598. *Homolytic Aromatic Substitution. Part XXVI.* The Reactions of Some Aroyl Peroxides with Naphthalene.*

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The products of reactions of *o*- and *p*-nitrobenzoyl, *o*- and *p*-chlorobenzoyl, and 1- and 2-naphthoyl peroxide with naphthalene have been subjected to quantitative study. The composition of the mixtures of isomeric naphthols arising from the hydrolysis of the naphthyl esters formed in these reactions, and of the mixtures of isomeric binaphthyls formed in the reactions with 1- and 2-naphthoyl peroxide, have been determined by infrared spectroscopy. The results are discussed in terms of the polar characteristics of the various radicals, and are shown to be consistent with current theory.

The results reported in Part XIII[1] indicate that the free radicals formed by the decomposition of benzoyl peroxide react with naphthalene in three distinct ways. These are: (*a*) substitution by benzoyloxy-radicals to give 1- and 2-naphthyl benzoate, (*b*) substitution by phenyl radicals to give 1- and 2-phenylnaphthalene, and (*c*) hydrogen abstraction by benzoyloxy-radicals to give 1- and 2-naphthyl radicals, which then react with naphthalene by substitution to give 1,1'- 1,2'-, and 2,2'-binaphthyl. The distribution of the various isomers of the different products was also measured. It was therefore considered of interest to investigate the reactions of some other aroyl peroxides with naphthalene, in order to determine the influence of substituents in the nuclei of the aryl and aroyloxy-radicals on the relative extent to which processes (*a*), (*b*), and (*c*) occur, and on the isomer distribution in the various products. In addition, in order to throw more light on the mechanism of process (*c*), the reactions of 1- and 2-naphthoyl peroxide with naphthalene were studied. The results of these experiments, in which *o*- and *p*-chlorobenzoyl, *o*- and *p*-nitrobenzoyl, and 1- and 2-naphthoyl peroxide were allowed to decompose in naphthalene, are now reported and discussed.

Experimental

Naphthalene was purified as described in Part XIII.[1] The aroyl peroxides were prepared from the corresponding acid chlorides by Hey and Walker's standard method.[2] The m. p.s of the products were all in agreement with those reported by Hey and Walker,[2] with the exception of *o*-chlorobenzoyl peroxide, which was not prepared by those workers. Our results for this compound are, however, in agreement with those of Breitenbach and Bremer[3] who reported its preparation.

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* Part XXV, preceding paper.

[1] Davies, Hey, and Williams, *J.*, 1958, 1878.

[2] Hey and Walker, *J.*, 1948, 2213.

[3] Breitenbach and Bremer, *Ber.*, 1943, **76**, 1124.

The isomeric binaphthyls were prepared as described in Part XIII.[1]

1-*Naphthyl* p-*chlorobenzoate* was prepared by reaction of 1-naphthol (4 g.) with *p*-chlorobenzoyl chloride (5 g.) in the presence of pyridine (10 ml.). The mixture was left overnight, diluted with water, and filtered. The ester (6·5 g.) after crystallisation from methanol had m. p. 115·5° (Found: C, 72·1; H, 3·9; Cl, 12·4. $C_{17}H_{11}ClO_2$ requires C, 72·2; H, 3·9; Cl, 12·5%). The other esters were prepared by analogous methods.

2-*Naphthyl* p-*chlorobenzoate*, after crystallisation from methanol, had m. p. 121·5° (Found: C, 71·6; H, 3·6; Cl, 12·9%). 1-*Naphthyl* o-*chlorobenzoate* had m. p. 53° (from methanol) (Found: C, 72·7; H, 3·7; Cl, 13·0%). 2-*Naphthyl* o-*chlorobenzoate* had m. p. 88·5° (from ethanol) (Found: C, 72·5; H, 4·0; Cl, 12·2%). 1- and 2-Naphthyl *p*-nitrobenzoate had m. p.s 143° and 169° respectively (lit.,[4] 143° and 169° respectively). 1-*Naphthyl* o-*nitrobenzoate* had m. p. 101° (from ethanol) (Found: C, 70·0; H, 4·0; N, 5·0. $C_{17}H_{11}NO_4$ requires C, 69·6; H, 3·8; N, 4·8%). 2-Naphthyl *o*-nitrobenzoate had m. p. 113·5° (lit.,[5] 112°) (Found: C, 69·7; H, 3·5; N, 4·6%).

