Orientation in Photochemical Substitution of Phenyl and Methyl Radicals in Toluene: MO Calculation

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The photochemical reaction of toluene with phenyl radicals generated from benzoyl peroxide affords methylbiphenyls, the order for the orientation of which is *ortho*/2 > *para* > *meta*/2; this result is the same as that for the thermal reaction. In contrast, the photochemical reaction with methyl radicals generated from acetyl peroxide affords xylenes in the order *ortho*/2 > *meta*/2 > *para* for 254 nm light, and *ortho*/2 > *para* > *meta*/2 for light >290 nm. The orientation of the products obtained with light at 254 nm is different from that obtained in thermal reaction: *ortho*/2 > *para* > *meta*/2. The electron density of toluene and the energies of intermediate cyclohexadienyl radicals have been calculated by molecular orbital methods and likely reaction mechanisms are discussed on the basis of these calculations.

ALTHOUGH thermally generated radicals usually give *ortho*-substituted aromatic products[1] as a result of resonance and inductive effects, toluene with ethyl chloroacetate gives an unusually high ratio of *meta*-substituted product.[2] This result may be ascribed to the participation of the excited state of the substrate.[3]

Here we report the results for reactions of irradiated toluene with phenyl and methyl radicals.

RESULTS

Toluene absorbs at 254 nm (Σ 157 l mol^{-1} cm^{-1}) but shows no absorption above 290 nm. In order to see the effect of orientation, two sets of reaction were carried out: (i) irradiation at 254 nm with a quartz cell and a 30-W low-pressure Hg lamp (*i.e.* excitation of toluene) and (ii) irradiation at >290 nm with a Pyrex cell and a 1-kW high-pressure Hg lamp (*i.e.* non-excitation of toluene). Benzoyl peroxide was used for both thermal and photochemical reactions.

TABLE 1

Yields [a] and isomer distributions [b] of some products in the thermolysis and photolysis of benzoyl peroxide in toluene

Condition	*o*-Methylbiphenyl Yield (%)	*o*-Methylbiphenyl Distribn. (%)	*m*-Methylbiphenyl Yield (%)	*m*-Methylbiphenyl Distribn. (%)	*p*-Methylbiphenyl Yield (%)	*p*-Methylbiphenyl Distribn. (%)	Biphenyl yield (%)	Benzene yield (%)
Temp. (80 °C)	22.2	65 (57)	7.17	21 (18)	4.78	14 (25)	1.19	62.8
hν (>290 nm)	7.45	68 (56)	1.95	18 (18)	1.53	14 (26)	1.80	29.2
hν (254 nm)	9.28	64 (60)	3.06	21 (16)	2.19	15 (24)	3.33	20.4

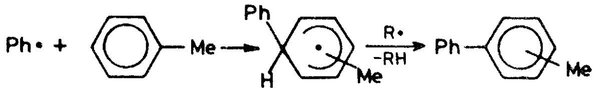
[a] Yields are based on the decomposed benzoyl peroxide. [b] Figures in parentheses mean the distribution in which a statistical factor of 2 for *ortho* and *meta* positions was taken into account.

Benzoyl peroxide has ε values of 3 538 and 30 at 254 and 313 nm respectively; while acetyl peroxide has ε values of 1 170 and 0.9 at 254 and 313 nm respectively.

Reaction of Benzoyl Peroxide.—Irradiation of a toluene solution of 0.1M-benzoyl peroxide in a quartz cell with a 30-W low-pressure Hg lamp at 254 nm for 9 h resulted in 82% decomposition of the benzoyl peroxide, while irradiation of an identical solution in a Pyrex cell with a 1-kW high-pressure Hg lamp (>290 nm light) for 3 h resulted in 87% decomposition. When heated at 80 °C under reflux for 15 h 62% decomposition occurred. The decomposition affords phenyl radicals, which react with toluene as shown in equations (1) and (2).[4]

The yields of some products are listed in Table 1. Other products formed (phenyl benzoate, tolyl benzoate, benzyl benzoate, dimethylbiphenyl *etc.*) were the result of the cage reaction of benzoyl peroxide, substitution of $PhCO_2\cdot$, and H-abstraction from the methyl group of toluene.

$$(PhCO_2)_2 \longrightarrow 2\,PhCO_2\cdot \longrightarrow 2\,Ph\cdot + 2\,CO_2 \qquad (1)$$

