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The Role of Aroyloxyl Radicals in the Formation of Solvent-derived Products in Photodecomposition of Diaroyl Peroxides. The Reactivity of Substituted Cyclohexadienyl Radicals and Intermediacy of ipso Intermediates

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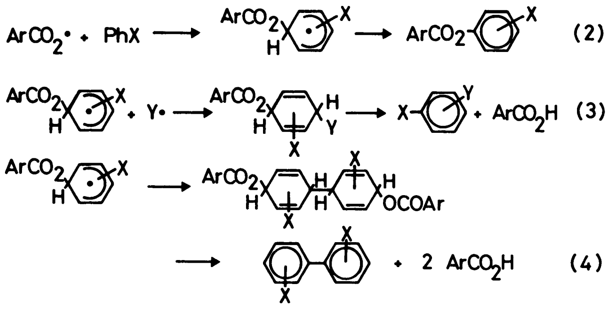
Photolyses of bis(2-thiophenecarbonyl) peroxide (TPO) in benzene and toluene afforded, among free-radical products, biphenyl and dimethylbiphenyls, respectively, which were solely derived from the aromatic solvents. The yields of biphenyls depended upon the rate with which the radical intermediates were generated from the peroxides in sufficiently high concentrations for their dimerization. Photolyses of TPO and dibenzoyl peroxide in 1,3,5-trimethylbenzene afforded also a solvent-derived product, 2,3′,4,5′,6-pentamethyldiphenylmethane. Its formation provides clear evidence for participation of cyclohexadienyl radicals bearing the aroyloxyl group on the methyl-substituted ipso carbon atom.

Aroyloxyl radicals, when generated in aromatic solvents, reversibly add to the solvents to produce aroylcyclohexadienyl radicals,[1,2] which are intercepted by a suitable oxidant to give aryl esters,[3,4] and also undergo recombination with other radicals followed by elimination of arenecarboxylic acid to give arylation products.[5,6] Dimerization of the cyclohexadienyl radicals[7] and subsequent elimination of two moles of the arenecarboxylic acid could be the course leading to biphenyls on decomposition of diaroyl peroxides in aromatic solvents. However, usually in benzene which has been employed as one of "inert" solvents, photochemical and free-radical reactions do not give biphenyl. On photochemical decomposition of bis(2-thiophenecarbonyl) peroxide (TPO) in aromatic solvents, we have found some remarkable features of the reactions of the aroylcyclohexadienyl radicals; 1) in benzene biphenyl was formed in a noticeable yield, particularly at low temperatures,[8] 2) in toluene among the possible dimethylbiphenyls 2,3′- and 3,3′-dimethyl isomers were formed together with a small amount of 2,2′-dimethyl isomer, and 3) in 1,3,5-trimethylbenzene 2,3′,4,5′,6-pentamethyldiphenylmethane was formed in a considerable yield.[9] In this paper we wish to report some new aspects of reactivities of aroyloxyl radicals with aromatic solvents and the role of ipso intermediates in the reaction.

$$\mathrm{ArCO_2OCOAr} \longrightarrow 2\ \mathrm{ArCO_2\cdot} \qquad (1)$$



Results

Photolysis and Thermolysis of Bis(2-thiophenecarbonyl) Peroxide in Benzene. Effects of Light Intensity and Temperature. Bis(2-thiophenecarbonyl) peroxide (TPO, 0.03 mol/dm^3) was irradiated at varying temperatures (5—60 °C) in benzene (3 cm^3) under argon and oxygen atmosphere for five times half-life periods with 313 nm light of varying intensities from a 400 W high pressure mercury lamp through a filter (85 min) or from a 1 kW high pressure mercury lamp directly (20—30 min), or with 337.1 nm laser pulses from a nitrogen laser (80 Hz, 20—30 min). TPO (0.03 mol/dm^3) was also heated in benzene at 80 °C for 2880 min (5 times half-life period) under degassed conditions. The products were determined quantitatively by GLPC except carbon dioxide, which was determined by gravimetry using an Ascarite tube. The results are summarized in Table 1.

TPO (0.03 mol/dm^3) was photolyzed in a mixture (400 cm^3) of varying fractions of benzene and styrene (1:0 to 3:1 by volume) in a nitrogen stream. The carbon dioxide evolved was absorbed with an Ascarite tube and determined by gravimetry. The results are summarized in Table 2 and depicted in Fig. 1.

Spin Trapping of 2-Thiophenecarbonyloxyl Radicals in Photolysis and Thermolysis of TPO. A solution of TPO (0.01 mol/dm^3) containing *N*-benzylidene-*t*-butylamine oxide (0.1 mol/dm^3) was irradiated at room temperature with a 1 kW high pressure mercury lamp or heated at 80 °C for several minutes in the cavity of an ESR spectrometer. The photolysis and thermolysis resulted in the same ESR signals (a_N=1.35 mT) attributable to the 2-thiophenecarbonyloxy spin adduct, *N*-{phenyl(2-thiophenecarbonyloxy)methyl}-*t*-butylaminyloxyl.[10,11]

Trapping of Phenyl Radicals Resulting from the Sol-

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TABLE 1. EFFECTS OF LIGHT INTENSITY AND TEMPERATURE ON PRODUCT YIELDS IN PHOTOLYSIS OF TPO IN BENZENE

Light source	Temp/°C	Product yield[a]				
		PhPh	2-ThPh	$ThCO_2Ph$	$ThCO_2H$	CO_2
Under deaerated conditions						
Δ[b]	80	0.02	—	0.01	0.68	0.30
Δ[c]	75—85	—	—	0.04	0.63	0.26
1 kW Hg[d]	60	0.02	trace	0.04	0.74	0.27
1 kW Hg	40	0.04	trace	0.06	0.62	0.27
1 kW Hg	29	0.07		0.05	0.48	
1 kW Hg	25	0.11	0.02	0.08	0.82	0.28
400 W Hg[e]	25	0.02	0.03	0.13	0.97	
N laser[f]	25	0.11	0.01	0.07	1.01	
1 kW Hg	15	0.11	0.01	0.06	0.45	
1 kW Hg	5	0.14	0.01	0.07	0.38	
N laser	5	0.17	trace	0.06	0.96	
Under oxygen						
1 kW Hg	60	0.01		0.28	1.06	
1 kW Hg	40	0.02		0.51	0.86	
1 kW Hg	29	0.03		0.61	0.60	
1 kW Hg	25	0.05		0.45	0.60	
1 kW Hg	15	0.06		0.45	0.60	
1 kW Hg	5	0.06		0.39	0.52	

a) Yields based on a mole of TPO. b) Thermolysis for 2880 min. c) Taken from Ref. 16. d) 20—30 min irradiation with a 1 kW high pressure mercury lamp. e) 85 min irradiation with a 400 W high pressure mercury lamp. f) 25—30 min irradiation with nitrogen laser pulses (80 Hz).

