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A New Assisted Reaction in the Photodecomposition Reaction of Dibenzoyl Peroxide

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2,2′-, 2,3′-, and 3,3′-Dimethylbiphenyls were found in the photodecomposition reaction of dibenzoyl peroxide using toluene as solvent. We carried out the experiments to study the external magnetic field, oxygen scavenging, and excitation light intensity effects on their yields. It is concluded that they are produced through the dimerization of (benzoyloxy)methylcyclohexadienyl radicals. This is a new case of the assisted reaction by benzoyloxyl radical. The yields of dimethylbiphenyls were found to be affected remarkably by the small variation of the concentration of benzoyloxyl radical through the three experiments.

The external magnetic field effect upon chemical reactions is one of the most challenging subjects of modern chemistry. We have studied the magnetic field effects upon the photolysis of dibenzoyl peroxide, and have found that the yields of some products in the reaction are dependent upon external magnetic field,[1,2] particularly the yields of newly found products of the reaction, dimethylbiphenyls, show very large magnetic field dependence.[3] In the present paper, the identification and formation mechanism of the newly found products will be discussed in detail, special attention being paid to the scavenger and the excitation light intensity effects on the product yields of this reaction.

During the study of the magnetic field effects upon the photolysis of dibenzoyl peroxide, we found that the yields of some products were sensitive to excitation light intensity. Therefore we have constructed a stabilized light source necessary for excitation and have measured the yields under constant light intensity.

Experimental

The toluene solution (0.5 ml) of dibenzoyl peroxide (**1**) (0.04 mol dm^{-3}) containing chrysene (**2**) (0.002 mol dm^{-3}) as a singlet sensitizer[4] in a Pyrex cell was degassed with the freeze-thaw technique, and was sealed under a nitrogen atmosphere. The irradiation system used in this study is shown in Fig. 1. The cell was set in a water bath with a quartz window. The temperature of the bath was kept 16.5±0.3 °C. The solution was irradiated with an ORC CHM-506-15 1 kW super high pressure mercury lamp through a water filter with Pyrex windows. In order to stabilize the excitation light intensity, we made a feed-back power supply. The light intensity was monitored by a Toshiba TPS 601 phototransister and its signal was returned to the power supply of the lamp. The response time of the feed-back system was about 1 s. The fluctuation of the light intensity was less than ±1.5% and its drift was less than ±2.5% per hour. The excitation light intensity was reduced by placing a copper mesh in front of the sample.

The decrease of **1** was monitored by iodometric titration. In order to decompose **1** almost completely, the irradiation time was set fivefold of the half life time of its disappearance.

The photodecomposition products with molecular weights less than 214 were identified with a Shimadzu 4CMPF gaschromatograph and a Hitachi RMU-6MG gaschromatograph-mass spectrometer. For the former, a 3 mm diameter × 1 m PEG 20 M and Silicone OV-1 columns and 3 mm diameter × 2 m Apiezone L, Polyphenylether 6-ring, Silicone OV-17, and Bentone 34 columns were used. For the latter, 3 mm diameter × 1 m Silicone OV-1 column was used.

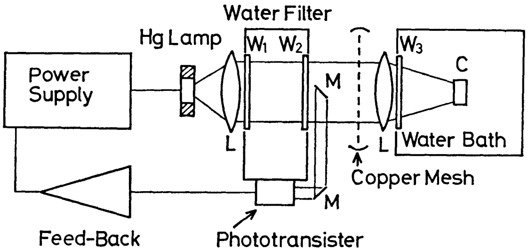


Fig. 1. Reaction apparatus of photodecomposition reaction.
C: Sample cell, L: quartz lens, M: mirror, W_1, W_2: Pyrex windows, W_3: quartz window.