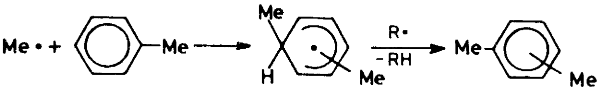


(2)

The total yield of methylbiphenyls is higher in the thermal reactions (34.2% based on the decomposed benzoyl peroxide)[1b] than in the photo-reactions (11—15%). This is ascribed to a cage reaction as described below. The isomer ratios observed in photo- and thermal reactions are analogous, *i.e. ortho* > *meta* > *para*. The orientation, in which the statistical factor of 2 for *ortho* and *meta* is used, is *ortho* > *para* > *meta* (Table 1). This orientation is well known with the thermal reactions of phenyl radicals.[5]

Reaction of Acetyl Peroxide.—Irradiation of a toluene–diethyl ether solution of 0.10M-acetyl peroxide in a quartz cell with a 30-W low-pressure Hg lamp (254 nm light) for 10.5 h resulted in 76% decomposition of acetyl peroxide, while irradiation of an identical solution in a Pyrex cell with a 1-kW high-pressure Hg lamp (>290 nm) for 5 h resulted in 78% decomposition. The decomposition affords methyl radicals, which reacts with toluene as shown in equation (3).[6, 7]

The yields of products are listed in Table 2. The total yield of xylenes was 2—3% based on the decomposed acetyl peroxide. The order of the xylene isomers was *ortho* > *meta* > *para* with > 290 nm light (*i.e.* nonexcited toluene). The orientation, in which the statistical factor of 2 for the *ortho*- and *meta*-positions was taken into account was *ortho* > *para* > *meta* for light > 290 nm, and *ortho* > *meta* > *para* for light at 254 nm (excited toluene). In the thermal reaction of toluene with acetyl peroxide, the ratio of isomers has been reported to be *ortho*, 56%; *meta*, 27%; *para*, 17% (*i.e. ortho*/2, 48%; *meta*/2, 23%; *para*, 29%).[8] The isomer ratio at >290 nm is analogous to this, while that of 254 nm light is quite different (*i.e. ortho* decreases, while *meta* increases).



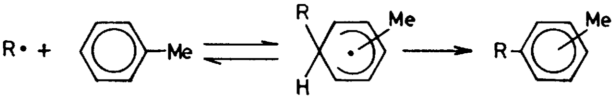
(3)

DISCUSSION

Reaction of Benzoyl Peroxide.—A cage reaction is favoured by irradiation[9] and in the case of benzoyl peroxide gives a stable product (phenyl benzoate); this results in a lowering of the degree of substitution to give methylbiphenyls in comparison with the thermal reaction. As shown in Table 1, there is no difference between the orientations of thermal and photochemical reactions. Hence both reactions may go by way of the same mechanism.[10]

The reaction of ground-state toluene with the radical R• may go through the addition of radical to form the cyclohexadienyl radical (I) [see equation (4)].

We calculated the energies of (1; R = Ph) by the MINDO/3 method,[11] and showed that the stability of (1) decreases in the order: *meta* (—2 986.97 eV) > *ortho* (—2 985.90 eV) > *para* (—2 985.30 eV). Hence the order is not in conformity with the observation: *ortho* > *para* > *meta*. The latter observation agrees with the order of the frontier electron densities for ground-state toluene by which we calculated by the HMO method: *ortho*, 0.381 62; *meta*, 0.301 06; *para*, 0.301 74. Hence the electronic state of the ground-state toluene governs the orientation; *i.e.* the transition state for Ph• substitution is reactant-like.[12,13] Phenyl radicals react principally with the abundant ground-state toluene, and little with photo-excited toluene.



(4)

(I)

As shown, the smaller electron density at the *meta*-position results in a slower rate of *meta*-attack compared with the *ortho*- and *para*- positions.

Reaction of Acetyl Peroxide.—The lower yield of xylenes is ascribed to the preference of the recombination (formation of CH_3-CH_3) and H-abstraction (formation of CH_4) of Me• radical (Table 2).

