one oxygen p_y orbital is used to form a σ bond to hydrogen, whereas, in the latter, it holds an unshared pair. The only difference in the π orbitals will arise from distortion of this system by the charge on the oxygens in the anion and from symmetry differences arising from the probable tendency of the oxygens of the ion to assume a "*trans*" rather that a "*cis*" orientation with respect to each other. The first of these factors may be expected to have relatively little influence on the separation of the first few energy levels which are reached by promotion of electrons from one π-orbital to another. Sklar[14] has pointed out that in the anilinium ion, a strong, local field does not distort the benzene 265 mμ band to any great extent. The change in the symmetry of the molecule would not be expected to affect the positions of the maxima but might alter intensities appreciably. No evidence for the latter effect is apparent in our data.

The spectra of both the enols show evidence that the long wave length band is actually an unresolved doublet. This feature disappears in the anions. Such a change is usually associated with some operation which creates a new symmetry element in some slightly unsymmetrical structure. That this is the case with the triketone is immediately obvious. In the case of the diketone it may indicate that even though the hydrogen bond is compressed slightly, the hydrogen does not assume a symmetrical position with respect to the two oxygens, but is, as we have assumed, bound to one oxygen by a covalent linkage.

Acknowledgment.—We are indebted to the Quaker Oats Company for financial support of of this research.

AMES, IOWA RECEIVED JUNE 7, 1951

(14) A. L. Sklar, *J. Chem. Phys.*, **7**, 987 (1939).

[CONTRIBUTION FROM THE MORLEY CHEMISTRY LABORATORY, WESTERN RESERVE UNIVERSITY]

Free Radical Aromatic Substitution. I. The Reaction of Benzoyl Peroxide with Naphthalene Derivatives[1,2]

BY RALPH L. DANNLEY AND MORRIS GIPPIN

The thermal decomposition of benzoyl peroxide in α-chloro-, α-bromo- and α-nitronaphthalene has been found to result in monosubstitution by a benzoyloxy group in the 2-, 4- or 5-positions of the naphthalene derivative. The yields of isomeric esters were determined semiquantitatively and the ratio of yields of homonuclear to heteronuclear substitution products indicated that toward attack by the benzoyloxy radical, the substituents had the following relative activating influences: $NO_2 > Br > Cl > H$.

A number of reactions of aromatic substitution proceed by free radical mechanisms. Such reactions (*e.g.*, the preparation of biaryls by the Hey and Gomberg–Bachmann methods) are characterized by universal ortho–para substitution. In the reaction of a free radical with an aromatic derivative, the substituent in the ring undoubtedly exerts not only a directive but also an activating or deactivating influence upon the attack by the entering radical. Such influences may be determined by means of competition reactions but very few experiments of this type have been reported.

One possible type of competition reaction would consist of the attack of a free radical upon a benzene derivative in which two substituents have opposing directive influences. Thus Grieve and Hey[3] decomposed sodium benzenediazotate in *o*-nitrotoluene and found an 8.7% yield of 4-nitro-3-methylbiphenyl and no trace of 3-nitro-4-methylbiphenyl. By applying the law of invariable ortho–para orientation, the substitution of the phenyl radical para to the nitro group (meta to the methyl group) must mean that the nitro group has a greater directive influence than the methyl group.

A second type of competitive reaction involves the decomposition of a free radical reagent in a mixture of two monosubstituted benzenes to determine which will be preferentially attacked. Grieve and Hey[3] heated an alkaline solution of benzenediazonium chloride (1.00 mole) with an equimolecular mixture of toluene and nitrobenzene to give 0.12 mole of nitrobiphenyls and 0.032 mole of methylbiphenyls. These relative yields indicate that the nitro group has an activating influence roughly four times that of the methyl group. This technique of decomposition of a free radical reagent in an equimolecular mixture of solvents has also been applied by De Tar and Scheifele[4] to the thermal decomposition of 0.12 mole of N-nitrosoacetanilide in a mixture of benzene and chlorobenzene to give 0.021 mole of biphenyl and 0.040 mole of chlorobiphenyl (determined by halogen analysis). These yields show that chlorobenzene is about twice as reactive as benzene toward substitution by phenyl free radicals.

A third possible type of competitive reaction had not been attempted until the present work. In the reaction of a free radical with a substance such as chloronaphthalene, the relative amount of substitution in the two rings would be a measure of the activating or deactivating influence of the chlorine atom. Huisgen and Sorge[5] have shown that substitution of the naphthalene nucleus by free radicals is possible for they obtained α-phenylnaphthalene from the thermal decomposition of N-nitrosoacetanilide in naphthalene.