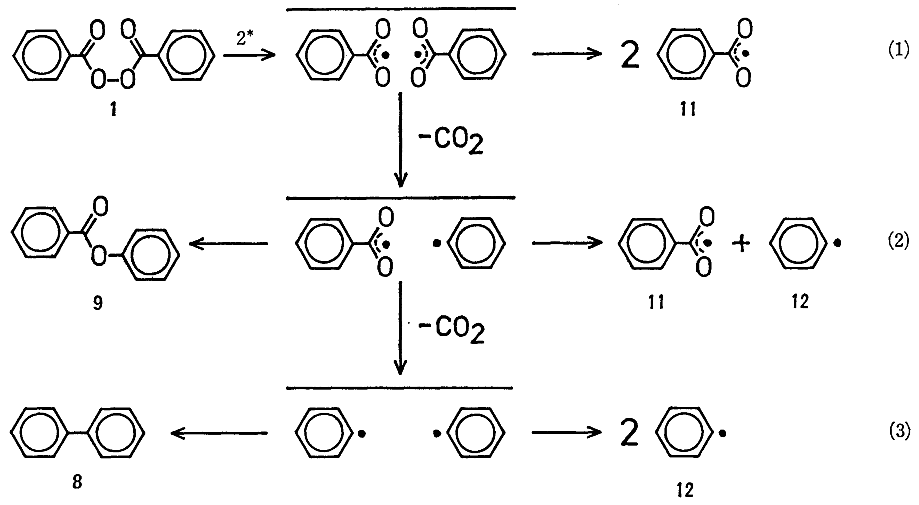
In addition to the established authentic samples[5,6] (biphenyl, 1,2-diphenylethane, diphenylmethane, *o*-, *m*-, and *p*-methylbiphenyls, phenyl benzoate, and *o*-, *m*-, and *p*-tolyl benzoates), 2,2′-, 2,3′-, 2,4′-, 3,3′-, 3,4′-, and 4,4′-dimethylbiphenyls, 2-, 3-, and 4-methyldiphenylmethanes, and benzyl benzoate were prepared for the authentic samples in the present study. Dimethylbiphenyls except for 4,4′-one (Tokyo Kasei) were synthesized after the method described in the literature.[7] 3- and 4-Methyldiphenylmethane were made by Wolff-Kishner reduction of the corresponding ketones.[8] 2-Methyldiphenylmethane was given by Dr. Sakuragi, The University of Tsukuba.[9] Benzyl benzoate was prepared from benzyl alcohol and benzoyl chloride.

The yields were measured by the gaschromatograph with a 3 mm diameter × 1 m PEG 20 M column, terephthalonitrile being used as an external standard. The respective peaks were integrated by a Shimadzu chromatopac ElA integrator and these data were treated statistically using a YHP 9825A desktop computer.

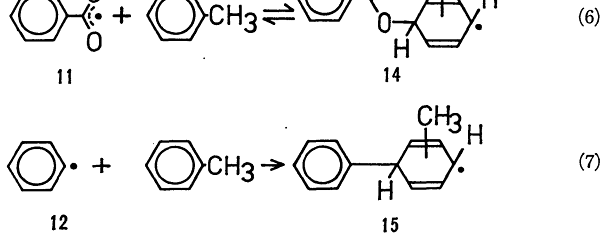
Results and Discussion

In this study, we identified 14 products with molecular weights less than 212.[3] They are listed in Table 1 together with their yields under the high and low excitation light intensities. At first, our consideration will be confined to the case of high intensity excitation. Among the products given in Table 1, dimethylbiphenyls (**3**'s) and benzyl benzoate (**10**) were found for the first time in the present study, while the others have already been identified.[5,6]

The photolysis of **1** proceeds as follows:[5]



As is seen in Eq. 1, the O–O bond of **1** is dissociated to produce a benzoyloxy-benzoyloxy radical pair $(\overline{PhCO_2\cdot\ PhCO_2\cdot})$. It releases carbon dioxide and produces benzoyloxy-phenyl and phenyl-phenyl radical pairs.(See Eqs. 2 and 3.) By the recombination within the cages, **8** and **9** are formed as cage products. The pair which retains from recombination, dissociates to escaping radicals. The escaping benzoyloxy (**11**) and phenyl (**12**) radicals react with solvent (toluene) and form new radicals as shown in the following equations.



The existence of benzyl radical (**13**) was proved by the formation of 1,2-diphenylethane (**5**).[10] Beside the formation of **13**, the cyclohexadienyl radicals (**14** and **15**) are formed as is shown in Eqs. 6 and 7. Their existences were proved by the formation of tolyl benzoates (**6**'s) and methylbiphenyls (**4**'s).[5,11–13] It is worth while to point out that diphenylmethane was not found under the present experimental conditions.[6] This suggests that the reactions of Eqs. 5 and 7 are very fast and the back reaction of Eq. 7 can be disregarded.[13] On the other hand, **11** can be supplied not only by the escaping from the cage but also by the back reaction of Eq. 6.[13]

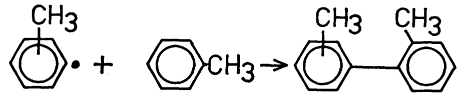
TABLE 1. PRODUCT YIELDS AND THEIR DEPENDENCES ON THE EXCITATION LIGHT INTENSITY[a)]