Decomposition of Aroyl Peroxides in Naphthalene.—The aroyl peroxide was allowed to decompose in molten naphthalene (100 g.) in a thermostat at 85° for 72 hr. The initial concentration of the peroxide was 0·02M. The products were worked up as described in Part XIII [1] for the reaction of benzoyl peroxide with naphthalene. The free aroic acid, and the acid formed by the hydrolysis of esters were generally obtained in a pure state, and had m. p.s very close to those recorded in the literature.

Reaction of p-*Nitrobenzoyl Peroxide with Naphthalene.*—In experiment 1 the esters were hydrolysed as described in Part XIII,[1] but only a trace of phenolic material was obtained from the hydrolysate together with a dark red viscous gum, from which no crystalline product could be isolated, in place of the expected *p*-nitrobenzoic acid. The same result was obtained when an authentic mixture of 1- and 2-naphthyl *p*-nitrobenzoate was hydrolysed under the same conditions. Similar results were also obtained when more dilute (2N) sodium hydroxide solution was used for the hydrolysis. The biaryl fraction obtained from this experiment contained no nitrogen, and its infrared spectrum showed it to be mixture of the isomeric binaphthyls. Fractional crystallisation of a portion of this mixture from light petroleum (b. p. 80—100°) gave white crystals the analysis of which was consistent with that required for binaphthyl (Found: C, 94·2; H, 5·5. Calc. for $C_{20}H_{14}$: C, 94·45; H, 5·55%).

In experiment 2, the hydrolysis stage was omitted, and the esters and biaryls were distilled together. The infrared spectrum of this fraction revealed the presence of 1- and 2-naphthyl *p*-nitrobenzoate. Specimens of both these esters were obtained by fractional crystallisation from methanol, and their m. p.s were in agreement with those reported in the literature and not depressed on admixture with authentic specimens. The results of these experiments are summarised in Table 2.

Reaction of o-*Nitrobenzoyl Peroxide with Naphthalene.*—In experiment 3 the esters were hydrolysed by refluxing the mixture for 24 hr. with two successive portions (100 ml.) of 2N-sodium hydroxide since a preliminary experiment showed that hydrolysis with 5N-sodium hydroxide, as described in Part XIII,[1] led to intractable, resinous products. Hydrolysis with 2N-alkali gave *o*-nitrobenzoic acid and a mixture of 1- and 2-naphthol. The biaryl fraction obtained from this experiment contained no nitrogen, and its infrared spectrum showed it to be a mixture of the isomeric binaphthyls. Fractional crystallisation of a portion of this mixture from light petroleum (b. p. 80—100°) gave white crystals (m. p. 130—135°) whose infrared spectrum showed it to be 1,1′-binaphthyl contaminated with a trace of the 1,2′-isomer (Found: C, 93·9; H, 5·6%).

No hydrolysis was carried out on the product of experiment 4, the esters and biaryls being distilled together. The infrared spectrum of this distillate revealed the presence of both 1- and 2-naphthyl *o*-nitrobenzoate, and fractional crystallisation from methanol gave a pure specimen of 1-naphthyl *o*-nitrobenzoate (m. p. and mixed m. p. 101°) (Found: C, 70·2; H, 3·7; N, 5·1%). The infrared spectrum of this compound was identical with that of an authentic specimen. The results of these experiments are summarised in Table 2.

Reaction of p-*Chlorobenzoyl Peroxide with Naphthalene.*—The product of experiment 5 was worked up as described in Part XIII,[1] and a mixture of 1- and 2-naphthol and *p*-chlorobenzoic

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[4] Vogel, " A Text-Book of Practical Organic Chemistry," Longmans, Green and Co. Ltd., London, 1948.