---

(1) From a thesis submitted by Morris Gippin to the Graduate School, Western Reserve University, in partial fulfillment of the requirements for the Doctor's degree, 1951.

(2) Presented at the Cleveland Meeting of the American Association for the Advancement of Science, December 27, 1950.

(3) W. S. M. Grieve and D. H. Hey, *J. Chem. Soc.*, 1797 (1934).

(4) D. F. De Tar and H. J. Scheifele, THIS JOURNAL, **73**, 1442 (1951).

(5) R. Huisgen and G. Sorge, *Ann.*, **566**, 162 (1950).

It was therefore decided to investigate the reaction of a free radical reagent with α-chloro-, α-bromo- and α-nitronaphthalene and from the ratios of homonuclear to heteronuclear substitution products, establish a table of relative activating influences of the groups. Benzoyl peroxide was selected as the source of free radicals as it is readily obtained in a high state of purity and decomposes smoothly at reasonable temperatures with a minimum of side reactions.

Experimental

Reaction of Benzoyl Peroxide with 1-Bromonaphthalene.—To 1200 ml. of 1-bromonaphthalene maintained at 70 ± 2° was added a suspension of 105.3 g. (0.435 mole) of 98%[6] pure benzoyl peroxide (Lucidol, recrystallized from chloroform–methanol) in 270 ml. of 1-bromonaphthalene. The addition required five hours and the reaction mixture was kept at 70° for three days. The 3.8 g. (0.008 mole) of carbon dioxide which was evolved was absorbed in an ascarite train after being passed through a trap which condensed 1.2 ml. (0.013 mole) of benzene. Ammonia gas was passed into the reaction mixture to precipitate 50.9 g. (0.42 mole) of benzoic acid as its ammonium salt which was removed by filtration. The filtrate was vacuum distilled at 0.5 mm. pressure to give 1-bromonaphthalene and (I) 5.2 g., 134–171°; (II) 98.8 g., 171–196°; (III) 7.9 g., 196–232°; and 13.8 g. of unidentified residual tar.

Chromatography of I upon alumina using carbon tetrachloride as a solvent and eluting with 1% ethanol in chloroform gave 2.6 g. of 1-bromonaphthalene. The oil which was obtained by extraction of the alumina with ethanol was rechromatographed upon alumina using carbon tetrachloride as a developing and eluting solvent. The 1.4 g. of material thus purified was saponified[7] and 0.43 g. of benzoic acid separated from the phenolic constituent. Recrystallization of the phenol from benzene–petroleum ether gave 0.76 g. of 1-bromo-2-naphthol, m. p. 76–79° (lit.[7] 83°); benzoate, m. p. 97.5–98° (lit.[7] 97–98°). This yield of naphthol corresponded to 1.12 g. (0.003 mole) of 1-bromo-2-benzoyloxynaphthalene.

II consisted of a mixture of 1-bromo-4-benzoyloxynaphthalene and 1-bromo-5-benzoyloxynaphthalene. The semiquantitative estimation of these two materials required two separate procedures.

Procedure A.—Chromatographic adsorption of a 5.2-g. aliquot of II upon alumina using petroleum ether for development and elution gave 3.56 g. of crude 1-bromo-4-benzoyloxynaphthalene. A portion of this crude ester after recrystallization from methanol had a m. p. of 105° (lit.[8] 105–106°). In order to get a semiquantitative result, 0.500 g. of the crude ester was saponified to produce 0.165 g. of benzoic acid and a phenolic fraction. Recrystallization of the phenolic component from dilute ethanol gave 0.31 g. of 1-bromo-4-naphthol, m. p. 127–128° (lit.[9] 127–128°); picrate, m. p. 168° (lit.[10] 168°). This yield of pure naphthol proved that a minimum of 63% of II consisted of 1-bromo-4-benzoyloxynaphthalene.

Procedure B.—Saponification of 5.54 g. of II produced 1.48 g. of benzoic acid and a phenolic fraction. The phenols were chromatographed upon alumina using carbon tetrachloride as a solvent and eluting with chloroform. The first fraction thus obtained was recrystallized from benzene–petroleum ether to give 1.08 g. of 1-bromo-5-naphthol, m. p. 137° (lit.[11] 137°); methyl ether, m. p. 67–68° (lit.[11] 67–68°). This yield of pure naphthol proved that (II) consisted of a minimum of 28.7% 1-bromo-5-benzoyloxynaphthalene.