Products		I_0	$1/3.5\,I_0$
2,2′-Dimethylbiphenyl	(2,2′-**3**)	0.2 %	0.1 %
2,3′-Dimethylbiphenyl	(2,3′-**3**)	2.36	1.44 (61)
3,3′-Dimethylbiphenyl	(3,3′-**3**)	3.56	2.23 (63)
2-Methylbiphenyl	(2-**4**)	6.21	6.86 (110)
Mixture[b)]		23.22	24.30 (105)
o-Tolyl benzoate	(*o*-**6**)	4.09	3.26 (80)
Benzoic acid	(**7**)	102.10[c)]	97.00[c)] (95)
Biphenyl	(**8**)	1.19	1.22 (103)
Phenyl benzoate	(**9**)	16.13	15.73 (98)
m-Tolyl benzoate	(*m*-**6**)	—[d)]	
p-Tolyl benzoate	(*p*-**6**)	—[d)]	
Benzyl benzoate	(**10**)	—[d)]	

a) The yields are presented in mole percent taking benzoyl peroxide as reference. Values in the parentheses are the percentages of the yields under $1/3.5\,I_0$ divided by those under I_0. The experimental errors are less than 5% of respective values for dimethylbiphenyls and biphenyl and less than 3% of those for the others. b) Given value is the sum of the yields of 3- and 4-methylbiphenyls (3- and 4-**4**'s) and 1,2-diphenylethane (1,2-**5**) because of incomplete separation under our VPC conditions. c) The absolute yield of benzoic acid is not so precise as others owing to the VPC conditions, but the relative value in the parentheses are as precise as others. d) These products were identified but their yields were not measured because of their low yields and the incomplete separation between them under our VPC conditions.

Concerning **3**'s six isomers (2,2′-, 2,3′-, 2,4′-, 3,3′-, 3,4′-, and 4,4′-**3**'s) may be expected to exist. But actually, the only three isomers (2,2′-, 2,3′-, and 3,3′-**3**'s) were detected in the present experiment and no para-substituted compounds (2,4′-, 3,4′-, and 4,4′-**3**'s) could be found. The observed ratio of the detected isomers is; 2,2′-**3**:2,3′-**3**:3,3′-**3**=6.8:60.2:100, showing that the yields of the meta-isomers are larger than those of the ortho-isomers.

The most intuitive path for formation of **3**'s is the addition of the methylphenyl (tolyl) radical (**16**) to toluene as follows:[14)]

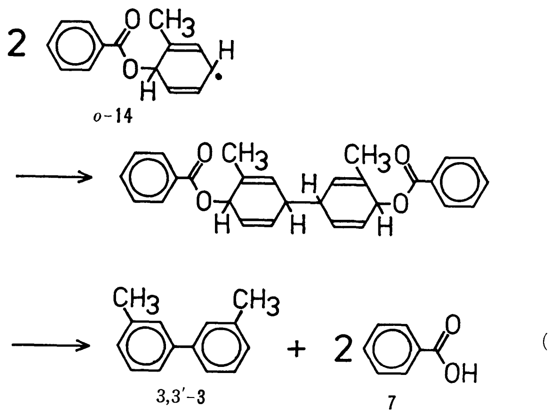


16

(8)

The consideration on the partial rate factors of tolylation, however, rejects the application of this mechanism to formation of **3**'s. The partial rate factors of the reaction shown by Eq. 8 can safely be considered to be similar to those of phenylation of toluene (f_i), the ratio of which was measured to be f_o:f_m:f_p=3.3:1.1:1.3.[15)] Thus this mechanism predicts that the yield of 2,x'-**3** should be larger than that of 3,x'-**3**. This prediction contradicts the observed ratio. Therefore, the direct tolylation mechanism is disregarded.