[5] Barnett and Nixon, *Chem. News*, 1924, **129**, 190.

acid was obtained by the hydrolysis of the esters. Slow crystallisation of the biaryl fraction (1·39 g.) from light petroleum (b. p. 80—100°) gave 2,2′-binaphthyl (0·041 g.; m. p. and mixed m. p. 186°). Analysis of the residue obtained on evaporation of the mother-liquors gave: C, 89·55; H, 5·35; Cl, 4·7%; and the infrared spectrum showed it to contain both 1,1′- and 1,2′-binaphthyl, together with some other material. If this residue is assumed to be a mixture of *p*-chlorophenylnaphthalenes and binaphthyls, the above analysis indicates that the chloro-compounds are present in the biaryl fraction to the extent of 30·4% (0·42 g.). It was not possible to separate quantitatively the *p*-chlorophenylnaphthalenes from the binaphthyls by distillation or by chromatography on alumina. However, fractional crystallisation from light petroleum (b. p. 80—100°) gave white crystals, m. p. 135°, whose analysis is consistent with their being a mixture of 1,1′- and 1,2′-binaphthyl (Found: C, 94·4; H, 5·5%).

No hydrolysis was carried out on the product of experiment 6, the esters and biaryls being distilled together. Fractional crystallisation of this mixture from methanol, followed by recrystallisation of the crude products to constant m. p. gave the following: (i) 2,2′-binaphthyl, m. p. and mixed m. p. 186° (Found: C, 94·35; H, 5·4%); (ii) 1,1′-binaphthyl, m. p. and mixed m. p. 160° (Found: C, 94·9; H, 5·8%); (iii) 1-naphthyl *p*-chlorobenzoate, m. p. and mixed m. p. 115·5° (Found: C, 72·3; H, 3·9; Cl, 12·8%). The infrared spectra of these compounds were identical with those of authentic specimens. No pure specimen of 2-naphthyl *p*-chlorobenzoate could be isolated, although its presence was indicated by the infrared spectra of the residues obtained by working up the mother-liquors remaining after the isolation of the above compounds. The results of these experiments are summarised in Table 2.

Reaction of o-*Chlorobenzoyl Peroxide with Naphthalene*.—The products of experiments 7 and 8 were worked up as described in Part XIII,[1] and biaryl fractions were collected which consisted of binaphthyls and *o*-chlorophenylnaphthalenes. These fractions were analysed for chlorine and their composition calculated from the analyses. These results are given in Table 1.

Crystallisation of a portion of the biaryl fraction from experiment 7 from light petroleum (b. p. 80—100°) gave a small amount of 2,2′-binaphthyl (0·005 g.) (m. p. and mixed m. p. 182°; correct infrared spectrum). Specimens of *o*-chlorobenzoic acid and mixtures of 1- and 2-naphthol were obtained from the ester hydrolysates. The results of these experiments are summarised in Table 2.

TABLE 1. *Analysis of biaryl fractions in Expts.* 7 *and* 8.

Expt.	Wt. of biaryl fraction (g.)	Cl (%)	*o*-Chlorophenylnaphthalenes (%)
7	1·50	6·95	47
8	1·48	5·7	39

TABLE 2. *Products of reactions of aroyl peroxides with naphthalene.*

Experiment No.:	1	2	3	4	5	6	7	8
Substituent in phenyl group of peroxide	p-NO$_2$	p-NO$_2$	o-NO$_2$	o-NO$_2$	p-Cl	p-Cl	o-Cl	o-Cl
Peroxide used (g.)	5·182	5·182	5·182	5·182	4·854	4·854	4·854	4·854
Free acid (g.)	2·91	2·88	2·76	2·76	3·15	3·14	2·70	2·71
Acid formed by hydrolysis of esters (g.)	0·98		2·28		1·49		1·66	1·65
Naphthols (g.)	0·19		1·43		0·94		0·80	0·86
Binaphthyls (g.)	0·46		0·24		0·97		0·80	0·91
Arylnaphthalenes (g.)	0·0		0·0		0·42		0·70	0·57
Esters and biaryls (g.)		4·10		4·16		3·97		
Esters (g.) *		3·64		3·92		2·58		
Non-volatile residue (g.)	0·02	0·18	0·02	0·19	0·02	0·18	0·13	0·10
Peroxide accounted for (%)		95·05	96·66	95·75	100·7	99·19	98·7	96·99

* These quantities were calculated by subtraction of the combined yields of binaphthyls and arylnaphthalenes obtained in experiments 1, 3, and 5 from the combined yields of esters and biaryls obtained from experiments 2, 4, and 6 respectively.

In a further experiment the hydrolysis stage was omitted, and the esters and biaryls were distilled together. Fractional crystallisation of this distillate from methanol gave 1,1′-binaphthyl (m. p. and mixed m. p. 160°) (Found: C, 94·2; H, 5·4%). No other pure compounds could be obtained from this mixture.

