382. *Homolytic Aromatic Substitution. Part XIII.* The Reaction of Benzoyl Peroxide with Naphthalene.*

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The decomposition of benzoyl peroxide in dilute solution in naphthalene at 85° and at 100° has been investigated. The main products have been found to be mixtures of the isomeric phenylnaphthalenes, naphthyl benzoates, and dinaphthyls, whose compositions have been measured by infrared spectroscopy. The results are discussed in terms of the mechanism of the various competing reactions and the relative reactivity of the 1- and the 2-position of the naphthalene nucleus towards attack by free radicals.

THE reaction of naphthalene with aryl radicals from various sources has been studied by several groups of workers with confusing and, in some instances, conflicting results. Möhlau and Berger [1] found that naphthalene and benzenediazonium chloride in the presence of a little aluminium chloride yielded a mixture of 1- and 2-phenylnaphthalene containing about 90% of the 1-isomer; chlorobenzene was also found among the products. Huisgen and Sorge [2] studied the reaction of phenyl radicals derived from *N*-nitroso-acetanilide with a solution of naphthalene in benzene, and isolated a mixture of 1- and 2-phenylnaphthalene in 33% yield. The mixture was found to contain about 16% of the 2-isomer. Diphenyl was also obtained from these reactions, and was considered to be formed by the reaction of the phenyl radicals with benzene. From the relative amounts of diphenyl and 1- and 2-phenylnaphthalene isolated, naphthalene was estimated to be

* Part XII, *J.*, 1956, 1475.

[1] Möhlau and Berger, *Ber.*, 1893, **26**, 1196.

[2] Huisgen and Sorge, *Annalen*, 1950, **566**, 162.

22 times more reactive than benzene towards attack by phenyl radicals. Waters[3] studied the decomposition of benzenediazonium chloride in a solution of naphthalene in acetone, to which zinc dust was gradually added. 2-Phenylnaphthalene was isolated from the resulting mixture, and the presence of 1-phenylnaphthalene was inferred from the isolation of *o*-benzoylbenzoic acid from the products of oxidation of the mixture with chromic acid. Grieve and Hey[4] studied the reaction of *o*-carboxymethylphenyl radicals, derived from methyl anthranilate, with a solution of naphthalene in carbon tetrachloride. From the products, methyl *o*-α-naphthylbenzoate and a little methyl *o*-chlorobenzoate were isolated. Boyland and Sims[5] studied the reaction between equimolar quantities of benzoyl peroxide and naphthalene in chlorobenzene as solvent. Carbon dioxide, benzoic acid, and a mixture of 1- and 2-naphthyl benzoate were the only products identified. Dannley and Gippin,[6] who studied the reaction of benzoyl peroxide with various 1-substituted naphthalenes, were able to isolate only mixtures of esters. No products of phenylation were found. Lynch and Pausacker[7] investigated the reaction of benzoyl peroxide with naphthalene and isolated from the reaction mixture carbon dioxide, benzoic acid, 1- and 2-naphthyl benzoate (as 1- and 2-naphthol and benzoic acid after hydrolysis), 1- and 2-phenylnaphthalene, a high-boiling substance which was thought to be 1 : 4-diphenylnaphthalene, and an involatile residue of unspecified physical properties. In the most recent publication on the phenylation of naphthalene, Huisgen and Grashey[8] have described the phenylation of naphthalene in benzene solution by phenylazotriphenylmethane at 45°, by nitroso-acetanilide at 20—25°, and by benzoyl peroxide at 80°. From these reactions mixtures of 1- and 2-phenylnaphthalene containing approximately 80% of the 1- and 20% of the 2-isomer were isolated. From a competitive reaction with a mixture of naphthalene and pyridine with nitrosoacetanilide, it was found that naphthalene was phenylated 13 times more rapidly than pyridine. From a reaction between benzoyl peroxide and naphthalene a fraction, b. p. 210—280°/11 mm., was isolated, which crystallised in colourless leaflets. On crystallisation from benzene–ethanol, this material had m. p. 143—145° but, when the fused compound was allowed to solidify, it had m. p. 159°. The authors suggested that this compound is a diphenylnaphthalene. However, it is almost certainly 1 : 1′-dinaphthyl, since Orchin and Friedel[9] describe 1 : 1′-dinaphthyl as having these properties.