TABLE 2. YIELDS OF CARBON DIOXIDE IN PHOTOLYSIS AND THERMOLYSIS OF TPO IN BENZENE-STYRENE MIXTURES

Ratio by volume		CO_2 yield[a]	
PhH	Styrene	Photolysis	Thermolysis
400	0	0.27	0.30
395	5		0.18
390	10	0.18	0.01
350	50	0.14	0.01
300	100	0.14	

a) Yields based on a mole of TPO.

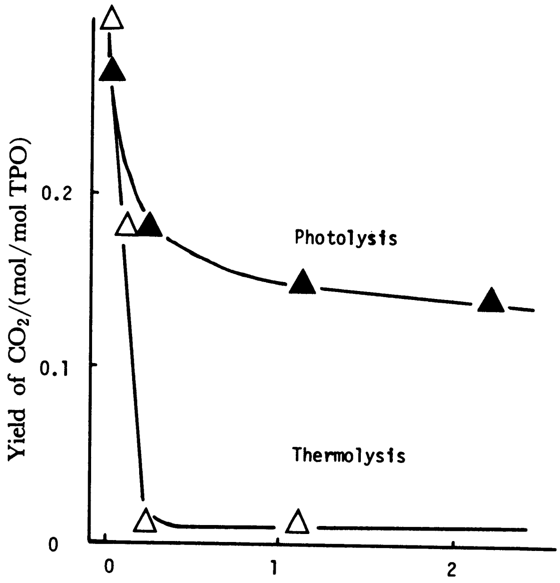


Fig. 1. Change of carbon dioxide yield with styrene concentration in thermolysis and photolysis of TPO in benzene.

TABLE 3. YIELDS OF BIPHENYL AND CHLOROBENZENE ON IRRADIATION OF TPO, BIS(4-METHOXYBENZOYL) PEROXIDE (MeOBPO), AND BENZOPHENONE IN A 1:1 MIXTURE OF BENZENE AND CARBON TETRACHLORIDE

Initiator	Product yield[a]	
	PhPh	PhCl
TPO	0.04	trace
MeOBPO	0.03	trace
Ph_2CO	trace	0.03

a) Yields based on a mole of substrate.

vent Benzene by Carbon Tetrachloride. TPO (0.03 mol/dm^3), bis(4-methoxybenzoyl) peroxide (0.03 mol/dm^3), and benzophenone (0.03 mol/dm^3) were irradiated, respectively, under nitrogen in a mixture of carbon tetrachloride and benzene (1:1 by volume, 3 cm^3) at room temperature with a 1 kW high pressure mercury lamp. The yields of biphenyl and chlorobenzene were determined by GLPC, and are listed in Table 3.

Photolysis and Thermolysis of TPO in Toluene. Effects of Wavelength and Temperature on Product Yields. TPO (0.03 mol/dm^3) was photolyzed in toluene (3 cm^3) by irradiating with 254 (low pressure mercury lamp), 313 (high pressure mercury lamp), and 337.1 nm light (nitrogen laser) at varying temperatures (5—22 °C). TPO was also thermolyzed at 80 °C in toluene. Table 4 compares the yields of 2-thiophenecarboxylates resulting from the photolysis with 313 nm light and thermolysis, and Table 5 summarizes the yields of dimethylbiphenyls afforded in the photolyses.

Photolysis of TPO and Dibenzoyl Peroxide in 1,3,5-

TABLE 4. YIELDS OF ISOMERIC METHYLPHENYL AND BENZYL 2-THIOPHENECARBOXYLATES IN PHOTOLYSIS AND THERMOLYSIS OF TPO IN TOLUENE

	Temp /°C	Benzyl ester Yield[a]	Methylphenyl ester Total yield[a]	Isomer ratio o-	m-	p-
Photolysis	20	0.01	0.09	63	11	26
Thermolysis[b]	80	0.03	0.04	69	8	23
Thermolysis[c]	80	0.02	0.18	48	17	35

a) Yields based on a mole of TPO. b) Thermolysis under degassed conditions. c) Thermolysis under oxygen.

TABLE 5. YIELDS OF ISOMERIC DIMETHYLBIPHENYLS IN PHOTOLYSIS OF TPO IN TOLUENE UNDER NITROGEN[a]

Light /nm	Temp /°C	Dimethylbiphenyl 2,2'-	2,3'-	2,4'-	3,3'-	3,4'-	4,4'-
254	5	0.02	0.10	trace	0.10	trace	0
	22	0.01	0.06	trace	0.06	trace	0
313	7-8	0.01	0.05	trace	0.05	trace	0
	22	0.01	0.03	trace	0.03	trace	0
337.1	5	0.01	0.06	trace	0.06	trace	0
	10	0.01	0.06	trace	0.06	trace	0
	20	trace	0.02	trace	0.02	trace	0

a) Yields based on a mole of TPO.

TABLE 6. PRODUCT YIELDS IN PHOTOLYSIS OF TPO IN 1,3,5-TRIMETHYLBENZENE[a]

Temp/°C	Product[b] TMPT	DMBT	BDPE	PMDM	TCA
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

a) Yields based on a mole of TPO. b) TMPT: 2,4,6-trimethylphenyl 2-thiophenecarboxylate, DMBT: 3,5-dimethylphenylmethyl 2-thiophenecarboxylate, BDPE: 1,2-bis(3,5-dimethylphenyl)ethane, PMDM: 2,3',4,5',6-pentamethyldiphenylmethane, TCA: 2-thiophenecarboxylic acid.

TABLE 7. PRODUCT YIELDS IN PHOTOLYSIS OF BPO IN 1,3,5-TRIMETHYLBENZENE[a]

Temp/°C	Product[b] TMPB	$PhCO_2Ph$	BDPE	PMDM
65	0.00	0.06	0.32	0.00
40	0.02	0.07	0.26	0.03
30	0.02	0.08	0.24	0.04
20	0.03	0.06	0.20	0.07
10	0.06	0.09	0.15	0.09
5	0.06	0.09	0.14	0.09

a) Yields based on a mole of BPO. b) TMPB: 2,4,6-trimethylphenyl benzoate, BDPE: 1,2-bis(3,5-dimethylphenyl)ethane, PMDM: 2,3',4,5',6-pentamethyldiphenylmethane.