Reaction of 1-*Naphthoyl Peroxide with Naphthalene.*—Experiments 9 and 10 were conducted as described in Part XIII.[1] When the peroxide was added to the molten naphthalene, an immediate, vigorous evolution of gas (probably carbon dioxide) was observed. This may be connected with the comparatively low percentage of the peroxide which could be accounted for in these reactions. The first distillation of the biaryl fractions gave products which were contaminated with 1-naphthoic acid and unhydrolysed esters. These compounds were removed by boiling the biaryl fractions under reflux for 24 hr. with further portions of 5N-sodium hydroxide. Although repeated attempts were made, no 2,2′-binaphthyl could be isolated from these fractions, and it is therefore concluded that little if any of this isomer was present. A small liquid fraction, b. p. 66°/0·1 mm., was also obtained in the distillation of these "biaryl fractions." This material was not identified, but its analysis indicates that it was not a hydrocarbon (Found: C, 83·9; H, 7·1%).

The products obtained in these experiments are summarised in Table 3.

Reaction of 2-*Naphthoyl Peroxide with Naphthalene.*—Experiment 11 was conducted as described in Part XIII.[1] During the hydrolysis of the esters a large quantity of a solid was precipitated, which was subsequently shown to be sodium 2-naphthoate (2-naphthoic acid liberated, m. p. and mixed m. p. 182—185°). Moreover, the biaryl fraction obtained by distillation of the neutral residue after the hydrolysis of esters was found to be contaminated with unhydrolysed esters and 2-naphthoic acid. Consequently, in experiments 12 and 13, the residues after removal of naphthalene and free 2-naphthoic acid were refluxed with two successive portions of sodium hydroxide solution to ensure complete hydrolysis, and water (250 ml.) was added when hydrolysis was complete in order to take up the precipitated sodium 2-naphthoate. The results obtained in these experiments are given in Table 3, and those of experiments 12 and 13 are considered to be the more reliable.

TABLE 3. *Products of reactions of* 1- *and* 2-*naphthoyl peroxides* (5·34 g.) *with naphthalene* (100 g.).

Experiment No.:	9	10	11	12	13
Naphthoyl peroxide	1-	1-	2-	2-	2-
Free acid (g.)	1·92	1·96	2·90	2·88	2·87
Acid formed by hydrolysis of esters (g.)	1·60	1·62	0·43	1·95	2·00
Naphthols (g.)	1·04	0·97	0·47	0·93	0·99
Liquid, b. p. 66°/0·1 mm. (g.)	0·06	0·05			
Binaphthyls (g.)	1·17	1·17	1·20	1·21	1·19
Non-volatile residue (g.)	0·12	0·19	0·14	0·18	0·17
Peroxide accounted for (%)	80·3 *	81·3 *	—	89·9 †	90·7 †

* Since no 2,2′-binaphthyl was isolated in this reaction, it is assumed for the purpose of this calculation that the binaphthyls were formed entirely by direct substitution of 1-naphthyl radicals, derived from the peroxide, in naphthalene; and hence the binaphthyls are taken into account in deriving these figures.

† These figures were arrived at without reference to the binaphthyls, since, because all three isomeric binaphthyls are formed, not all of them could have been formed by direct substitution of 2-naphthyl radicals in naphthalene. It is, therefore, impossible to obtain an accurate estimate of the amount of binaphthyls formed by direct substitution.

TABLE 4. *Ratio of isomeric naphthols and binaphthyls formed in experiments* 1—13.

		Naphthols (%)		2,2′-Binaphthyl	Total Binaphthyls (%)		
Expt. No.	Peroxide	1-	2-	(g.)	1,1′-	1,2′-	2,2′-
1	*p*-Nitrobenzoyl	72·3	27·7				
3	*o*-Nitrobenzoyl	81·0	19·0				
5	*p*-Chlorobenzoyl	75·4	24·6				
7	*o*-Chlorobenzoyl	70·8	29·2				
8	*o*-Chlorobenzoyl	75·2	24·8				
9	1-Naphthoyl	82·1	17·9	0·0	69·0	31·0	0·0
10	1-Naphthoyl	82·2	17·8	0·0	69·6	30·4	0·0
12	2-Naphthoyl	68·6	31·4	0·098	36·7	55·2	8·1
13	2-Naphthoyl	66·9	33·1	0·107	34·8	56·3	8·9

The infrared spectra of the biaryl fractions were consistent with their being mixtures of the three isomeric binaphthyls. Pure specimens of 1,1′- and 2,2′-binaphthyl were isolated from them.

