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PHOTOLYSES OF BIS(2-THIOPHENECARBONYL) AND BIS(3-THIOPHENECARBONYL) PEROXIDES IN BENZENE. PRODUCTION OF BIPHENYL FROM THE SOLVENT BENZENE CONTROLLED BY THE PHOTOLYSIS RATE#

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Direct and sensitized photolyses of bis(2-thiophenecarbonyl) (2-TPO) and bis(3-thiophenecarbonyl) peroxide (3-TPO) in benzene afforded biphenyl derived solely from the solvent among the products. The yield of biphenyl depended upon the rate with which the radical intermediates were generated from the peroxides in sufficiently high concentrations to dimerize.

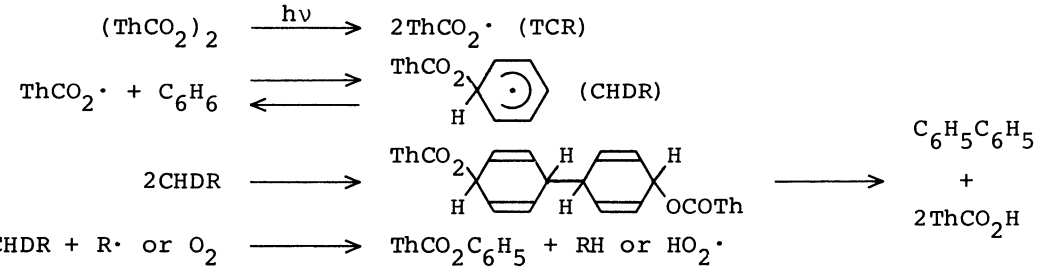
Benzene has been employed as one of "inert" solvents in many photochemical reactions. Usually, photochemical and free-radical reactions carried out in benzene do not give biphenyl, both phenyl groups of which are derived from the solvent. However, we now wish to report a remarkable formation of biphenyl in photolyses of bis(2-thiophenecarbonyl) (2-TPO) and bis(3-thiophenecarbonyl) peroxide (3-TPO) in benzene. The effects of reaction temperature and sensitizers on the yield of biphenyl show that biphenyl is produced when the peroxides are decomposed efficiently to generate high stationary concentrations of radical intermediates enough to undergo bimolecular reactions.

2-TPO and 3-TPO (0.03 mol dm^{-3}) were photolyzed in benzene (3 ml) with a 1 kW high pressure mercury lamp directly (313-nm light obtained through an aqueous potassium chromate solution filter or through a Pyrex filter) and in the presence of sensitizers (366-nm light obtained through a Toshiba UV-D36B glass filter; concentrations of the sensitizers were adjusted to have the optical density of more than unity) under degassed condition or under argon atmosphere until the peroxides were completely decomposed. The products were characterized by actual isolation and quantitatively determined by GLPC as summarized in Table 1 together with results of their thermolyses at 80°C and control irradiation of triplet sensitizers in benzene in the absence of the peroxides. As Table 1 shows, most photolysis products except biphenyl are the same as those produced from the thermolyses,[2-4] and their production can be understood in terms of the conventional free-radical pathways.[5]

The production of biphenyl is noticeable, since decomposition of various types of radical generators except sources of phenyl radicals in benzene has never given such a high yield of biphenyl.[5] It is also remarkable that the yield of biphenyl is highly dependent on the photolysis conditions.

Dedicated to Professor Osamu Simamura on the occasion of his 70th birthday.

The formation of biphenyl can be reasonably understood by the following scheme; thiophenecarbonyloxyl radicals (TCR) generated from TPO reversibly add to benzene to give cyclohexadienyl radicals (CHDR),[6] which undergo recombination into tetrahydrobiphenyl derivatives followed by elimination of two moles of thiophenecarboxylic acid.[7,8] This mechanism is supported by the results of photolyses carried out under oxygen atmosphere which gave phenyl thiophenecarboxylate in much higher yield than under argon atmosphere at the expense of biphenyl (Table 1).



(Th: 2- or 3-thienyl group; R·: free radicals. An isomer of tetrahydrobiphenyls is expressed above.)

For efficient production of biphenyl, TCR effectively adds to benzene, in competition with decarboxylation, to shift the equilibrium to the right side, which is in contrast with other kinds of aroyloxyl radicals failing in production of biphenyl in benzene.[5] Reluctance of 2-TCR to decarboxylation can be seen from the much lower yield of carbon dioxide (0.27 mol) liberated in benzene from 2-TPO than from other diaroyl peroxides like dibenzoyl peroxide (1.4 mol) in benzene.[9] Although decomposition of other diaroyl peroxides in benzene usually gives only negligible amounts of phenyl aroates in the absence of oxidants like oxygen,[6,10] 2-TPO gives a non-negligible amount of phenyl 2-thiophenecarboxylate.[11] This fact can be taken as a piece of evidence for the higher reactivity of TCR towards benzene than the other aroyloxyl radicals. The higher reactivity and stability of TCR probably arise from electronic effects of the sulfur atom.

Effects of temperature on product formation in direct photolysis of 2-TPO were examined as summarized in Table 2, which indicates that the yield of biphenyl is very sensitive to temperature and remarkably reduced above 40°C. 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 or TCR. Therefore, the reduction of the yield of biphenyl indicates that at higher temperatures above 40°C CHDR tends to effectively dissociate into TCR and benzene rather than undergo recombination.