In the present work, which was completed before the publication of Lynch and Pausacker's and Huisgen and Grashey's papers, an attempt has been made partly to resolve the confusion which surrounds the reactions of naphthalene with free radicals by a detailed study of the relatively simple case of the decomposition of benzoyl peroxide in dilute solution in naphthalene. The formation of 1- and 2-phenylnaphthalene and 1- and 2-naphthyl benzoate has been confirmed, although at the lower temperature (85°) the yields are somewhat lower than might have been expected. In addition, the formation of 1 : 1′-, 2 : 2′-, and 1 : 2′-dinaphthyl, which have been found in the product to an appreciable extent (30—35%), is now reported for the first time. The discovery of the isomeric dinaphthyls in the product implies that Lynch and Pausacker's interpretation[7] of the stoicheiometry of the reaction must be regarded as incorrect. The proportions in which the isomeric phenylnaphthalenes, naphthyl benzoates, and dinaphthyls are formed have also been measured.

EXPERIMENTAL

Reagents.—Benzoyl peroxide (from Messrs. May and Baker) was purified according to the procedure described in Part II.[10] *NN*-Dimethylformamide (from B.D.H.) was dried (CaSO₄)

[3] Waters, *J.*, 1939, 864.
[4] Grieve and Hey, *J.*, 1938, 108.
[5] Boyland and Sims, *J.*, 1953, 2966.
[6] Dannley and Gippin, *J. Amer. Chem. Soc.*, 1952, **74**, 332.
[7] Lynch and Pausacker, *Austral. J. Chem.*, 1957, **10**, 165.
[8] Huisgen and Grashey, *Annalen*, 1957, **607**, 46.
[9] Orchin and Friedel, *J. Amer. Chem. Soc.*, 1946, **68**, 573.
[10] Augood, Hey, and Williams, *J.*, 1952, 2094.

and distilled through a 25 cm. helix-packed column (b. p. 152°). Naphthalene (B.D.H.; May and Baker) was purified by crystallisation from ethanol to constant m. p. 80°. *cyclo*Hexane (May and Baker) was washed repeatedly with concentrated sulphuric acid, saturated sodium hydrogen carbonate solution, and water. After drying (CaCl$_2$) it was distilled through a 25 cm. helix-packed column (b. p. 81·6°/778 mm., n_D^{15} 1·4286, m. p. 6·5°). *n*-Heptane (May and Baker) was shaken with concentrated sulphuric acid until the washings were colourless, then with water, then dilute potassium hydroxide, and finally water again until the washings were neutral to litmus. It was dried (KOH) and fractionally distilled, and the fraction of b. p. 98° was collected.

1-Phenylnaphthalene, prepared by the reaction of 1-naphthoyl peroxide with benzene, was distilled twice *in vacuo* (b. p. 117°/0·1 mm.). A specimen of 2-phenylnaphthalene prepared by Hey and Lawton [11] was crystallised from aqueous ethanol to constant m. p. 102°. 1- and 2-Naphthol (B.D.H.) were treated with activated charcoal in ethanol and crystallised to constant m. p. 96° and 123° respectively. 1- and 2-Naphthyl benzoate were crystallised from aqueous ethanol to constant m. p. 55° and 106° respectively. 1 : 1′-Dinaphthyl was prepared by an Ullmann reaction from 1-iodonaphthalene, and recrystallised from ethanol to constant m. p. 160° (Found: C, 94·4; H, 5·5. Calc. for C$_{20}$H$_{14}$: C, 94·45; H, 5·55%). Orchin and Friedel [9] report m. p. 145—147° and 159·5—160·5°. The present specimen of 1 : 1′-dinaphthyl showed no sign of melting in the region of 145° and melted only at 160°. When this form was recrystallised from benzene–ethanol it melted first at 144—146°, but subsequently solidified and re-melted at 159—160°. The infrared spectra in *cyclo*hexane solution of the single- and double-melting forms were identical, whereas the infrared spectra of Nujol mulls of the two forms showed differences. This peculiar behaviour of 1 : 1′-dinaphthyl is now under investigation. 1 : 2′-Dinaphthyl, prepared by Hooker and Fieser's method [12] from 2-bromonaphthalene and α-tetralone, was crystallised from light petroleum (b. p. 80—100°) to constant m. p. 75°. Hooker and Fieser [12] report m. p. 74·5—75°. 2 : 2′-Dinaphthyl was prepared by means of an Ullmann reaction, using 2-bromonaphthalene and copper bronze. It was obtained as white plates, m. p. 186—186·5° (Hooker and Fieser [12] report m. p. 185—186°) (Found: C, 94·4; H, 5·5. Calc. for C$_{20}$H$_{14}$: C, 94·45; H, 5·55%).