Saponification of (III) yielded 0.74 g. of benzoic acid, 1.43 g. of phenolic fraction and 5.65 of unidentified unsaponified residue. Purification of the phenol by the chromatographic and recrystallization procedure previously described gave 1.34 g. of 1-bromo-5-naphthol, m. p. 137°. Therefore this fraction contained 1.96 g. (0.006 mole) of 1-bromo-5-benzoyloxynaphthalene.

Reaction of Benzoyl Peroxide with 1-Chloronaphthalene.—This reaction was carried out in a manner identical with the decomposition in 1-bromonaphthalene. The use of 25.9 g. of benzoyl peroxide (98% pure) produced 0.6 cc. (0.007 mole) of benzene, 0.079 g. (0.002 mole) of carbon dioxide, and 11.6 g. (0.095 mole) of benzoic acid. Vacuum distillation at about 0.5 mm. pressure removed the excess 1-chloronaphthalene and gave (I) 7.01 g., 120–132°; (II) 6.46 g., 132–174°; and 12.1 g. of residual unidentified tar. Much decomposition occurred during the latter part of the distillation.

Chromatography of a 3.51-g. aliquot of I upon alumina using carbon tetrachloride as a solvent gave 2.86 g. of IA and 0.33 g. of IB. Recrystallization of a portion of IA from ethyl alcohol yielded 1-chloro-4-benzoyloxynaphthalene, m. p. 100–101° (lit.[8] 101–102°). To determine semiquantitatively the amount of this ester, a 1.50-g. aliquot of (IA) was saponified to produce 0.544 g. of benzoic acid and 0.893 g. of a crude phenol. Chromatography of this phenol upon alumina using carbon tetrachloride as a solvent yielded 0.804 g. of 1-chloro-4-naphthol, m. p. 118–119° (lit.[12] 120°); bromination product, m. p. 95.5–96° (lit.[13] 96°). Saponification of (IB) gave 0.130 g. of benzoic acid and 0.174 g. of phenolic component. Chromatography of this component upon alumina using carbon tetrachloride as a solvent produced 0.128 g. of 1-chloro-2-naphthol, m. p. 69–70° (lit.[14] 72°); benzoyl ester, m. p. 99–100° (lit.[15] 101°). The yields of 0.804 g. of 1-chloro-4-naphthol and 0.128 g. of 1-chloro-2-naphthol proved that (I) consisted of a minimum of 69.3% and 5.8% of the respective benzoate esters.

Chromatography of a 3.23-g. aliquot of Fraction (II) upon alumina using petroleum ether as a solvent and eluting with carbon tetrachloride produced a principal fraction IIa weighing 2.95 g. A 1.54-g. aliquot of IIa was saponified to give 0.49 g. of benzoic acid and 0.83 g. of a phenolic fraction. Chromatography of this phenolic fraction upon alumina using carbon tetrachloride as a solvent and eluting with chloroform yielded 0.71 g. of 1-chloro-5-naphthol, m. p. 128–130°. Recrystallization from carbon disulfide raised the m. p. to 131.5–132° (lit.[16] 131.5°); picrate, m. p. 161–162° (lit.[16] 160°). The 0.71-g. yield of pure naphthol proved that II consisted of a minimum of 66% 1-chloro-5-benzoyloxynaphthalene.

Reaction of Benzoyl Peroxide with 1-Nitronaphthalene.—Inasmuch as 1-nitronaphthalene has a m. p. of 60°, the reaction procedure necessarily differed from those preceding, in that benzoyl peroxide in solid form was added to the molten reaction mixture. The decomposition of 72.6 g. (0.30 mole) of benzoyl peroxide in 1297 g. (7.5 moles) of 1-nitronaphthalene produced 0.37 g. (0.008 mole) of carbon dioxide, 0.3 ml. (0.003 mole) of benzene, and 33.6 g. (0.275 mole) of benzoic acid. Distillation of the reaction mixture at 0.003 mm. pressure gave 1-nitronaphthalene, and (I) 0.90 g., 93–99°; (II) 26.9 g., 99–127°; (III) 1.34 g., 127–183°; and 36 g. of unidentified residual tar.