With triplet sensitized photolyses, the sensitizers with higher triplet excitation energies like acetophenone, xanthone, and benzophenone afforded biphenyl in more than 0.1 mol based on the peroxide; however, the sensitizers with lower triplet energies like 2-benzoylnaphthalene gave biphenyl in lower yield. Furthermore, the sensitizers with much lower triplet energies like biacetyl and benzil did not sensitize the decomposition of the peroxide.

The above effect of the triplet energy of the sensitizers on the efficiency of peroxide decomposition indicates that the sensitizers carrying triplet excitation

Table 1. Products from Photolyses of 2-TPO and 3-TPO in Benzene[a)]

Sensitizer (E_T)[b)]	Concentration /mol dm^{-3}	Half-life /min	Yield[c)] PhPh	ThPh	$ThCO_2Ph$	$ThCO_2H$
2-TPO						
Unsensitized[d)]		20-30	0.11	0.02	0.08	0.82
Unsensitized[d,e)]		85	0.02	0.03	0.13	0.97
Unsensitized[d,f)]		20-30	0.05	-	0.45	0.60
Acetophenone (74)	0.27	9.5	0.13	-	0.05	0.79
Xanthone (74)	0.09	9.0	0.12	-	0.04	0.68
Benzophenone (69)	0.05	16	0.19	0.02	0.06	0.69
2-Benzoyl-naphthalene (60)	0.05	28	0.06	0.02	0.03	0.93
Biacetyl (56)	0.06	-	-	-	-	-
Benzil (53)	0.05	-	-	-	-	-
Thermolysis (80°C)[g)]			0.02	-	0.01	0.68
Thermolysis (75-85°C)[h)]			-	-	0.04	0.63
3-TPO						
Unsensitized[d)]		40	0.03	0.04	0.05	1.1
Benzophenone (69)	0.05	12	0.10	trace	0.04	0.90
2-Benzoyl-naphthalene (60)	0.05	63	0.02	trace	trace	0.74
Thermolysis (80°C)[i)]			0.04	0.03	0.02	1.3
Thermolysis (80°C)[j)]			-	0.02	0.02	0.91
With no peroxides						
Acetophenone (74)[k)]	0.05		-	-	-	-
Benzophenone (69)[l)]	0.05		0.02	-	-	-

a) Concentration of the peroxides: 0.03 mol dm^{-3}. Irradiated at room temperature with 366-nm light from a 1 kW high pressure mercury lamp under degassed condition or under argon atmosphere unless otherwise noted. b) Triplet excitation energy in kcal/mol (S. L. Murov, "Handbook of Photochemistry," Marcel Dekker, New York, 1973). c) Yield based on a mole of peroxide. d) Irradiated with 313-nm light from a 1 kW high pressure mercury lamp. e) A 400 W high pressure mercury lamp was employed with a filter to reduce light intensity. f) Under oxygen. g) Heated for 2880 min. h) Ref. 3. i) Heated for 750 min. j) Ref. 4. k) Irradiated for 78 min. l) Irradiated for 60 min.

Table 2. Effects of Temperature on Product Yields in Direct Photolysis of 2-TPO in Benzene[a)]

Temperature/°C	PhPh	2-ThPh	2-$ThCO_2Ph$	2-$ThCO_2H$	CO_2
60	0.02	trace	0.04	0.74	0.27
40	0.04	trace	0.06	0.62	0.27
29	0.07	0.01[b)]	0.05	0.48	0.28[b)]
15	0.11	0.01	0.06	0.45	
5	0.14	0.01	0.07	0.38	

a) Concentration of 2-TPO: 0.03 mol dm^{-3}. Yield based on a mole of 2-TPO. b) At 25°C.

energies more than 60 kcal/mol can sensitize the decomposition. Actually, triplet benzophenone was quenched by 2-TPO with a nearly diffusion-controlled rate constant of 6.0×10^9 $dm^3mol^{-1}s^{-1}$ as determined by the quenching of phosphorescence of benzophenone at room temperature with single photon counting technique.

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 peroxides. In Table 1, actually the shorter the half-life of 2-TPO in its photolysis, the higher the yield of biphenyl. For example, in direct photolysis of 2-TPO, when the apparent half-life was increased from 25 to 80 min by use of lower light intensity, the yield of biphenyl was decreased from 0.11 to 0.02 mol. This is attributed to a reduced decomposition rate of the peroxide to give lower stationary concentration of TCR, which subsequently resulted in less effective recombination of CHDR into the tetrahydrobiphenyl derivatives. Likewise, 2-benzoylnaphthalene did not so effectively accelerate the decomposition of 2-TPO (half-life: 28 min) as benzophenone (half-life: 16 min) to give a lower yield of biphenyl. Moreover, 3-TPO, on direct photolysis as well as thermolysis, did not give biphenyl effectively; however, benzophenone accelerated the decomposition of the peroxide to give a higher yield of biphenyl.

Finally, it should be noted that the present reaction illustrates an interesting effect of the rate for the radical production on the yield of a product resulting from bimolecular interaction of free radicals.

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