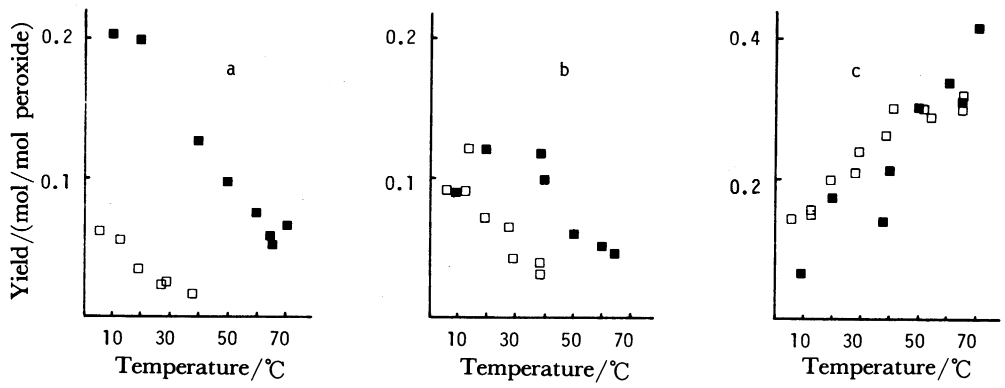


Fig. 2. Temperature dependence of product yields in photolysis of TPO (■) and BPO (□) in TMB; a) TMPT (■) and TMPB (□), b) PMDM, c) BDPE.

TABLE 8. PRODUCT YIELDS IN THERMOLYSES OF BPO AND TPO IN 1,3,5-TRIMETHYLBENZENE AT 80 °C[a]

Peroxide	Conditions	Product[b]			
BPO		TMPB	$PhCO_2Ph$	BDPE	PMDM
	degassed	0.02	0.00	0.37	0.00
	air	0.06	0.00	0.03	0.03
TPO		TMPT	$ThCO_2Th$	BDPE	PMDM
	degassed	0.07	0.02	0.32	0.03
	air	0.19	0.01	0.00	0.11

a) Yields based on a mole of peroxide. d) TMPB: 2,4,6-trimethylphenyl benzoate, TMPT: 2,4,6-trimethylphenyl 2-thiophenecarboxylate, BDPE: 1,2-bis(3,5-dimethylphenyl)ethane, PMDM: 2,3',4,5',6-pentamethyldiphenylmethane, Th: thienyl.

Trimethylbenzene. Temperature Effects on Product Yields. TPO (0.03 mol/dm^3) was irradiated in 1,3,5-trimethylbenzene (TMB, 3 cm^3) at varying temperatures (20—70 °C) under nitrogen with 313 nm light, and the products were determined by GLPC. The results are summarized in Table 6 and depicted in Fig. 2. Dibenzoyl peroxide (BPO, 0.03 mol/dm^3) was similarly photolyzed in TMB at varying temperatures (5—65 °C), and the results are summarized in Table 7 and depicted in Fig. 2. Thermolyses of TPO and BPO were carried out at 80 °C in TMB under deaerated and aerated conditions. Table 8 lists the results.

Generation of 3,5-Dimethylphenylmethyl Radicals in TMB and Temperature Effects on the Product Distribu-

tion. Attempts were made to generate 3,5-dimethylphenylmethyl radicals in the absence of any aroyloxyl radicals by photochemical and thermal procedures in TMB.

a) Photolysis of 1,3-Bis(3,5-dimethylphenyl)-2-propanone. 1,3-Bis(3,5-dimethylphenyl)-2-propanone (0.01 mol/dm^3) in TMB (3 cm^3) was irradiated with 313 nm light under degassed conditions. The product yields at varying temperatures (10—68 °C) are summarized in Table 9.

Table 9. Photolysis of 1,3-bis(3,5-dimethylphenyl)-2-propanone in 1,3,5-trimethylbenzene

Temp/°C	Conversion/%	Yield/%	
		PMDM	BDPE
10	95	<6	84
19	100	<6	92
30	100	<6	91
47	96	<6	73
68	84	<6	40

Table 10. Photoreaction of benzophenone in 1,3,5-trimethylbenzene

Temp/°C	Product yield/%		
	PMDM	BDPE	$Me_2C_6H_3CH_2CPh_2OH$
30	0	29	35
40	0	27	35
55	0	27	36

b) Photoreaction of Benzophenone in TMB. Degassed and sealed samples of benzophenone (0.03 mol/dm^3) in TMB (3 cm^3) were irradiated with 366 nm light at varying temperatures (30—55 °C). The results are summarized in Table 10.

c) Thermolysis of Di-t-butyl Diperoxyoxalate. Di-*t*-butyl diperoxyoxalate (0.03 mol/dm^3) was heated at 35—55 °C in TMB (3 cm^3) under degassed conditions. Table 11 summarizes the results.

MO Calculations of Some Models for Ipso- and Non-ipso-substituted Cyclohexadienyl Radicals. Open shell restricted SCF-MO calculations were performed

Table 11. Thermolysis of di-*t*-butyl diperoxyoxalate in 1,3,5-trimethylbenzene

Temp/°C	Product yield/%	
	PMDM	BDPE
35	0	75
45	0	77
55	0	77

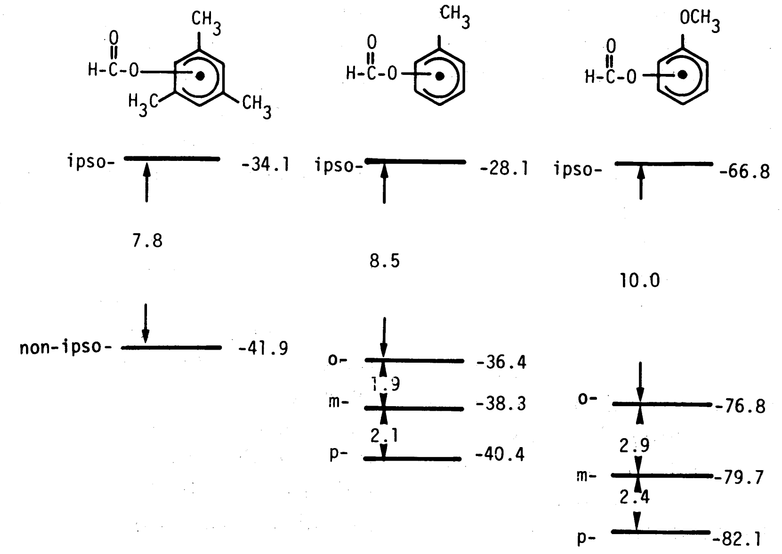


Fig. 3. Total and relative energies of substituted cyclohexadienyl intermediates (kcal/mol).

