[Contribution from the Baker Laboratory of Chemistry of Cornell University]

A Quantitative Study of the Orienting Influence of the Nitro Group in the Formation of Nitrobiphenyls by Reaction of Nitrobenzene with N-Nitrosoacetanilide, with Benzoyl Peroxide, and with Benzenediazonium Chloride and Alkali[1]

By DeLos F. DeTar and Harry J. Scheifele, Jr.[2]

Previous workers have shown qualitatively that the usual orientation rules are not followed in the formation of biaryls by reaction of benzoyl peroxide, benzenediazonium chloride and alkali, and of N-nitrosoacetanilide with aromatic solvents. A quantitative determination of the mononitrobiphenyls formed by reaction of these reagents with nitrobenzene has shown that the nitro group of nitrobenzene is largely ortho–para directing, and that the ratio of nitrobiphenyls formed (60–70% 2-, 0–10% 3-, 30–40% 4-) is nearly the same for each of the three reactants. These results provide additional support for the hypothesis that free radicals are involved in the formation of biaryls by the above reactions. Further experiments with N-nitrosoacetanilide have shown that it reacts with an equimolar mixture of benzene and chlorobenzene to form principally chlorobiphenyls, a result which is also indicative of a reaction involving free radicals rather than phenyl cations. The acetoxyl portion of N-nitrosoacetanilide (benzenediazoacetate form) does not undergo decarboxylation. It appears as acetic acid to the extent of 80–85%.

A free radical mechanism has been postulated for the formation of biaryls by reaction of diacyl peroxides, of diazonium salts and alkali, and of N-nitrosoacylanilides with aromatic solvents.[3] We have found it desirable to re-examine the bases for postulating a free radical rather than an ionic process for these reactions in order to establish a secure foundation for a continuation of our work[4] on the details of the reactions. Of the various types of evidence discussed,[3] that pertaining to the orienting and activating influence observed for various substituent groups appears to be reasonably unambiguous.[5,6]

In order to ascertain the orienting influence of a given substituent it is necessary to know the relative amounts of the isomeric biaryl products formed. The presently available orientation data have accumulated as a result of preparative investigations involving the physical separation of biaryls from the reaction mixture and from one another. Because of the experimental difficulties involved, it is not surprising that a large proportion of the biaryl fraction usually remains unidentified. The most complete recovery and separation has been accomplished with the less soluble products such as the dinitrobiphenyls and the *p*-terphenyl derivatives. Representative data are summarized in Tables I, II and III.

Although these data as a whole lend support to the idea that substituent groups are generally ortho–para directing in the Gomberg–Bachmann reaction and in the reaction of N-nitrosoamides with aromatic solvents, quantitative information is clearly desirable for comparison of these reactions with halogenation, nitration and other ionic reactions.[7,8] Furthermore, a direct quantitative intercomparison of the three biaryl formation reactions is of interest.

Table I

Orienting Influence of Substituents in the Gomberg-Bachmann Reaction of Benzenediazonium Salts[9]

Solvent	Biaryls formed[a]	Yield, %	Ref.
C_6H_5CN	$C_6H_5C_6H_4CN$-4[b]	10	10
$C_6H_5COOCH_3$	($C_6H_5C_6H_4COOCH_3$-4)[b]	..	10
$C_6H_5CH_3$	($C_6H_5C_6H_4CH_3$-2 and -4)[c]	..	11
$C_6H_5NO_2$	$C_6H_5C_6H_4NO_2$-4	36	12
$C_6H_5NO_2$	($C_6H_5C_6H_4NO_2$-2 and -4)[d]	..	13
C_5H_5N[e]	$C_6H_5C_5H_4N$-2, -3, and -4[e]	(40)	14
$C_6H_5NO_2$[f]	4-$O_2NC_6H_4C_6H_4NO_2$-4	75	12

[a] Inclusion of a product in parentheses indicates that only a trace of the product was actually identified. [b] Identified by m.p. [c] Identified by oxidation to biphenylcarboxylic acids. [d] 4-Nitrobiphenyl isolated, 2-isomer identified as 2-acetamidobiphenyl. [e] Pyridine. The phenylpyridines were separated by recrystallization of the picrates. [f] *p*-Nitrobenzenediazonium salt of 1,3-naphthalenedisulfonic acid. Para substitution with *o*- and *m*-nitrobenzenediazonium salts and nitrobenzene is reported in 30 and 54% yields.

We have studied the orienting influence of the nitro group of nitrobenzene in its reaction with benzoyl peroxide, with benzenediazonium chloride and alkali, and with N-nitrosoacetanilide. The nitrobiphenyl fraction was isolated from the reaction mixture by steam-distillation, and then 2-, 3- and 4-nitrobiphenyl and residual nitrobenzene were determined in the presence of each other by spectrophotometric means. The results, summarized in Table IV, show that the three reactions are alike in producing mostly 2-nitrobiphenyl, a somewhat smaller amount of 4-nitrobiphenyl, and only traces of 3-nitrobiphenyl. The high yield of 2-nitrobiphenyl is unexpected and serves to emphasize the incompleteness of data based only on isolation experiments. The more soluble 2- and 3-isomers are harder to isolate than the 4-isomers, a situ-

---

(1) Presented before the Division of Organic Chemistry at the 118th Meeting of the American Chemical Society, Chicago, 1950.

(2) This paper is based for the most part on a thesis presented by Harry J. Scheifele, Jr., to the Graduate School of Cornell University in partial fulfillment of the requirements for the M.S. degree.

(3) W. A. Waters, "The Chemistry of Free Radicals," Oxford University Press, New York, N. Y., 1946.

(4) D. F. DeTar and S. V. Sagmanli, This Journal, **72**, 965 (1950).