Decomposition of Benzoyl Peroxide in Naphthalene.—Experiment 1 was conducted with a relatively high concentration of benzoyl peroxide in order to identify the various products formed, and the results are therefore not quantitative. Benzoyl peroxide (15 g.) was allowed to decompose in naphthalene (100 g.) in a thermostat at 85° for 72 hr. In addition to free benzoic acid (9 g.) the following products were isolated by standard methods: (*a*) a pale yellow liquid (8 g.; b. p. 117—145°/0·1 mm.), which solidified and was shown to be a mixture of 1- and 2-phenylnaphthalene and 1- and 2-naphthyl benzoate by a comparison of its infrared spectrum with the spectra of authentic specimens of the four components; (*b*) 2 : 2′-dinaphthyl, m. p. and mixed m. p. 185—186·5° (Found: C, 94·6; H, 5·5%), whose ultraviolet spectrum was identical with that recorded in the literature [13] and whose infrared spectrum with that of an authentic specimen; and (*c*) a mixture of 1 : 1′- and 1 : 2′-dinaphthyl, from which the less soluble 1 : 1′-isomer, m. p. and mixed m. p. 158—160° (Found: C, 94·4; H, 5·6%), was obtained by crystallisation from dilute ethanol (cf. Smith [14]). The ultraviolet spectrum was identical with that recorded in the literature [13] and the infrared spectrum (*cyclo*hexane solution) was identical with that of a similar solution of authentic 1 : 1′-dinaphthyl.

Experiments 2—7 were carried out quantitatively, with benzoyl peroxide (5 g.) in naphthalene (150 g.), at 85° for 72 hr. (experiments 2—5) or at 100° for 24 hr. (experiments 6 and 7). When the decomposition was complete the reaction mixtures were diluted with benzene (400 ml.) and extracted exhaustively with saturated sodium hydrogen carbonate solution (10 × 50 ml.) to remove free benzoic acid. They were then worked up by the general procedure described in Part II,[10] except that 5N-sodium hydroxide was used to hydrolyse the esters and that the aqueous solution obtained from this hydrolysis was treated by standard methods for the isolation of 1- and 2-naphthol as well as benzoic acid. In the final distillation of the diaryl mixture at 0·1 mm., it was found that all the phenylnaphthalenes distilled below 140°, and that the dinaphthyls distilled at 160—200° at this pressure. The amount of involatile residue was extremely small. The results are given in Table 1.

[11] Hey and Lawton, *J.*, 1940, 374.

[12] Hooker and Fieser, *J. Amer. Chem. Soc.*, 1936, **58**, 1216.

[13] Friedel and Orchin, " Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, New York, 1951.

[14] Smith, *J.*, 1877, **32**, 551.

Experiment 8 was conducted in order to determine whether any benzene is formed in the reaction. Benzoyl peroxide (5 g.) was allowed to decompose in naphthalene (150 g.) in a thermostat at 80° for 72 hr. The reaction flask was connected with a reflux condenser to prevent loss of benzene. Ten minutes before the flask was removed from the thermostat, *n*-heptane (50 ml.) was added to the mixture, so that on removal from the thermostat a homogeneous

TABLE 1.