Saponification of I produced 0.255 g. of benzoic acid and 0.507 g. of a phenolic fraction. This phenolic fraction was purified by boiling an aqueous alkaline solution with charcoal and finally recrystallizing from benzene to give 0.472 g. of 1-nitro-2-naphthol, m. p. 102–103° (lit.[17] 103°); benzoate m. p. 141–142° (lit.[18] 142°). The isolation of 0.472 g. of the pure phenol proved that a minimum of 81% of (I) consisted of 1-nitro-2-benzoyloxynaphthalene.

A 4.66-g. aliquot of (II) was chromatographed upon alumina using carbon tetrachloride as the solvent and eluting agent. A principal fraction IIa, 3.54 g., was obtained and extraction of the alumina with absolute ethanol gave IIb, 0.564 g. IIb upon saponification produced 0.19 g. of benzoic acid and 0.25 g. of 1-nitro-2-naphthol, m. p. 102–103°. A sample of IIa was recrystallized from ethanol to yield 1-nitro-4-benzoyloxynaphthalene, m. p. 176–177° not depressed by an authentic sample. A semiquantitative

---

[6] V. R. Kokatnur and M. Jelling, This Journal, **63**, 1432 (1941).

[7] S. E. Hazlet, *ibid.*, **62**, 2156 (1940).

[8] W. Autenrieth and P. Mülhinghaus, *Ber.*, **40**, 748 (1907).

[9] F. Reverdin and H. Kaufmann, *ibid.*, **28**, 3054 (1895).

[10] F. Bodroux, *Bull. soc. chim.*, [3] **31**, 35 (1904).

[11] R. C. Fuson, This Journal, **46**, 2779 (1924).

[12] H. Kast, *Ber.*, **44**, 1337 (1911).

[13] R. Willstätter and L. Schuler, *ibid.*, **61**, 367 (1928).

[14] K. Fries and K. Schimmelschmidt, *Ann.*, **484**, 293 (1930).

[15] W. Autenrieth, *Arch. Pharm.*, **233**, 34 (1895).

[16] H. Erdmann and R. Kirchoff, *Ann.*, **247**, 372 (1888).

[17] C. Liebermann and P. Jacobson, *ibid.*, **211**, 46 (1882).

[18] W. Bottcher, *Ber.*, **16**, 1935 (1883).

determination of this material was made by saponification of a 1.71-g. aliquot of IIa to produce 0.57 g. of benzoic acid and 1.03 g. of a phenolic component. Recrystallization of the phenolic component from chloroform gave 0.85 g. of pure 1-nitro-4-naphthol, m. p. 164–165° (lit.[19] 164°); benzoate m. p. 176–177° (lit.[20] 176°). The isolation of 0.25 g. of 1-nitro-2-naphthol and 0.85 g. of 1-nitro-4-naphthol proved that fraction II contained a minimum of 8.3% and a 58.3% of the respective benzoate esters.

Saponification of III produced 0.42 g. of benzoic acid and 0.64 g. of a phenol. Purification of the phenol by decolorizing an alkaline solution with charcoal and precipitation with acetic acid gave 0.57 g. of 1-nitro-5-naphthol, m. p. 170–171° (lit.[21] 171°); methyl ether, 95–96° (lit.[21] 96–97°). The 0.57-g. yield of pure phenol proved that 66% of III consisted of 1-nitro-5-benzoyloxynaphthalene.

Discussion.—The yields of products are listed in Table I. The quantities of carbon dioxide and benzene are of limited accuracy but are included because, as they are of similar magnitude, they indicate that the free phenyl radicals which did form probably produced benzene and did not substitute the aromatic nucleus.

TABLE I

Product	Moles of products per mole of $(C_6H_5COO)_2$ $1\text{-}BrC_{10}H_7$	$1\text{-}ClC_{10}H_7$	$1\text{-}NO_2C_{10}H_7$
CO_2	0.01	0.02	0.03
C_6H_5COOH	.98	.91	.92
C_6H_6	.03	.07	.01
1,2-Ester	.007	.009	.03
1,4-Ester	.41	.16	.18
1,5-Ester	.20	.14	.10

The formation of quantities of esters is unusual, for in general the decomposition of benzoyl peroxide in aromatic solvents produces phenylated products.[22] Substitution by aroyloxy radicals is not unknown, however, for the decomposition of benzoyl peroxide in phenols[23] results in substitution by the benzyloxy group. Also, the decomposition of α-naphthoyl peroxide in carbon tetrachloride[24] produces some 4-α-naphthoyloxy-1-naphthoic acid. As the benzoyloxy radical is a logical precursor to the phenyl radical, it seems possible that benzoyloxylation occurs with nuclei highly susceptible to free radical attack while phenylation occurs with less reactive substances.