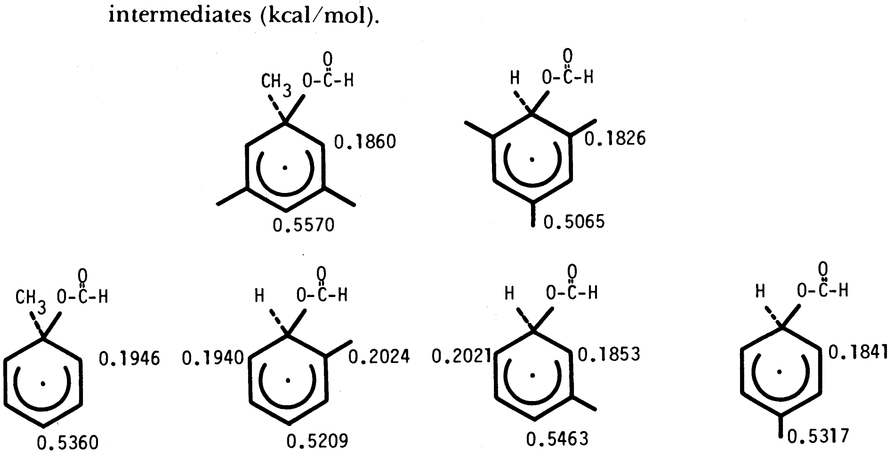
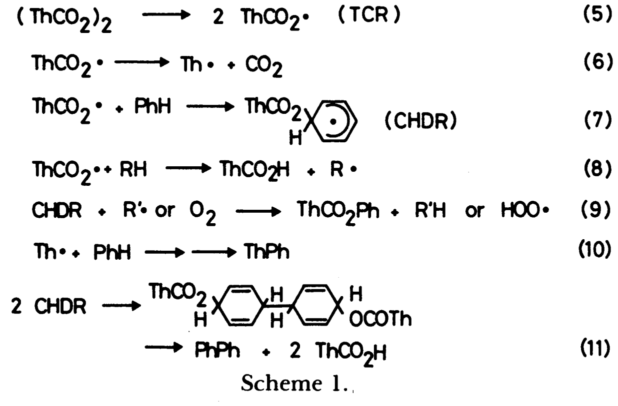


Fig. 4. Spin density of substituted cyclohexadienyl intermediates.

for cyclohexadienyl radicals derived from addition of formyloxyl radicals to toluene, anisole, and 1,3,5-trimethylbenzene by the MINDO/3 method[12] on a FACOM M-200 system. First, the structure of the unsubstituted cyclohexadienyl radical was optimized under C_{2v} constraint.[13] Then, by using this optimized planar ring structure, 6-formyloxycyclohexadienyl and 6-formyloxy-6-methylcyclohexadienyl radicals were optimized. Here, the formyloxyl group was fixed to the conformations for the C–O single bond in which the cyclohexadienyl group and carbonyl oxygen are cis and the carbonyl and *O*-cyclohexadienyl bonds are coplanar, since esters, in general, prefer strongly such a conformation.[14,15] Finally, based on these conformations, the total energies, relative energies, and spin densities of the ipso- and non-ipso-substituted cyclohexadienyl radicals were determined. The results are shown in Figs. 3 and 4. The total energy of the formyloxy-substituted cyclohexadienyl radicals decreases in the order of ipso, ortho, meta, and para isomers. The energy difference between the ipso- and ortho(non-ipso)-substituted cyclohexadienyl radicals is 7.8kcal/mol in the case of 1,3,5-trimethylbenzene, which is the smallest value among the substituted benzenes employed. The difference of energies among the substituted cyclohexadienyl radicals increases in the order of trimethyl-, methyl-, and methoxy-substitution.

Discussion

Mechanism for Formation of Biphenyls. As Table 1 shows, most of the products from the photolysis of TPO in benzene are the same as those from its thermolysis,[16] and their production can be understood in terms of the conventional free-radical pathways.[1,2] The following scheme shows the formation processes of the products except biphenyl; TPO is thermally or photochemically decomposed to give 2-thiophenecarbonyloxyl radicals (TCR) (Eq. 5), which decarboxylate to give 2-thienyl radicals (TR) and carbon dioxide (Eq. 6), add to benzene to give cyclohexadienyl radicals (CHDR) (Eq. 7),[3] or abstract a hydrogen atom to give 2-thiophenecarboxylic acid (TCA)(Eq. 8). CHDRs are oxidized by radicals or oxygen to give phenyl 2-thiophenecarboxylate (Eq. 9). TRs add to benzene to give finally 2-phenylthiophene (Eq. 10).



$$(\mathrm{ThCO_2})_2 \longrightarrow 2\ \mathrm{ThCO_2}\cdot\ (\mathrm{TCR}) \qquad (5)$$

$$\mathrm{ThCO_2}\cdot \longrightarrow \mathrm{Th}\cdot + \mathrm{CO_2} \qquad (6)$$

$$\mathrm{ThCO_2}\cdot + \mathrm{RH} \longrightarrow \mathrm{ThCO_2H} + \mathrm{R}\cdot \qquad (8)$$

$$\mathrm{CHDR} + \mathrm{R'}\cdot \text{ or } \mathrm{O_2} \longrightarrow \mathrm{ThCO_2Ph} + \mathrm{R'H} \text{ or } \mathrm{HOO}\cdot \qquad (9)$$

$$\mathrm{Th}\cdot + \mathrm{PhH} \longrightarrow \longrightarrow \mathrm{ThPh} \qquad (10)$$

Scheme 1.