Experiment no.:	2	3	4	5	6	7 *
Free benzoic acid (g.)	2·79	2·83	2·85	2·82	2·49	2·48
Naphthols (g.)	0·95	0·96	0·93	0·94	0·70	0·73
Benzoic acid from esters (g.)	1·43	1·35	1·38	1·39	1·11	1·17
Phenylnaphthalene fraction (g.)	0·87	0·84	0·85	0·87	1·83	1·89
Dinaphthyl fraction (g.)	1·54	1·60	1·65	1·65	1·40	1·41
High-boiling residue (g.)	0·21	0·19	0·19	0·16	0·19	0·16
Peroxide accounted for (%)	94·0	92·9	94·0	93·8	93·1	94·8

* Experiments 2—5 at 85°, and 6 and 7 at 100°.

mixture was obtained. About 40 ml. of the solvent were then distilled out of the mixture through a 25 cm. helix-packed column. Any benzene formed in the reaction would be expected to co-distil with this *n*-heptane. The distillate was treated with a mixture of concentrated sulphuric acid (10 ml.) and fuming nitric acid (10 ml.) at room temperature. When addition of the mixed acids was complete the mixture was boiled under reflux for 15 min., and poured on ice (25 g.). The mixture was extracted with ether (5 × 40 ml.), and the extracts were washed repeatedly with water to remove all trace of acids, and finally dried (Na_2SO_4). The solvents were distilled off, leaving a small yellowish-brown residue which was dissolved in ethanol (10 ml.). This solution was poured into ice-water (50 ml.), and the residue removed by filtration. The residue (0·24 g.) was semi-solid and its infrared spectrum showed no correlation with that of *m*-dinitrobenzene. Thus it can be inferred that only very little, if any, benzene is formed in the reaction. When the *n*-heptane was distilled out of the mixture, a small amount of naphthalene sublimed with it, and it is probable that the semi-solid obtained on treatment with nitric acid was composed mainly of nitro-derivatives of naphthalene.

Determination of Ratios of Isomers.—The spectrographic analysis of the mixtures of phenylnaphthalenes, dinaphthyls, and naphthols obtained from reactions 2—7 was carried out with a Grubb-Parsons double-beam infrared spectrometer fitted with an automatic pen-recorder. For each analysis of a mixture of isomers the spectra of the pure isomers were first recorded in the range 2—15 μ, Nujol mulls between rock-salt plates being used in order to locate the " key bands " for the analysis. These were all found to lie in the range 12—14 μ, so that dimethylformamide and *cyclo*hexane were suitable solvents for all the analyses. The spectra of solutions of known concentration of the pure isomers and of the mixtures, in a 0·01″ rock-salt cell, were then recorded. The calculations of the composition of the mixtures from the infrared spectra were carried out as described in Part III.[15]

(i) *Naphthols*. Dimethylformamide was used as solvent and measurements were made at the following characteristic absorption maxima: 1-naphthol, 12·52 μ, 2-naphthol, 13·26 μ. The weights of the two components were calculated directly. The accuracy of the method was tested by the analysis of two synthetic mixtures (A) and (B) of known composition. These

TABLE 2. *Analyses of mixtures of known composition.*

	Naphthols					Phenylnaphthalenes					Dinaphthyls			
	Known (%)		Found (%)			Known (%)		Found (%)			Known (%)		Found (%)	
	1-	2-	1-	2-		1-	2-	1-	2-		1 : 1′-	1 : 2′-	1 : 1′-	1 : 2′-
A	59·2	40·8	59·2	40·8	C	79·6	20·4	80·2	19·8	E	29·4	70·6	30·4	69·6
B	75·1	24·9	74·7	25·3	D	77·0	23·0	76·9	23·1	F	58·7	41·3	58·6	41·4

results are given in Table 2. The results of the analysis of the mixtures obtained from experiments 2—7 are given in Table 3. The purity of the naphthol mixtures is indicated by the sum of the weights of the two components as determined by the analysis, which in all the experiments is not less than 97% of the weight of the original naphthol mixture taken. The data given in Tables 2 and 3 were calculated by expressing the weight of each component in turn as a percentage of the sum of the determined weights of both components.

[15] Augood, Hey, and Williams, *J.*, 1953, 44.