Another possible mechanism for formation of **3**'s is an assisted reaction mechanism which have been applied to formation of tetraarylmethanes[16)] and *N*-aryldiphenylmethanimines[17)] by **11**. For example, 3,3'-**3** can be formed through the 4-benzoyloxy-3-methyl-2,5-cyclohexadienyl radical (*o*-**14**) as follows:

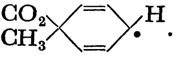


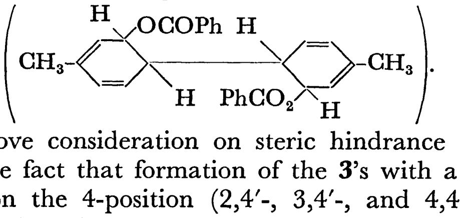
o-14

3,3'-3

7

(9)

The benzoyloxylation of toluene preferably occurs on the *o*-position through the hyperconjugation of the methyl group. The steric hindrance of the methyl group may block benzoyloxylation on the methylsubstituted ring carbon atom leading to  .
Furthermore, the steric hindrance of benzoyloxy residue in **14** is considered to disturb the dimerization reaction at its ortho-position



The above consideration on steric hindrance can explain the fact that formation of the **3**'s with a methyl group on the 4-position (2,4'-, 3,4'-, and 4,4'-**3**'s) is prohibited. Thus the assisted reaction scheme explains the observed yields of **3**'s. According to this mechanism, **3**'s are escape products.

In order to prove this assisted reaction scheme, we have studied the following effects on the reaction yields.

1) The effect of external magnetic field.
2) The effect of oxygen scavenging.
3) The effect of excitation light intensity.

TABLE 2. OXYGEN SCAVENGING EFFECT ON THE YIELDS OF THE PRODUCTS[a)]

Products		Degassed	Aerated	
2,3'-Dimethylbiphenyl (2,3'-**3**)		2.26%	1.45%	(64)
3,3'-Dimethylbiphenyl (3,3'-**3**)		3.47	2.37	(68)
2-Methylbiphenyl	(2-**4**)	5.68	9.34	(165)
Mixture[b)]		20.06	13.92	(68)
o-Tolyl benzoate	(*o*-**6**)	3.24	9.57	(296)
Benzoic acid	(**7**)	81.27[c)]	84.80[c)]	(104)
Biphenyl	(**8**)	1.23	1.12	(91)
Phenyl benzoate	(**9**)	16.28	15.50	(95)

a) The yields and the values in the parentheses have similar meanings as those in Table 1. The experimental errors are the same as those in Table 1. b) Given value is the sum of the yields of 3- and 4-methylbiphenyls (3- and 4-**4**'s) and 1,2-diphenylethane (1,2-**5**) because of incomplete separation under our VPC conditions. c) Same as the note c) in Table 1.

The yields of **3**'s were decreased and increased by the application of the low (9.75 and 78 mT) and high (4.3 T) magnetic field, respectively.[3)] Since this reaction occurs through a singlet precursor in which two radicals in the benzoyloxy-benzoyloxy, benzoyloxy-phenyl, or phenyl-phenyl radical pair have the antiparallel unpaired electron spins, the observed magnetic field dependence corresponds to that of the escape product belonging to the (a-3) type of the theoretical classification.[2,3)] Therefore, from the magnetic field effect, **3**'s are proved to be escape products in accordance with the above mentioned assisted reaction mechanism.

Next, we tried to scavenge escaping radicals. Because this reaction yields various kinds of products, organic scavenger may disturb analysis of the products. So the dissolved oxygen in the solution was used as a radical scavenger. The product yields from the samples with and without degassing are listed in Table 2.[18)] The excitation light intensity was kept constant during the two series of the experiments. The reaction time was 30 min for these experiments. We can see from Table 2 that the yields of 2,3'- and 3,3'-**3**'s were decreased by the dissolved oxygen. This decrease and the increase of the yield of *o*-**6** seem to indicate that **14**'s react with oxygen forming **6**'s and the dimerization reaction of **14**'s to form **3**'s are inhibited by the oxidation. **15**'s are also oxidized forming **4**'s. The increase of 2-**4** is remarkable as is shown in Table 2. But the sum of the yields for 3- and 4-**4** and 1,2-**5** is decreased by oxygen, because **13** is oxidized forming benzyl alcohol and benzaldehyde as final products[19)] and like the case of **14**'s, the dimerization of **13** is also inhibited. On the other hand, the yields of **8** and **9** were not so much changed by oxygen. Therefore, the yields of cage products can be considered to be nearly insensitive to dissolved oxygen. This is also one of the proofs of the fact that **3**'s are escape products.