The production of biphenyl is noticeable, since decomposition of various types of radical generators except for phenyl radicals in benzene has never given such a high yield of biphenyl.[1,2] Biphenyl is not produced from phenyl radicals which could be formed from the reaction medium, since chlorobenzene was not detected in the photolysis of TPO in the presence of carbon tetrachloride as a phenyl radical scavenger in contrast with irradiation of benzophenone under similar conditions (Table 3). The formation of biphenyl in the photolysis of TPO in benzene can be reasonably understood by the following scheme; CHDRs generated from addition of TCRs to the solvent benzene undergo dimerization into tetrahydrobiphenyl derivatives[7] followed by elimination of two moles of thiophenecarboxylic acid (Eq. 11). This mechanism is supported by the results of photolyses carried out under oxygen atmosphere which gave phenyl 2-thiophenecarboxylate in a much higher yield than under argon atmosphere at the expense of biphenyl (Table 1).

Efficient production of biphenyl requires that TCRs effectively add to benzene, in competition with decarboxylation, to give CHDRs. This is in contrast with other kinds of aroyloxyl radicals which fail in production of biphenyl in benzene.[1,2] Reluctance of TCR to decarboxylation can be seen in a much lower yield of carbon dioxide (*ca.* 0.3 mol/mol TPO in Table 1) in benzene than from other diaroyl peroxides such as BPO (1.4 mol)[10] and in the efficient formation of the acyloxy spin adduct in the photolysis and thermolysis of TPO in the presence of the nitrone. Although decomposition of other diaroyl peroxides in benzene usually gives only negligible amounts of phenyl arenecarboxylates in the absence of oxidants such as oxygen,[3,17] TPO gives a non-negligible amount of phenyl 2-thiophenecarboxylate (Table 1). This fact can be taken as a piece of evidence for the higher reactivity of TCR towards benzene than other aroyloxyl radicals. The higher reactivity and stability of TCR probably arise from electronic effects of the sulfur atom.[16]

The yield of biphenyl is highly dependent on the photolysis conditions; it is very sensitive to temperature and remarkably reduced with increasing temperature. Since the yield of carbon dioxide was not varied in the temperature range examined, the effect of temperature is not due to acceleration of the decarboxylation rate of TCR. Therefore, the reduction of the yield of biphenyl indicates that TCR is in an addition equilibrium with CHDR and that at higher temperatures than 40 °C CHDR tends to decrease its stationary concentration by dissociating into TCR and benzene rather than undergoing recombination.

According to the above mechanism for biphenyl formation, the yield of biphenyl should be controlled by the stationary concentration of CHDR, and thus by the decomposition rate of the peroxide. In Table 1, when the apparent half-life period of TPO is decreased from 80 to 25 min by use of higher light intensity, the yield of biphenyl is increased from 0.02 to 0.11 (high pressure mercury lamp) and 0.17 mol (nitrogen laser).

In the presence of styrene as a radical scavenger, carbon dioxide was produced in much higher yield (0.14 mol) in photolysis than in thermolysis (0.01 mol), as shown in Fig 1. This result exhibits the decarboxylation from photoexcited TPO is more efficient than that from vibrationally excited TPO; in the thermolysis carbon dioxide almost results from decarboxylation of out-of-cage TCRs (Eq. 6), while in the photolysis, carbon dioxide results not only from decarboxylation of the out-of-cage TCRs but also from the two-bond fission (O-O and C(α)-C(carbonyl) bonds) of photoexcited TPO in either simultaneous or successive way (Eq. 12) and/or decarboxylation of in-cage TCRs (Eq. 13).[10]

$$(\mathrm{ThCO_2})_2 \longrightarrow \mathrm{ThCO_2}\cdot + \mathrm{CO_2} + \mathrm{Th}\cdot \qquad (12)$$

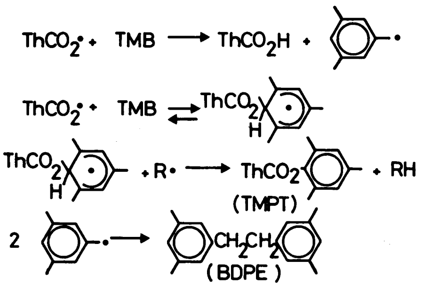
$$\begin{aligned}(\mathrm{ThCO_2})_2 &\longrightarrow (2\mathrm{ThCO_2}\cdot)_{\mathrm{cage}}\\ &\longrightarrow \mathrm{ThCO_2}\cdot + \mathrm{CO_2} + \mathrm{Th}\cdot \qquad (13)\end{aligned}$$

Photolysis of TPO in toluene under similar conditions to the above resulted in the formation of dimethylbiphenyls among usual radical reaction products[1,2] (Tables 4 and 5). The isomer ratio of dimethylbiphenyls was high in meta- and ortho-substituted derivatives and very low in para-substituted ones[18] (Table 5). As discussed above on the formation of biphenyl in benzene, dimethylbiphenyls are considered to arise from recombination of cyclohexadienyl radicals formed through addition of TCR to toluene. Temperature effects on the yield of dimethylbiphenyls are consistent with this mechanism. The total yield and isomer ratio of methylphenyl 2-thiophenecarboxylates are 0.1 mol and 63:11:26 for ortho:meta:para isomers, respectively. The isomer ratio is in good agreement with that in the thermolysis of TPO in toluene. In thermolysis oxygen increased the ester yield and gave the isomer ratio which was lower in the ortho and higher in the para ratio. An intermediate isomer ratio (57:16:27) was reported for thermolysis of TPO in acetonitrile containing toluene in the presence of a copper(II) salt.[19]

The isomer ratio of dimethylbiphenyls is highly remarkable, since the ratio depends, according to the above mechanism, to the population of isomeric cyclohexadienyl intermediates (for their structures, see Fig. 4). As mentioned above, the photolysis of TPO in toluene under deaerated conditions afforded the isomer ratio of methylphenyl thiophenecarboxylates different from that given by the thermolysis under oxygen. Since the oxidants such as oxygen would scavenge the initially formed cyclohexadienyl intermediates to afford the corresponding esters, their isomer ratios would reflect the population of the isomeric cyclohexadienyl radicals.[20,21] The para-substituted derivatives among dimethylbiphenyls would arise from recombination of the meta or ipso intermediate. Therefore, if the isomer ratio of the esters under oxygen reflects the ratio of the corresponding cyclohexadienyl radicals, the absence of any para-substituted dimethylbiphenyls means that the adjacent positions to the carbon atoms substituted by a thiophenecarbonyloxyl group are almost unreactive in recombination with other acyloxycyclohexadienyl radicals, as previously discussed for photolysis of BPO in toluene.[18] However, since it is expected that the ipso intermediate could undergo recombination at the 3 position with other intermediates to give para-substituted dimethylbiphenyls, the above facts indicate that ipso intermediate would not play an important role in the dimethylbiphenyl formation.