The reaction of acetyl peroxide with 254 nm light affords an order of orientation of *ortho* > *meta* > *para*, which is different from that of the thermal reaction and suggests the operation of a different mechanism. This is tentatively explained by the participation of excited toluene. As we reported previously,[3] the frontier electron densities calculated by the CI method for the first-excited state of toluene for radical reactions has an order of orientation of *ortho* > *meta* > *para*, although the order of the stability of the cyclohexadienyl radical was calculated by the MINDO/3 method to be *meta* (—191 0.55 eV) > *ortho* (—190 9.03 eV) > *para* (—190 8.90 eV). Hence the orientation at 254 nm agrees with the order of the first-excited frontier electron densities, but not with the order of stability of the cyclohexadienyl radical. Therefore, the electronic state of excited toluene, or the partial contribution of the stability of cyclohexadienyl radicals along with other unknown factors, increase the proportion of the *meta*-fraction.

On the other hand, the reaction with >290 nm light or with heating in the dark shows an order of orientation similar to that for benzoyl peroxide. The orientation in these cases, *ortho* > *para* > *meta*, is in accord with the expectation from the ground-state frontier electron density of toluene, but not with that of (I). This suggests that the transition state is reactant-like[12,14] and that excited toluene does not participate.

TABLE 2

Yields[a] and isomer distribution[b] of some products in the photolysis of acetyl peroxide in toluene

	o-Xylene		*m*-Xylene		*p*-Xylene				
Wavelength (nm)	Yield (%)	Distribn. (%)	Yield (%)	Distribn. (%)	Yield (%)	Distribn. (%)	Ethylbenzene yield (%)	Ethane yield (%)	Methane yield (%)
>290	2.03	57 (49)	0.96	27 (23)	0.55	16 (28)	4.55	32.5	100
254	0.90	51 (45)	0.61	35 (31)	0.24	14 (24)	14.9	54.9	50.4

[a] Yields are based on the decomposed acetyl peroxide. [b] Figures in parentheses mean the distribution in which a statistical factor of 2 for *ortho* and *meta* positions was taken into account.

The lower reactivity of methyl radicals compared with phenyl would give rise to the efficient reaction of Me• with photo-excited (at 254 nm) toluene, the latter having a reactivity much higher than that of the ground-state compound; highly reactive phenyl radicals are, however, less selective and there would be little rate enhancement on excitation of toluene, the radicals reacting with the ground-state compound.

EXPERIMENTAL

Materials.—Toluene (b.p. 110—112 °C) was of guaranteed grade. Benzoyl peroxide, m.p. 104—106 °C, was first grade. No impurities were detected by g.l.c. in these materials. An ethereal solution of acetyl peroxide was prepared by reaction of acetic anhydride with sodium peroxide in ether[16] The solution was diluted with toluene and evaporated by the passage of nitrogen in order to prepare on 0.10M-toluene–ether solution; this avoided the possibility of an explosion on isolation of acetyl peroxide. Authentic samples of methylbiphenyls were prepared [17] by a Gomberg reaction of diazotised toluidines with benzene; *ortho* (3%); *meta* (6%); *para* (7%). All these materials were identified by i.r. and n.m.r. spectroscopy; they had single g.l.c. peaks.

Photo-reaction.—A toluene solution of 0.1M-benzoyl peroxide or 0.1 M-acetyl peroxide was irradiated by a 30-W low-pressure Hg lamp in a cylindrical 10 × 200 nm quartz cell and a 1-kW high-pressure Hg lamp in a Pyrex cell.

Thermal Reaction of Benzoyl Peroxide.—A toluene solution of 0.1 M-benzoyl peroxide was refluxed at 80 °C for 15 h.

Analysis.—The peroxide content of the solution was determined iodometrically according to the following procedure. The peroxide solution (1 ml) was added to a water–acetic acid–methanol (1 : 1 : 2) mixture (30 ml) and then a saturated solution of KI (1 ml) was added. In the case of benzoyl peroxide, the mixture was titrated directly with $Na_2S_2O_3$ after being kept at room temperature for 30 min. For acetyl peroxide, the mixture was boiled for a few minutes and the warm solution was then titrated.

The reaction products were analysed by g.l.c. using a Yanagimoto GCG 180 gas chromatograph and GC-MS with a Shimadzu GCMS-7000 mass spectrometer. A Bentone 34 column (2 m) for benzoyl peroxide solution and a Bentone 34 + DIDP (5 + 5%) column (2 m) for acetyl peroxide solution were used. The identification of products was done by g.c.–mass spec. as well as by comparison of g.l.c. peaks with those of authentic samples. The estimation of yield was done by g.l.c. using internal standards of anisole for benzoyl peroxide and mesitylene for acetyl peroxide.

Gaseous products, methane and ethane, produced in the reaction of acetyl peroxide, were also analysed by g.l.c. using a Porapak QS column (2 m).

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