Determination of Ratios of Isomers.—The spectrographic analysis of the mixtures of binaphthyls and naphthols from experiments 1—13 was conducted by the method described in Part XIII.[1] The results are given in Table 4. The results of tests of the accuracy of the methods of analysis of mixtures of binaphthyls and naphthols (by the analysis of synthetic mixtures of known composition) were also described in Part XIII.[1]

DISCUSSION

The molar yields of the various products of the reactions of the aroyl peroxides with naphthalene are summarised in Table 5.

Since both the free acid and the acid formed by the hydrolysis of esters were invariably obtained in a reasonably pure state, very little further substitution of these acids or esters could have occurred. This supports the contention [1] that naphthalene is a " fast " solvent towards homolytic attack. This view is also supported by the small amounts of involatile residue formed in these reactions.[6]

The most striking feature of these results is the decrease in the yield of esters, and the concomitant increase in the yield of arylnaphthalenes along the series nitrobenzoyl peroxides, chlorobenzoyl peroxides, benzoyl peroxide. These phenomena appear to be linked with the electrophilic character of the corresponding aroyloxy-radicals, which might be expected to decrease in the order, *o*- and *p*-$NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}O{\cdot} >$ *o*- and *p*-$Cl{\cdot}C_6H_4{\cdot}CO{\cdot}O{\cdot} >$ $C_6H_5{\cdot}CO{\cdot}O{\cdot}$. Since naphthalene is very reactive towards electrophilic reagents reaction of the aroyloxy-radicals with naphthalene tends to supersede the competing reaction of decarboxylation as the electrophilic character is increased. The effect of nuclear substituents on the ease of decarboxylation is difficult to predict as neither the aroyloxy- nor the aryl radical can be appreciably stabilised by nuclear substituents. The only additional canonical forms which can be written for these radicals necessarily contain an additional dipole, and hence can make only very small contributions. Any such effects are therefore likely to be small, and consequently the effect of substituents on the reactivity of aroyloxy-radicals in nuclear substitution is, as discussed above, likely to be the dominating influence on their fate.

The position of the naphthoyl peroxides in this series (cf. Table 5) indicates that 1- and 2-naphthoyloxy-radicals are not very different from benzoyloxy-radicals with regard either to polarity or to stability.

Although the formation of binaphthyls in these reactions is due, in the first instance, to attack on the nucleus of naphthalene by aroyloxy-radicals (cf. Part XIII [1]), the yield of binaphthyls (Table 5) varies with the nature of the aroyl peroxide in the opposite sense to that of the esters formed as a result of substitution by aroyloxy-radicals. This is reasonable since the binaphthyls arise by attack of aroyloxy-radicals on hydrogen attached to nuclear carbon, giving the appropriate aroic acid together with 1- and 2-naphthyl radicals which then effect substitution in the 1- and the 2-position of other naphthalene molecules. The esters, on the other hand, are formed by attack of the aroyloxy-radicals on the nuclear carbon atoms. Whereas the latter process would be expected to become

TABLE 5. *Yields, in moles/mole of peroxide, of the products of aroyl peroxide–naphthalene reactions.*

Peroxide	Free acid	Esters	Arylnaphthalenes	Binaphthyls
Benzoyl[1]	1·12	0·55	0·20	0·29
p-Nitrobenzoyl	1·11	0·80	0·0	0·12
o-Nitrobenzoyl	1·06	0·87	0·0	0·06
p-Chlorobenzoyl	1·29	0·61	0·11	0·24
o-Chlorobenzoyl	1·11	0·68	0·17	0·21
1-Naphthoyl	0·72	0·60	0·29	
2-Naphthoyl	1·07	0·72	0·30	

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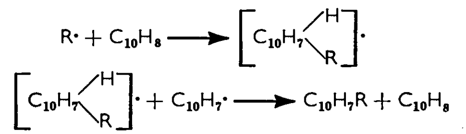
[6] Williams, " Homolytic Aromatic Substitution," Pergamon Press Ltd., London, 1960, pp. 59, 65.

more favoured as the electrophilic character of the attacking radical is increased, the results indicate that the former has the opposite polar requirement since the two reactions are direct competitors. Hambling, Hey, Pengilly, and Williams [7] have shown that the analogous reaction of hydrogen-abstraction from the side-chain of toluene by *para*-substituted aryl radicals is favoured by increasing nucleophilic character on the part of the radicals, and similar considerations might be expected to apply in the present reactions.