(ii) *Phenylnaphthalenes.* The reaction mixture was twice redistilled at 0·1 mm. to ensure removal of any dinaphthyls. The product was a pale yellow liquid which partly solidified. *cyclo*Hexane was used as solvent and measurements were made at the following characteristic absorption maxima: 1-phenylnaphthalene, 12·48 μ; 2-phenylnaphthalene, 12·22 μ. The accuracy of the determination was tested by the analysis of synthetic mixtures (C) and (D) of

TABLE 3. *Products obtained from the reactions of benzoyl peroxide with naphthalene.*

Expt. no.	Naphthols (%)		Phenyl-naphthalenes (%)		2 : 2'-Di-naphthyl (g.)	1 : 1'- and 1 : 2'-Dinaphthyls (%)		Total dinaphthyls (%)		
	1-	2-	1-	2-		1 : 1'-	1 : 2'-	1 : 1'-	1 : 2'-	2 : 2'-
2	73·9	26·1	82·2	17·8	0·064	56	44	54	42	4
3	72·7	27·3	83·1	16·9	0·064	57	43	55	41	4
4	72·2	27·8	82·3	17·7	0·066	56	44	54	42	4
5	72·7	27·3	80·5	19·5	0·065	55	45	53	43	4
6	68·9	31·1	80·0	20·0	0·043	56	44	54	42	4
7	67·4	32·6	79·4	20·6	0·041	56	44	54	43	3

known composition (Table 2). The method of calculation employed was similar to that used in the analysis of the mixtures of 1- and 2-naphthol. The sum of the weights of the two components as determined in the analysis was, in all the experiments, not less than 99% of the weight of the phenylnaphthalene mixture taken. The results of the analysis of the mixtures obtained from experiments 2—7 are given in Table 3.

(iii) *Dinaphthyls.* The dinaphthyl fraction was digested with light petroleum (b. p. 80—100° 20 ml.), and the resulting solution allowed to cool. Pale yellow crystals of 2 : 2'-dinaphthyl were deposited and were removed by filtration (m. p. and mixed m. p. 182—184°). The weights of 2 : 2'-dinaphthyl obtained in experiments 2—7 are given in Table 3. The filtrate, after removal of 2 : 2'-dinaphthyl, was transferred to a small flask packed with glass wool, and the light petroleum was removed by distillation at atmospheric pressure. The dinaphthyls distilled at 0·1 mm. as a pale yellow viscous liquid which solidified, and this product was used for isomer analysis of 1 : 1'- and 1 : 2'-dinaphthyl.

1 : 2'-Dinaphthyl has absorption maxima of medium intensity at 12·17 and 13·42 μ. At these wavelengths the absorption due to 1 : 1'-dinaphthyl is negligible. The analysis of the mixtures of 1 : 1'- and 1 : 2'-dinaphthyl for 1 : 2'-dinaphthyl by measuring the intensity of absorption of mixtures in *cyclo*hexane at these wavelengths was carried out. The amounts of 1 : 1'-dinaphthyl were obtained by difference. The accuracy of the method was estimated by analysis of mixtures (E) and (F) of known composition (Table 2).

The spectra of mixtures from experiments 2—7 in solution in *cyclo*hexane contained a band of very weak intensity at 13·13 μ which was not present in the spectra of either 1 : 1'- or 1 : 2'-dinaphthyl. Also, the intensity of the absorption band at 13·42 μ was slightly greater than that expected when the percentage of 1 : 2'-dinaphthyl in the mixtures was calculated on the basis of the intensity of absorption at 12·17 μ. Thus it appears that the dinaphthyl fractions contained a small amount of extraneous material, possibly diphenylnaphthalenes. It is, of course, conceivable that this extraneous material is 2 : 2'-dinaphthyl. This is, however, considered unlikely, since the solubility of 2 : 2'-dinaphthyl in *cyclo*hexane at room temperature is extremely low and, moreover, a saturated solution of 2 : 2'-dinaphthyl in *cyclo*hexane showed negligible absorption at this wavelength. Likewise, the spectrum of 2 : 2'-dinaphthyl as a mull in Nujol showed negligible absorption at 13·13 μ. The intensity of the band at 13·13 μ was greater in spectra of mixtures from reactions at 100° than from those at 85°, and it was estimated that the dinaphthyl mixtures from reactions at 85° and 100° contained approximately 5% and 15%, respectively, of the extraneous material. Taking this into account, we obtained isomer ratios by using the absorption maximum at 12·17 μ and assuming the absorption due to the extraneous material to be small at this wavelength (Table 3). Taking into account the 2 : 2'-dinaphthyl already isolated, we obtained figures (Table 3) for the proportions of the isomeric dinaphthyls in the original mixtures.

