3,5-dimethylphenylmethyl radicals with cyclohexadienyl radicals generated by attack of 2-thiophenecarbonyloxyl radicals on the ipso positions of 1,3,5-trimethylbenzene, followed by elimination of 2-thiophenecarboxylic acid (Eqs. 5' and 9).

Attempts were made to eliminate the possibility of addition of benzyl-type radicals to 1,3,5-trimethylbenzene and to confirm contribution of aroyloxyl radicals to **4** formation. Thus, 3,5-dimethylphenylmethyl radicals were generated in 1,3,5-trimethylbenzene in the absence of any aroyloxyl radicals by the following photochemical and thermal procedures; first, 1,3-bis(3,5-dimethylphenyl)-2-propanone (0.01 mol/dm^3) was photolyzed[3] at 10-50 °C to generate 3,5-dimethylphenylmethyl radicals through Norrish I cleavage.[6] 1,2-Bis(3,5-dimethylphenyl)ethane **3** was produced almost quantitatively and only a slight amount of **4** was detected on GLPC at all temperatures employed. Second, hydrogen atom abstraction by triplet benzo-

Table 1. Product Yields in Photolysis of TPO in 1,3,5-Trimethylbenzene at Various Temperatures (mol/mol peroxide)

Temperature /°C	Product				
	Ester **1**	Ester **2**	Ethane **3**	Methane **4**	$ThCO_2H$
70	0.06	0.07	0.42	trace	1.66
60	0.07	0.07	0.34	0.05	1.56
50	0.10	0.07	0.32	0.06	1.62
40	0.12	0.07	0.21	0.10	1.59
20	0.20	0.07	0.17	0.12	1.48

phenone was used to generate the benzyl-type radicals.[7] Thus, benzophenone (0.03 mol/dm^3) was irradiated in 1,3,5-trimethylbenzene at 25-55°C to give **3** (0.30 mol/mol benzophenone used) and 3,5-$C_6H_3Me_2CH_2CPh_2OH$ (0.35 mol) but almost none of **4**.[3] Finally, di-t-butyl peroxyoxalate (0.03 mol/dm^3) was heated at 35-55°C in 1,3,5-trimethylbenzene to result in formation of **3** (0.75 mol/mol peroxide) but almost none of **4**. In this case t-butoxyl radicals abstract hydrogen atoms from methyl groups of the solvent to generate 3,5-dimethylphenylmethyl radicals.[8] These results show that 3,5-dimethylphenylmethyl radicals can neither add to 1,3,5-trimethylbenzene by themselves (Eq. 11) nor recombine at the ring carbons, the potential radical centers of their resonance forms (Eq. 12), but undergo exclusively recombination (dimerization) at their benzyl carbons (Eq. 7).



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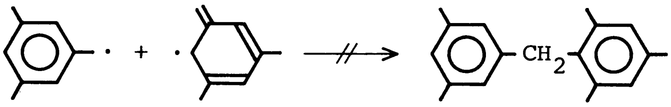

(12)

In order to confirm involvement of the aroyloxyl radicals in the formation of **4**, temperature dependence of product yields in the photolysis of TPO was examined, since, as previously explored, aroyloxyl radicals reversibly add to aromatic solvents.[2,9] The results are summarized in Table 1 and depicted in Fig. 1, which show that the yield of **3** increases but those of **1** and **4** decrease with increasing temperature. These results are consistent with the above mechanism; at higher temperatures the addition equilibria (Eqs. 5 and 5') tend to be shifted to the side of 2-thiophenecarbonyloxyl radicals and 1,3,5-trimethylbenzene,[2] and thus the former tend to abstract hydrogen atoms from methyl groups of the latter.[10]

Formation of pentamethyldiphenylmethane **4** and similar temperature effects on the product yields were observed in the photolysis of BPO (0.03 mol/dm^3) in 1,3,5-trimethylbenzene (Fig. 1).[3] The mechanism for product formation can be accounted for by the same processes as mentioned above. When the yields of products are compared between the two peroxides at the same temperatures, the yields of **3** are almost of the same magnitude; however, the yields of 2,4,6-trimethylphenyl esters, **1** or $PhCO_2C_6H_2Me_3$, and **4** are higher from TPO than from BPO. The difference in yield is much remarkable in the esters, and this can be understood by the difference in stability between 2-thiophenecarbonyloxyl and benzoyloxyl radicals, the

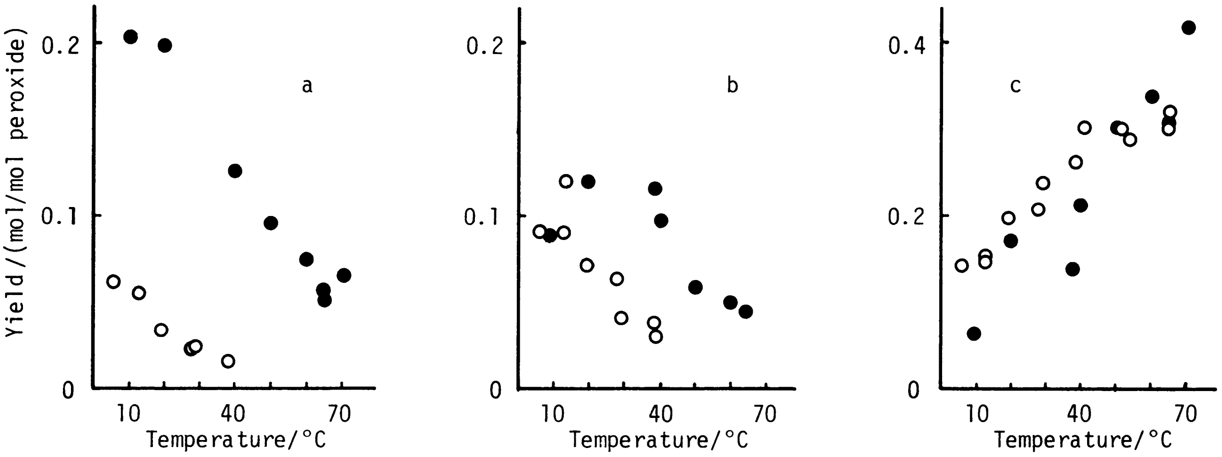

Fig. 1. Temperature Dependence of Product Yields in Photolysis of TPO (●) and BPO (o) in 1,3,5-Trimethylbenzene; a) ester **1** (●) and $PhCO_2C_6H_2Me_3$ (o), b) methane **4**, c) ethane **3**.

latter decarboxylating faster.$^{5)}$ That **1** is much higher in yield and suffers more remarkable temperature effects than $PhCO_2C_6H_2Me_3$ (Fig. 1a) indicates that **1** is formed not only through addition of 2-thiophenecarbonyloxyl radicals to 1,3,5-trimethylbenzene followed by disproportionation (Eqs. 5 and 6) but also through recombination of 2-thiophenecarbonyloxyl radicals with the ipso intermediate followed by acid elimination (Eq. 10).

Therefore, it is quite reasonable to conclude that the formation of **4** in photolyses of TPO and BPO provides clear evidence for intermediacy of the ipso intermediates formed in attack of aroyloxyl radicals to 1,3,5-trimethylbenzene.

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3) Irradiation was carried out with 1 kW high pressure mercury lamp through a Pyrex wall. The yields of products were determined by GLPC except the acid which was determined by HPLC.

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10) In the control experiments mentioned above, no temperature effects were observed on the product yields.

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