The amounts of the products obtained in reactions with 1-naphthoyl peroxide, especially with regard to the free 1-naphthoic acid formed, seem to be out of harmony with the other members of the series. Also (cf. Experimental Section), the amount of this peroxide accounted for as identified products was unusually low. These anomalies are probably connected with the vigorous evolution of much carbon dioxide which occurs in this reaction. 1-Naphthyl radicals must therefore be formed rapidly and in high yield. These entities have a certain amount of resonance stabilisation and consequently may be present in sufficient concentration to contribute to the dehydrogenation of the intermediate σ-complexes of substitution reactions, thereby giving rise to the formation of naphthalene:



$$R\cdot + C_{10}H_8 \longrightarrow \left[C_{10}H_7{<}^{H}_{R}\right]\cdot$$

$$\left[C_{10}H_7{<}^{H}_{R}\right]\cdot + C_{10}H_7\cdot \longrightarrow C_{10}H_7R + C_{10}H_8$$

where $R = C_{10}H_7$ or $C_{10}H_7{\cdot}CO{\cdot}O$.

It is, of course, impossible to distinguish naphthalene formed in this way from solvent naphthalene, except by the use of isotopically labelled reagents, and the observable results of such a process should be (*a*) a decrease in the yield of 1-naphthoic acid, and (*b*) a decrease in the amount of the peroxide accounted for. These are, in fact, the observed phenomena.

The ratios of the isomeric naphthols arising from hydrolysis of the esters formed on the decomposition of aroyl and naphthoyl peroxides in naphthalene are given in Table 4. These may be compared with the corresponding ratio for the decomposition of benzoyl peroxide in naphthalene [1] (1-naphthol, 72·9%; 2-naphthol, 27·1%). The results obtained with *p*-nitrobenzoyl peroxide are unreliable, since the hydrolysis of the esters obtained from its reaction with naphthalene gave only a very low yield of naphthols together with a red gum in place of the expected *p*-nitrobenzoic acid; these figures are, therefore, disregarded in the following discussion. The results indicate that the presence of nitro- (and to a smaller extent chloro-) substituents in the attacking aroyloxy-radicals increases the amount of substitution which occurs at the 1-position of naphthalene. This is consistent with the increased electrophilic character of these radicals, since naphthalene is substituted predominantly in the 1-position by electrophilic reagents.[8] This interpretation is in accord with the results obtained by Marshall and Waters [9] on the reaction of naphthalene with aryl radicals containing substituents of various polar characteristics. It was found that electron-withdrawing substituents in the aryl radicals increased, and electron-repelling substituents decreased, the proportion of 1-substitution.

On the basis of the above argument, and in view of the results given in Table 4, it might be inferred that the 1-naphthoyloxy-radical is more, and the 2-naphthoyloxy-radical less, electrophilic than the benzoyloxy-radical. However, an alternative interpretation, which is peculiarly applicable to these reactions, namely, that some 1- and 2-naphthyl naphthoate may be formed by the intramolecular loss of carbon dioxide from 1- and 2-naphthoyl peroxide, respectively, cannot be ruled out at present.

The mean ratios in which the isomeric binaphthyls are formed from the reactions of 1- and 2-naphthoyl and benzoyl [1] peroxide with naphthalene are given in Table 6. The

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[7] Hambling, Hey, Pengilly, and Williams, unpublished observations.

[8] Cf. Dewar and Mole, *J.*, 1956, 1441.