The high ratio of methylphenyl thiophenecarboxylates in the ortho isomer in the decomposition of TPO under the deaerated conditions indicates the contribution of the rearrangement of the ipso intermediate to the ortho one, though the possibility cannot be ruled out that a selectivity in the disproportionation step determined the isomer ratio of the esters.[22]

Intermediacy of ipso Intermediates. Photolysis of TPO in 1,3,5-trimethylbenzene(TMB) at 20 °C afforded thiophenecarboxylate esters, 2,4,6-trimethylphenyl 2-thiophenecarboxylate(TMPT) and 3,5-dimethylphenylmethyl 2-thiophenecarboxylate(DMBT), dimers from the solvent, 1,2-bis(3,5-dimethylphenyl)ethane(BDPE) and 2,3′,4,5′,6-pentamethyldiphenylmethane(PMDM), and 2-thiophenecarboxylic acid (TCA) (Table 6). The formation of TMPT and BDPE can be understood in terms of the usual radical processes (Eqs. 14—17).[1,2] The yield of DMBT is rather higher compared with that of the corresponding esters from other diaroyl peroxides such as BPO (Table 7). Taking into account the stability of TCR, DMBT is reasonably assumed to be formed through recombination of TCR with 3,5-dimethylphenylmethyl radicals (Eq. 18).

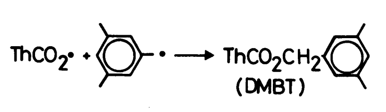


(14)

(15)

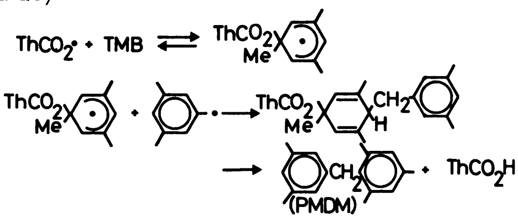
(16)

(17)



(18)

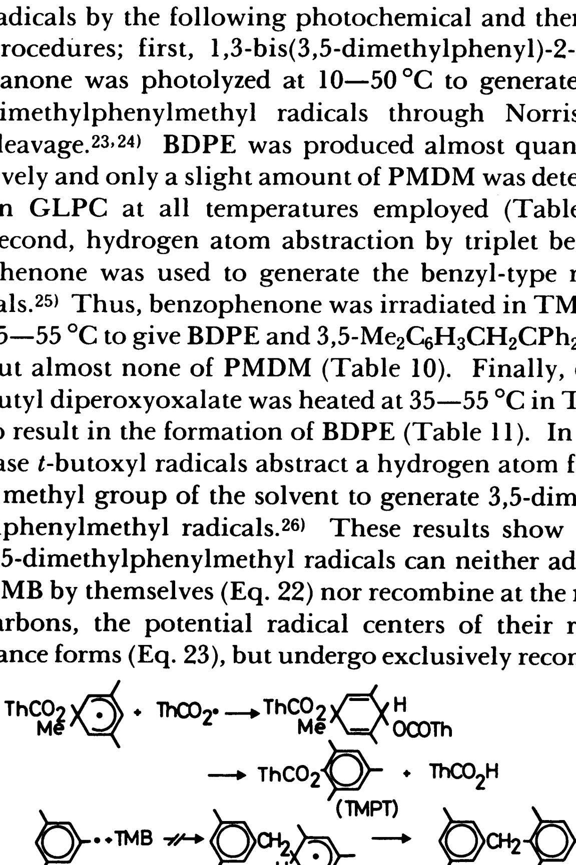
The formation of PMDM is quite unusual since, as the following control experiments show, benzyl-type radicals in general do not facilely add to aromatic rings.[1,2] Therefore, it is reasonably proposed that PMDM is formed through recombination of 3,5-dimethylphenylmethyl radicals with cyclohexadienyl radicals generated by attack of TCR on the ipso positions of TMB, followed by elimination of TCA (Eqs. 19 and 20).



(19)

(20)

Attempts were made to eliminate the possibility of addition of benzyl-type radicals to TMB and to confirm contribution of aroyloxyl radicals to PMDM formation. Thus, 3,5-dimethylphenylmethyl radicals were generated in TMB in the absence of any aroyloxyl radicals by the following photochemical and thermal procedures; first, 1,3-bis(3,5-dimethylphenyl)-2-propanone was photolyzed at 10—50 °C to generate the dimethylphenylmethyl radicals through Norrish I cleavage.[23,24] BDPE was produced almost quantitatively and only a slight amount of PMDM was detected on GLPC at all temperatures employed (Table 9). Second, hydrogen atom abstraction by triplet benzophenone was used to generate the benzyl-type radicals.[25] Thus, benzophenone was irradiated in TMB at 25—55 °C to give BDPE and 3,5-$Me_2C_6H_3CH_2CPh_2OH$ but almost none of PMDM (Table 10). Finally, di-*t*-butyl diperoxyoxalate was heated at 35—55 °C in TMB to result in the formation of BDPE (Table 11). In this case *t*-butoxyl radicals abstract a hydrogen atom from a methyl group of the solvent to generate 3,5-dimethylphenylmethyl radicals.[26] These results show that 3,5-dimethylphenylmethyl radicals can neither add to TMB by themselves (Eq. 22) nor recombine at the ring carbons, the potential radical centers of their resonance forms (Eq. 23), but undergo exclusively recombination (dimerization) at their benzyl carbons (Eq. 17).



(21)

(22)

(23)

Scheme 2.

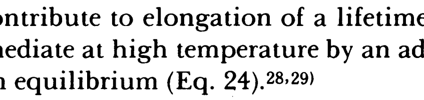
In order to confirm involvement of the aroyloxyl radicals in the formation of PMDM, temperature dependence of product yields in the photolysis of TPO was examined, as summarized in Table 6 and depicted in Fig. 2, since aroyloxyl radicals reversibly add to aromatic solvents. Figure 2 shows that the yield of BDPE increases but those of TMPT and PMDM decrease with increasing temperature. These results are consistent with the above mechanism; at higher temperatures the addition equilibria (Eqs. 15 and 19) tend to be shifted to the side of TCR and TMB, and thus TCR tends to abstract a hydrogen atom from a methyl group of TMB.

As to elimination of ipso substituents, products from homolytic substitution of a methyl group by TCR such as 3,5-dimethylphenyl 2-thiophenecarboxylate were not detected in the photolysis of the peroxides in TMB.