DISCUSSION

The results reported in this communication are summarised in Tables 4, 5, and 6. The mean molar yields of the various products of the reaction at the two temperatures at which it was investigated are given in Table 4.

The mean percentage compositions of the mixtures of isomeric naphthols and phenyl-naphthalenes at the two temperatures are given in Table 5, and those of the mixtures of of dinaphthyls in Table 6.

TABLE 4.

	Mean yield (moles/mole benzoyl peroxide)	
Product	85°	100°
Free benzoic acid	1·12	0·99
Naphthols	0·32	0·24
Benzoic acid from esters	0·55	0·45
Phenylnaphthalenes	0·20	0·44
Dinaphthyls *	0·29	0·23
Peroxide not accounted for	0·06	0·06

* Calc. on the basis that the dinaphthyl fraction at 85° contains 95% of dinaphthyls and at 100° 85% of dinaphthyls.

TABLE 5.

	Mean composition (%)				Mean composition (%)	
	1-	2-			1-	2-
Naphthols (85°)	72·9	27·1	Phenylnaphthalenes (85°)		82·0	18·0
,, (100°)	68·2	31·8	,,	(100°)	79·7	20·3

TABLE 6.

	Mean percentage composition		
	1 : 1'-	1 : 2'-	2 : 2'-
Dinaphthyls (85°)	54	42	4
,, (100°)	54	42	4

The major hydrocarbon products of the reaction are seen to be phenylnaphthalenes and dinaphthyls. Very little polyphenylation, which would yield, for example, diphenyl-naphthalenes, was found. This contention is supported by the observation that the free benzoic acid isolated was pure, as indicated by its melting point, and contained little or no diphenylcarboxylic acids. This is in contrast to the situation which obtains when further phenylation of the primary reaction products takes place to an appreciable extent, diphenyl-carboxylic acids, arising from phenylation of the benzoic acid formed as a primary product, being then formed and sometimes isolated (see, for example, Hey, Pengilly, and Williams [16]). The product which was isolated and thought to be 1 : 4-diphenylnaphthalene by Lynch and Pausacker [7] is almost certainly a mixture of dinaphthyls, which these authors did not identify as reaction products. The appreciable amount of high-boiling residue found by these workers may also consist largely of dinaphthyls, which would probably be involatile under the conditions of Lynch and Pausacker's final distillation. The absence of polyphenylation products in this reaction is consistent with the high reactivity of naphthalene towards attack by phenyl radicals (Huisgen and Sorge [2]). This point has also been discussed by Augood and Williams,[17] who pointed out that the formation of polyphenylation products was inconsistent with the high reactivity of naphthalene. This anomaly is now resolved by the demonstration that the high-boiling material consists of dinaphthyls, very little, if any, polyphenylnaphthalenes being formed.

The phenylnaphthalenes are undoubtedly formed by direct phenylation of naphthalene by phenyl radicals derived from the benzoyl peroxide. The proportions in which the 1- and the 2-isomers are formed demonstrate the greater reactivity of the 1-position to free-radical attack, and are in this respect in accord with the predictions of theoretical treatments depending on the calculation of free-valence numbers [18] and of atom localisation energies.[19]

[16] Hey, Pengilly, and Williams, *J.*, 1955, 6.

[17] Augood and Williams, *Chem. Rev.*, 1957, **57**, 123.

[18] Sandorfy, *Bull. Soc. chim. France*, 1949, **16**, 615; Burkitt, Coulson, and Longuet-Higgins, *Trans. Faraday Soc.*, 1951, **47**, 553; Coulson and Longuet-Higgins, *Rev. Sci.*, 1947, **85**, 929; Coulson, *J. Chim. phys.*, 1948, **45**, 243.

[19] Wheland, *J. Amer. Chem. Soc.*, 1942, **64**, 900.