In order to determine whether **3**'s are formed through the dimerization of **14**'s, we studied the excitation light intensity dependence of their yields. On the assumption that **1** decomposes exponentially and the concentration of radical **n**, [**n**], is proportional to the decomposition rate of **1**, then the yield of the products coming from **n** has the following excitation light intensity dependence.[20] When the formation rate of the product has a first order dependence on [**n**], the product yield does not depend on the excitation light intensity. When the rate has a second order dependence on [**n**], the product yield depends linearly on the excitation light intensity. The above-mentioned excitation light intensity dependence is calculated through an over-simplified model. Thus the actual dependence may be more complex than the above prediction. But it can be used for a qualitative argument.

On the second column of Table 1 are listed the yields in the low excitation light intensity experiment in which the light intensity was reduced to 1/3.5 of that in the high intensity experiment and the reaction time was increased to 70 min from 20 min in the high intensity experiment. We can see from Table 1 that the yields of **3**'s are reduced by lowering the excitation light intensity. The yield of *o*-**6** is also somewhat decreased. These findings may be explained by the following consideration. Owing to the elongation of reaction time, the concentrations of the initially prepared benzoyloxy and phenyl radicals decrease. Thus bimolecular termination reactions between escaping radicals are retarded and the probability of the decomposition of **11** to **12**, which is an unimolecular reaction, increases relatively. This means that the yields of **3**'s and *o*-**6** coming from **11** decrease. Table 1 shows that the decrement is much larger for **3**'s than *o*-**6** which is considered to be produced depending linearly on the concentration of **14**. Therefore it is most probable that the formation rates of **3**'s are nearly proportional to the square of the concentration of **14**. This supports the mechanism that **3**'s are formed by the dimerization of **14**.

The decrease in the yields of the products which come from **11** reflected on the increase in the yields of the products coming from **12**. As is shown in Table 1, by lowering the excitation light intensity the yield of 2-**4** increased a little and the sum of the yields of 3- and 4-**4** and 1,2-**5** increased slightly. The yields of **8** and **9** are not affected so much by the change of the excitation light intensity. This can be interpreted by the fact that they are cage products.

The above-mentioned three experiments show that dimethylbiphenyls are escape products which are formed through the dimerization of (benzoyloxy)methylcyclohexadienyl radicals. This shows the rationality of the assumed assisted dimerization scheme.

This is a new assisted reaction by the benzoyloxy radical. The other cases which have hitherto been studied are formation of tetraarylmethane through the reaction with the triphenylmethyl radical[16] and formation of *N*-aryldiphenylmethanimine through the reaction with the diphenylmethaniminyl radical.[17] Compared with these two cases, the present process is more essential, because **3**'s are produced from two **14**'s and their formation does not need the other radicals.

The excitation light dependence of the radical reaction induced by photodecomposition can be anticipated as the possibility to elucidate the mechanism, although the experiments concerning the change in the excitation light intensity have not been preferred because it can provoke complexities in the reaction by the change in the radical concentrations. The present study shows that the experiment of light intensity dependence is useful for the classification of reaction mechanisms.

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18) The values in the left columns in Tables 1 and 2 except for **7** are somewhat different from each other. This is due to the difference in the excitation light intensity. The fairly large discrepancy of the yield of **7** comes from the VPC conditions. However the values presented in left and right columns within each table do not have such discrepancies between them, because they were obtained under

the same experimental conditions.

19) We identified them under the existence of oxygen but we did not measure their yields.

20) The concentration of **1**, [**1**], decays as follows:

$$[\mathbf{1}](t)=[\mathbf{1}](0)\exp(-\alpha It),$$

here [**1**](0) is its initial concentration. I is the excitation light intensity, and α is the decomposition rate constant. When **n** is formed in proportion to [**1**], [**n**] can be given as follows:

$$[\mathbf{n}](t)=C_{\mathbf{n}}\left(-\frac{\mathrm{d}[\mathbf{1}](t)}{\mathrm{d}t}\right)=C_{\mathbf{n}}\alpha I\exp(-\alpha It),$$

here $C_{\mathbf{n}}$ is the fractional coefficient. If a product is produced in proportion to [**n**] or to the square of [**n**], the yield, $^{1\,\mathrm{or}\,2}Y$ is given respectively as follows:

$$^{1}Y=\lambda_1\int_0^{\infty}[\mathbf{n}](t)\mathrm{d}t=\lambda_1 C_{\mathbf{n}}$$

$$^{2}Y=\lambda_2\int_0^{\infty}([\mathbf{n}](t))^2\mathrm{d}t=\lambda_2 C_{\mathbf{n}}^2\frac{I}{2},$$

here λ_i is the reaction probability.

Thus ^{1}Y is independent of I, and ^{2}Y is linearly dependent on I.