Formation of PMDM and similar temperature effects on the product yields were observed in the photolysis of BPO in TMB (Table 7 and Fig. 2). The product formation can be accounted for by processes similar to those mentioned above except phenyl benzoate, the geminate product,[10] which was not detected in the thermolysis. When the yields of products are compared between the two peroxides at the same temperatures, the yields of BDPE are almost of the same magnitude; however, the yields of PMDM and 2,4,6-trimethylphenyl esters, TMPT and $PhCO_2C_6H_2Me_3$ (TMPB), 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 TCR and benzoyloxyl radicals, the latter decarboxylating faster.[27] That TMPT is much higher in yield and suffers more remarkable temperature effects than TMPB (Fig. 2) indicates that TMPT is formed not only through addition of TCR to TMB followed by disproportionation (Eqs. 15,16) but also through recombination of TCR with the ipso intermediate followed by acid elimination (Eq. 21).

Therefore, it is quite reasonable to conclude that the formation of PMDM in photolyses of TPO and BPO provides clear evidence for intermediacy of the ipso intermediates formed by attack of aroyloxyl radicals to TMB.

Thermolysis of the peroxides in TMB shows some intriguing trends. The formation of 2-thienyl 2-thiophenecarboxylate is noticeable, since BPO did not give any corresponding phenyl benzoate. This fact provides another piece of evidence for the stability (slow decarboxylation) of TCR. More remarkable is the increase of the PMDM yield for both peroxides under aerated conditions. Although the cause has not been clarified, it can be tentatively proposed that oxygen will contribute to elongation of a lifetime of the ipso intermediate at high temperature by an addition-elimination equilibrium (Eq. 24).[28,29]



(24)

Estimation of Stability of ipso Intermediates from MO Calculations. Open shell restricted SCF-MO MINDO/3 calculations showed that the energy difference between ipso and non-ipso intermediates from TMB (7.8 kcal/mol) is smaller than that from toluene (8.5 kcal/mol) (Fig. 3). This may indicate that the ipso intermediate from TMB is relatively stabilized more than that from toluene. For anisole as a model compound for diphenyl ether, of which the phenoxyl group has been established to be substituted by benzoyloxyl radicals,[30] the difference of the total energy between the ipso and non-ipso intermediates is much larger (10.0 kcal/mol) than the above two cases. In all three cases, the energy difference among the non-ipso intermediates is small compared with the above values. Similar results have been reported on substituted cyclohexadienyl radicals on the basis of CNDO/2[22] and *ab initio* MO calculations.[31] The relative energies of the isomeric intermediates have been similarly assessed by MINDO/3 calculations based on isodesmic reactions.[32] As discussed above, PMDM is apparently formed from the reaction of 6-aroyloxy-1,3,5-trimethylcyclohexadienyl radicals, of which the model is estimated to be higher in energy than the non-ipso intermediates. Therefore, the stability of substituted cyclohexadienyl radicals seems not to play an important role in the selectivity in the addition step of the aroyloxyl radicals, but to contribute to the ipso →ortho rearrangement as proposed in the case of toluene; the positions of the initial addition of aroyloxyl radicals to aromatic solvents can be predicted by the frontier orbital theory.[22,33]

The calculated spin density predicts that all cyclohexadienyl radicals depicted in Fig. 4 are the most reactive at the 3-position. The isomer ratio of dimethylbiphenyls indicates low reactivity of the 1- and 5-positions as discussed above. Based on the product distributions in toluene and the spin densities, the four cyclohexadienyl intermediates are considered to behave as follows; the ortho and meta intermediates are predominantly responsible for the dimethylbiphenyl formation by recombining at the 3-position, and the para intermediate reacts at the 1- or 5-position because of low reactivity of the 3-position due to the methyl substitution. On the contrary, the ipso intermediate is not responsible for biphenyl formation but rearranges to the ortho one.

Conclusion

The high reactivity of TCR towards aromatic solvents and the high stationary concentration of cyclohexadienyl radical intermediates in photolysis of TPO bring about their bimolecular reactions giving dimeric products of the solvents. Biphenyl and dimethylbiphenyls are formed in noticeable yields in benzene and toluene, respectively, through dimerization of the corresponding cyclohexadienyl radicals followed by acid elimination. In TMB PMDM arises from recombination of the ipso intermediates generated by attack of TCR and benzoyloxyl radicals to TMB with the benzyl-type radicals derived from TMB.

Experimental

Materials. Bis(2-thiophenecarbonyl) peroxide was prepared from 2-thiophenecarbonyl chloride and hydrogen peroxide (30% aqueous solution) in the presence of sodium hydroxide,[16] and dibenzoyl peroxide was commercially obtained. The peroxides were purified by precipitating from dichloromethane–methanol.

Di-*t*-butyl diperoxyoxalate was prepared by adding a pentane solution of *t*-butyl hydroperoxide to a cooled mixture of oxalyl dichloride, pyridine, and pentane, and reprecipitated from pentane.[26]

1,3-Bis(3,5-dimethylphenyl)-2-propanone was prepared by the reaction of 3,5-dimethylphenylmethyl bromide with nonacarbonyldiiron(0) in hexane,[34,35] and purified by recrystallization from petroleum ether.

2,4,6-Trimethylphenyl 2-thiophenecarboxylate was prepared by the reaction of 2,4,6-trimethylphenol and 2-thiophenecarboxylic acid in trifluoroacetic anhydride,[36] and recrystallized from hexane. Mp 89.3—89.8 °C. ^{1}H-NMR ($CDCl_3$): δ=2.12 (s, 6H), 2.24 (s, 3H), 6.79 (s, 2H), 7.06 (m, 1H), 7.50 (d, 1H), 7.86 (d, 1H). IR (KBr): $\nu_{C=O}$ 1720 cm^{-1}. Found: C, 68.13; H, 5.68%. Calcd for $C_{14}H_{14}O_2S$: C, 68.26; H, 5.72%.

3,5-Dimethylphenylmethyl 2-thiophenecarboxylate was prepared by the reaction of sodium 2-thiophenecarboxylate with 3,5-dimethylphenylmethyl bromide in acetic acid.[37] Bp 148.3—149.2 °C/1100 Pa. ^{1}H-NMR ($CDCl_3$): δ=2.32 (s, 6H), 5.29 (s, 2H), 7.0—7.3 (m, 4H), 7.58 (d, 1H), 7.86 (d, 1H). Found: C, 68.42; H, 5.82%. Calcd for $C_{14}H_{14}O_2S$: C, 68.26; H, 5.72%.