[9] Marshall and Waters, *J.*, 1959, 381.

wide differences revealed are expected, since, in the reactions with the naphthoyl peroxides, binaphthyls can be formed in two ways, according as the naphthyl radicals are derived by decarboxylation of naphthoyloxy-radicals (*a*) or by hydrogen-abstraction from solvent naphthalene (*b*):

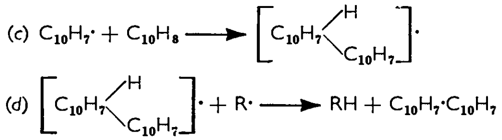
TABLE 6. *Formation of isomeric binaphthyls in reactions with naphthalene.*

Peroxide	1,1′-Binaphthyl (%)	1,2′-Binaphthyl (%)	2,2′-Binaphthyl (%)
1-Naphthoyl	69	31	0
2-Naphthoyl	36	56	8
Benzoyl	54	42	4

$$(a)\ C_{10}H_7{\cdot}CO{\cdot}O{\cdot} \longrightarrow C_{10}H_7{\cdot} + CO_2$$

$$(b)\ C_{10}H_7{\cdot}CO{\cdot}O{\cdot} + C_{10}H_8 \longrightarrow C_{10}H_7{\cdot}CO_2H + C_{10}H_7{\cdot}$$

The naphthyl radicals formed by either of these processes may then effect nuclear substitution in naphthalene [reactions (*c*) and (*d*)]:



$$(c)\ C_{10}H_7{\cdot} + C_{10}H_8 \longrightarrow \left[C_{10}H_7\left\langle{}^{H}_{C_{10}H_7}\right.\right]{\cdot}$$

$$(d)\ \left[C_{10}H_7\left\langle{}^{H}_{C_{10}H_7}\right.\right]{\cdot} + R{\cdot} \longrightarrow RH + C_{10}H_7{\cdot}C_{10}H_7$$

where R· is any radical present in solution which is capable of oxidising the intermediate σ-complex. If all the naphthyl radicals were formed by reaction (*b*), then it can be predicted that the ratio of the isomeric binaphthyls formed should be similar to that formed in the reaction of benzoyl peroxide with naphthalene, in which this is the only source of naphthyl radicals, provided that the assumption is made that benzoyloxy- and naphthoyloxy-radicals behave similarly in the hydrogen-abstraction reaction (*b*). Since the course of this reaction is largely determined by polar influences (see above), and since there is no *a priori* reason to suppose that the polar characteristics of benzoyloxy- and naphthoyloxy-radicals differ widely, this assumption is accepted as reasonable. The extent of the divergence from the isomer ratio obtained with benzoyl peroxide can therefore be regarded as a measure of the incidence of the direct naphthylation [(*a*) followed by (*c*) and (*d*)]. In the reaction with 2-naphthoyl peroxide, 1,1′-binaphthyl can arise only as a result of the abstraction reaction [(*b*) followed by (*c*) and (*d*)]. If it is now assumed that 1,2′- and 2,2′-binaphthyl are also formed by this reaction in the same ratio to 1,1′-binaphthyl as in the corresponding reaction with benzoyl peroxide, the following isomer ratio for binaphthyls formed in this way can be obtained: 1,1′- 35·7; 1,2′- 27·7; 2,2′- 2·6%. The sum of these figures, 66%, represents the proportion of the total yield of binaphthyls which is formed by the abstraction process. It then follows that the remainder of the binaphthyl (34%) represents the binaphthyls formed by direct substitution, and in the ratio obtained by subtraction, namely, 1,2′- 28·1; 2,2′- 5·9%. Thus the direct 2-naphthylation of naphthalene gives 1,2′- and 2,2′-binaphthyl in the following ratio: 1,2′- 82·6; 2,2′- 17·5%. These figures are very similar to those obtained for the ratio of isomeric phenylnaphthalenes (the corresponding products of direct substitution) obtained in the reaction of benzoyl peroxide with naphthalene (1-, 82; 2-, 18%),[1] thus confirming the postulated similarity in polar characteristics of the radicals derived from benzoyl and naphthoyl peroxides.

No calculation of this type can, however, be performed on the results obtained for the reaction of 1-naphthoyl peroxide with naphthalene, since no 2,2′-binaphthyl could be isolated from the products of this reaction. The complete absence of this product is hardly to be expected, since this would mean that no hydrogen-abstraction took place. The amount of 2,2′-binaphthyl would, however, be expected to be very small since the

2-position is much the less reactive in two successive reactions, and it may well be that this small amount escaped detection by the experimental techniques employed.

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