The formation of the isomeric dinaphthyls is believed to be due to the abstraction of hydrogen from the nucleus of naphthalene to give 1- and 2-naphthyl radicals, which in turn attack the solvent naphthalene in much the same way as phenyl radicals. This process results in the formation of all three dinaphthyls, since both 1- and 2-naphthyl radicals are capable of effecting substitution at the 1- and the 2-position of naphthalene. The proportions in which the isomeric dinaphthyls are formed $(1 : 1'- > 1 : 2'- > 2 : 2'-)$ are consistent with the reasonable assumptions (a) that for hydrogen-abstraction, as for substitution, the 1-position is the more reactive, and therefore that more 1- than 2-naphthyl radicals are formed, and (b) that the order of reactivity of the 1- and the 2-position in naphthalene $(1- > 2-)$ is the same for naphthylation as for phenylation, so that substitution by both 1- and 2-naphthyl radicals takes place more readily at the 1-position. The radical responsible for the initial abstraction of hydrogen from the naphthalene nucleus is thought to be benzoyloxy rather than phenyl, on account of the failure to identify benzene among the products, since benzene must be formed if phenyl radicals participate in the hydrogen-abstraction. The participation of the benzoyloxy- rather than the phenyl radical in this reaction is probably due to the high reactivity of the naphthalene nucleus towards free-radical attack. Consequently it appears that direct reaction of the normally unstable benzoyloxy-radicals becomes a sufficiently advantageous reaction path to allow it to compete with the more usual processes of decarboxylation and subsequent reaction of the resulting phenyl radicals. The benzoyloxy-radicals react with naphthalene in two ways, namely, by hydrogen-abstraction, to give naphthyl radicals and ultimately dinaphthyls, and by direct substitution to give naphthyl benzoates. Since, as established above, phenyl radicals do not react with naphthalene by hydrogen abstraction, in contrast with benzoyloxy-radicals, it is obvious that the alternative reaction of direct substitution is energetically favoured in this case. The source of this energetic advantage is probably the extra resonance energy associated with the formation of a diaryl, which results in a measure of stabilisation of the transition state and consequent lowering of the activation energy for substitution relative to hydrogen-abstraction by phenyl radicals, as compared with the corresponding quantities for substitution and hydrogen-abstraction by benzoyloxy-radicals. The inability of phenyl radicals to react with naphthalene by hydrogen-abstraction is also demonstrated by the fact that dinaphthyls do not appear to be formed when sources of phenyl radicals are used which do not involve the intermediation of benzoyloxy-radicals.[1,2]

As implied in the foregoing discussion, the naphthyl benzoates are formed most probably by direct substitution in the naphthalene nucleus by benzoyloxy-radicals. The proportion in which the 1- and the 2-isomers are formed is given by the proportion in which 1- and 2-naphthol occur in their hydrolysis product, and it may be seen from Table 5 that while the 1-position is still the more reactive, more substitution in the 2-position takes place in benzoyloxylation than in phenylation. This difference may be due to the difference in polar character of the benzoyloxy- and the phenyl radical, or to steric difficulty of substitution by the benzoyloxy-radical in the 1-position, or to a combination of both factors. The experimental evidence is at present insufficient to permit further profitable discussion of these effects and of other possible modes of formation of the naphthyl benzoates, which may include, for instance, the reaction between naphthyl radicals and benzoyl peroxide. The experimental results show that for both benzoyloxylation and phenylation of naphthalene the amount of the 2-isomer increases slightly with rise in temperature. This is in accordance with most other substitution reactions in which isomer distribution becomes more nearly statistical as the temperature is raised. The extent of arylation of naphthalene by phenyl radicals from benzoyl peroxide increases markedly as the reaction temperature is increased. This is presumably a result of easier decarboxylation of the benzoyloxy-radicals at higher temperatures. Consequently, the extent of substitution in naphthalene by benzoyloxy-radicals to give naphthyl benzoates decreases as the temperature is raised, and this is amply demonstrated by the experimental results.

In addition to the results presented in this paper we have investigated the reactions of di-*o*-, -*m*-, and -*p*-nitrobenzoyl peroxides with naphthalene. The main product in each case is a mixture of naphthyl nitrobenzoates, accompanied by a relatively small quantity of a mixture of dinaphthyls. No arylation of naphthalene takes place with any of these reagents. These and other results on the homolytic reactions of naphthalene will be presented in future papers.

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