3,5-Dimethylphenyl 2-thiophenecarboxylate was prepared by the reaction of 2-thiophenecarbonyl chloride with 3,5-dimethylphenol in a mixture of benzene and pyridine. Mp 39.2—42.3 °C. ^{1}NMR ($CDCl_3$): δ=2.30 (s, 6H), 6.75 (s, 2H), 6.98 (s, 1H), 7.08 (m, 1H), 7.55 (d, 1H), 7.86 (d, 1H). Found: C, 67.21; H, 5.22%. Calcd for $C_{13}H_{12}O_2S$: C, 67.21; H, 5.20%.

2,4,6-Trimethylphenyl benzoate,[38] phenyl,[16] 2-methylphenyl,[16] 3-methylphenyl,[16] 4-methylphenyl,[16] and benzyl 2-thiophenecarboxylate[39] were prepared similarly from 2-thiophenecarbonyl chloride and the corresponding phenols.

2-Thienyl 2-thiophenecarboxylate was prepared by the thermolysis of TPO in the presence of copper(II) chloride in acetonitrile containing thiophene.[16]

2,2′-Dimethyl- and 3,3′-dimethylbiphenyl were prepared by heating 2-iodo- and 3-iodotoluene, respectively, with copper powder (Ullman reaction),[40] and 4,4′-dimethylbiphenyl was commercially obtained.

2,3′-Dimethylbiphenyl was prepared in the following way.[41,42] 3-Methyl-1-(2-methylphenyl)cyclohexanol was prepared by Grignard reaction of 2-bromotoluene with 3-methylcyclohexanone. The cyclohexanol was heated with oxalic anhydride to give a mixture of 3-methyl-1-(2-methylphenyl)cyclohexene and 5-methyl-1-(2-methylphenyl)-cyclohexene. This mixture was refluxed with sulfur in quinoline to afford 2,3′-dimethylbiphenyl.

2,4′-Dimethyl- and 3,4′-dimethylbiphenyl were prepared in a similar way from 4-bromotoluene with 2-methyl- and 3-methylcyclohexanone, respectively.

2,2′,4,4′,6,6′-Hexamethylbiphenyl was prepared by heating 2,4,6-trimethylphenylmagnesium bromide with anhydrous copper(II) chloride.[43]

2-Methyl-, 3-methyl-, and 4-methyldiphenylmethane were prepared from the corresponding methylbenzophenones by modified Wolff-Kishner reaction.[44]

2,3′,4,5′,6-Pentamethyldiphenylmethane was prepared by

Friedel-Clafts reaction of 3,5-dimethylphenylmethyl bromide with 1,3,5-trimethylbenzene in the presence of iron(III) trichloride.[45]

1,2-Bis(3,5-dimethylphenyl)ethane were prepared by heating the corresponding dimethylphenylmethylmagnesium bromide with anhydrous copper(II) chloride.[45]

Benzophenone commercially obtained was recrystallized from methanol and petroleum ether.

Toluene and 1,3,5-trimethylbenzene (special grade, Wako) were purified by distilling over calcium hydride.

Photolyses and Thermolyses of Diacyl Peroxides. A solution (3 cm^3) of a peroxide (0.03 mol/dm^3) in benzene, toluene, or 1,3,5-trimethylbenzene in a Pyrex tube was degassed by the usual freeze-thaw cycles or by bubbling with argon, and irradiated with a 1 kW or a 400 W high pressure mercury lamp using a merry-go-round type Riko Rotary Photochemical Reactor or with a nitrogen laser (Lambda Physik M100B; 337.1 nm, 3.5 mJ/pulse, 80Hz). On irradiation with 254 nm light, a peroxide solution in a quartz tube was deaerated by bubbling with nitrogen, and irradiated with a 160 W low pressure mercury lamp. Irradiation was continued for more than five times the half-life period of the peroxide determined by iodometric analysis or high-performance liquid chromatography (Shimadzu LC2; column, ODS 25cm) under the experimental conditions.

Thermolyses of peroxides were carried out in the following manner. A solution of a peroxide degassed by the usual freeze-thaw cycles or under oxygen in a Pyrex tube was heated in a thermostat for more than five times the half-life period of the peroxide determined under the experimental conditions.

Photolysis of 1,3-Bis(3,5-dimethylphenyl)-2-propanone in 1,3,5-Trimethylbenzene. A solution of 1,3-bis(3,5-dimethylphenyl)-2-propanone in 1,3,5-trimethylbenzene (0.01 mol/dm^3, 3 cm^3) was degassed by the usual freeze-thaw cycles, and irradiated by a 1 kW high pressure mercury lamp for 70 min in a thermostat.

Irradiation of Benzophenone in 1,3,5-Trimethylbenzene. A solution of benzophenone in 1,3,5-trimethylbenzene (0.03 mol/dm^3, 3 cm^3) was degassed and irradiated by a 1 kW high pressure mercury lamp for 3 h in a thermostat.

*Thermolysis of Di-*t*-butyl Diperoxyoxalate in 1,3,5-Trimethylbenzene.* A solution of di-*t*-butyl diperoxyoxalate in 1,3,5-trimethylbenzene (0.03 mol/dm^3, 3 cm^3) was degassed and heated in a thermostat for five times the half-life period (1.0 h at 55 °C, 3.5 h at 45 °, and 14.2 h at 35 °) estimated from the reported decomposition rate constants.[26]

Product Analyses. Biaryls, diphenylmethanes, diphenylethanes, and esters were determined quantitatively by GLPC analysis on a Shimadzu GC-4CM PF gas chromatograph equipped with a flame ionzation detector. Acids were determined on a Shimadzu LC2 high-performance liquid chromatograph.

Trapping of Carbon Dioxide in the Presence of Styrene. TPO (0.03 mol/dm^3) in a mixture of varying fractions of benzene and styrene was thermolyzed at 80 °C and photolyzed at room temperature with a 400 W high pressure mercury lamp through a Pyrex wall. The resulting carbon dioxide was absorbed with an Ascarite tube and determined by gravimetry.

Spin Trapping of 2-Thiophenecarbonyloxyl Radicals. A solution of TPO (0.91 mol/dm^3) containing *N*-benzylidene-*t*-butylamine oxide (0.1 mol/dm^3) was heated at 80 °C or irradiated at room temperature with a 1 kW high pressure mercury lamp in the cavity of an ESR spectrometer (JEOL JES-ME-1X) for several minutes.

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