Direct comparison of the sum of the moles of 1,2-ester and 1,4-ester to the moles of 1,5-ester gives the following relative activating influences toward benzoyloxy free radical attack: NO_2, 19 > Br, 2.0 > Cl, 1.2 > H, 1.0. As these values are based on yields of only 31–62% identified products, their accuracy does not warrant including corrections for the number of positions available for substitution in the two rings.

---

[19] H. Hubner and P. Ebell, *Ann.*, **208**, 325 (1881).

[20] G. Doak, H. Eagle and H. Steinman, THIS JOURNAL, **64**, 1065 (1942).

[21] F. Fichter and T. Kuhnel, *Ber.*, **42**, 4751 (1910).

[22] D. H. Hey and W. A. Waters, *Chem. Revs.*, **21**, 169 (1937).

[23] S. L. Cosgrove and W. A. Waters, *J. Chem. Soc.*, 3189 (1949).

[24] M. S. Kharasch and R. L. Dannley, *J. Org. Chem.*, **10**, 406 (1945).

CLEVELAND 6, OHIO RECEIVED APRIL 23, 1951

[CONTRIBUTION FROM THE INSTITUTE OF POLYMER RESEARCH, POLYTECHNIC INSTITUTE OF BROOKLYN]

Allyl Polymerization. II. Decomposition of Benzoyl Peroxide in Allyl Esters[1,2]

BY NORMAN G. GAYLORD[3] AND FREDERICK R. EIRICH

The decomposition of benzoyl peroxide in the course of the bulk polymerization of allyl esters is almost first order, the rate constant increasing with increasing initial peroxide concentration. The order of rate of decomposition in the allyl esters is trimethylacetate > propionate > acetate > ethyl carbonate. It is suggested that the chain reaction accompanying the spontaneous unimolecular decomposition may involve products arising from, in addition to attack upon α-methylenic hydrogen, an attack on the acyl group of the esters as well as from a free radical displacement reaction on the allylic carbon causing cleavage of the carbon–oxygen bond, particularly in the case of allyl trimethylacetate.

In a previous paper[4] it was shown that the decomposition of benzoyl peroxide in allyl alcohol and allyl bromide, as in other solvents,[5] can be considered as a spontaneous first-order reaction accompanied by a free radical induced chain decomposition. This results in a variation of the rate of decomposition with the initial concentration of peroxide.[5a,c,d,6,7] The rates of decomposition in solutions containing polymerizable monomers are generally increased over those in the nonpolymerizing solvent alone[8,9] although it is reported[5d] that 3,4-dichlorostyrene suppresses induced decomposition with a resultant lowered rate of decomposition. The present work reports an investigation of the decomposition of benzoyl peroxide in the course of the bulk polymerization of several allyl esters.

Results and Discussion

Decomposition in Allyl Esters.—The decomposition of benzoyl peroxide was followed as a function of time during the bulk polymerization of several allyl esters at 80° under vacuum, in the presence of various initial concentrations of peroxide. Peroxide concentrations were determined by iodometric titration as described in the Experimental section and are expressed in moles per kilo-

---

[1] This work was carried out with the support of the U. S. Navy, Bureau of Aeronautics.

[2] Abstracted from a portion of the dissertation submitted by Norman G. Gaylord to the Graduate Faculty of the Polytechnic Institute of Brooklyn, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1950.

[3] E. I. du Pont de Nemours and Co., Yerkes Research Laboratory, Buffalo, N. Y.

[4] Part I of this series: THIS JOURNAL, **73**, 4981 (1951).

[5] (a) K. Nozaki and P. D. Bartlett, *ibid.*, **68**, 1686 (1946); (b) W. E. Cass, *ibid.*, **68** 1976 (1946); (c) B. Barnett and W. E. Vaughan, *J. Phys. Colloid Chem.*, **51**, 926, 942 (1947); (d) C. G. Swain, W. H. Stockmayer and J. T. Clarke, THIS JOURNAL, **72**, 5426 (1950).

[6] (a) D. J. Brown, *ibid.*, **62**, 2657 (1940); (b) S. G. Cohen, *ibid.*, **67**, 17 (1945).

[7] P. D. Bartlett and R. Altschul, *ibid.*, **67**, 816 (1945).

[8] S. Kamenskaya and S. S. Medvedev, *Acta Physicochim. U. R. S. S.*, **13**, 565 (1940).

[9] J. W. Breitenbach and V. Taglieber, *Ber.*, **76B**, 272 (1943).