(5) Excellent discussions of the mechanism of the substitution reactions are given by P. D. Bartlett, "Organic Chemistry," edited by H. Gilman, 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1943, p. 205, and G. W. Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 256.

(6) For further examples of anionic substitution *cf.* A. Wohl, *Ber.*, **32**, 3486 (1899); A. Wohl and W. Aue, *Ber.*, **34**, 2444 (1901). For other examples see German Patent 116,790; *Friedlaender*, **6**, 113 (1904).

(7) A. F. Holleman, *Chem. Revs.*, **1**, 187 (1924).

(8) J. S. Reese, *ibid.*, **14**, 55 (1934).

(9) W. E. Bachmann and R. A. Hoffman; "Organic Reactions," Vol. 2, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 224.

(10) M. Gomberg and W. E. Bachmann, This Journal, **46**, 2339 (1924).

(11) M. Gomberg and J. C. Pernert, *ibid.*, **48**, 1372 (1926).

(12) H. H. Hodgson and E. Marsden, *J. Chem. Soc.*, 208 (1940).

(13) W. S. M. Grieve and D. H. Hey, *ibid.*, 1797 (1934).

(14) J. W. Haworth, I. M. Heilbron and D. H. Hey, *ibid.*, 349 (1940).

TABLE II

ORIENTING INFLUENCE OF SUBSTITUENTS IN THE REACTION OF BENZOYL PEROXIDE WITH AROMATIC SOLVENTS

Solvent	Biaryls formed^a	Yield of isomer mixture, %	Ref.
C_6H_5Cl	($C_6H_5C_6H_4Cl$-4)^b	35	15
$C_6H_5NO_2$	($C_6H_5C_6H_4NO_2$-2 and 4)^c	42	15
$C_6H_5COOC_2H_5$	($C_6H_5C_6H_4COOC_2H_5$-3 and -4)^d	35	15
$C_6H_5CH_3$	($C_6H_5C_6H_4CH_3$-4)^e	..	16
C_5H_5N	($C_6H_5C_5H_4N$-2, -3, and -4)^f	37	17

^{a} Inclusion of a product in parentheses indicates that only a trace of the product was actually identified. ^{b} Identified by oxidation to 4-chlorobenzoic acid and by bromination to 4-chloro-4′-bromobiphenyl. ^{c} 4-Nitrobiphenyl isolated; 2-isomer identified as 2-acetamidobiphenyl. ^{d} Identified by hydrolysis to 3- and 4-biphenylcarboxylic acids, the latter is stated to predominate. ^{e} Identified by oxidation to *p*-phenylbenzoic acid. Other methylbiphenyls also present as indicated by m.p. ^{f} Phenylpyridines identified as picrates.

TABLE III

ORIENTING INFLUENCE OF SUBSTITUENTS IN THE REACTION OF N-NITROSOACETANILIDE WITH AROMATIC SOLVENTS

Solvent	Biaryls formed^a	Yield, %	Ref.
$C_6H_5NO_2$	($C_6H_5C_6H_4NO_2$-2 and -4)^b	..	13
C_6H_5CHO	($C_6H_5C_6H_4CHO$-4)^c	..	13
1,2-$CH_3C_6H_4NO_2$	($C_6H_5C_6H_5NO_2CH_3$-4,3)^d	..	13
C_5H_5N	$C_6H_5C_5H_4N$-2, -3 and -4^e	(60)	18
$C_6H_5Cl^f$	4-$C_6H_5C_6H_4C_6H_4Cl$-2	17	19
	4-$C_6H_5C_6H_4C_6H_4Cl$-3	13	
	4-$C_6H_5C_6H_4C_6H_4Cl$-4	26	
$C_6H_5Br^f$	4-$C_6H_5C_6H_4C_6H_4Br$-2	7	19
	4-$C_6H_5C_6H_4C_6H_4Br$-3	16	
	4-$C_6H_5C_6H_4C_6H_4Br$-4	28	
$C_6H_5NO_2$	4-$C_6H_5C_6H_4C_6H_4NO_2$-2	36	19
	4-$C_6H_5C_6H_4C_6H_4NO_2$-4	31	

^{a} Inclusion of a product in parentheses indicates that only a trace of the product was actually identified. ^{b} 4-Nitrobiphenyl identified by m.p.; 2-isomer identified as 2-acetamidobiphenyl. ^{c} Identified as the 2,4-dinitrophenylhydrazone. ^{d} Identified as 4-acetamido-3-methylbiphenyl. ^{e} Phenylpyridines separated as picrates. ^{f} N-Nitroso-4-acetamidobiphenyl used in this experiment; products were substituted *p*-terphenyls as listed.

ation pointed out by Hey and Waters.[20] Allowing for this, France, Heilbron and Hey (Table III) obtained results similar to ours in the reaction of N-nitroso-4-acetamidobiphenyl with nitrobenzene.

The fact that the nitro group is ortho–para directing is consistent only with a nucleophilic substitution step or with a process involving free radical intermediates. Since cleavage of either benzenediazo compounds or of benzoyl peroxide in such a way as to give the required nucleophilic agent (a phenyl anion, which might be formed only in the transition state complex) is improbable, the free radical process is the alternative and seems adequately established.

TABLE IV

THE YIELD OF THE ISOMERIC BIPHENYLS FORMED IN THE REACTIONS OF N-NITROSOACETANILIDE, OF BENZOYL PEROXIDE AND OF BENZENEDIAZONIUM CHLORIDE AND ALKALI WITH NITROBENZENE

Reactant^a	Total yield of NB,^{b} g.	%	Non-steam-volatile residue, g.	Yield of nitrobiphenyl,^{b,c} % 2-NB	3-NB	4-NB
NA^d	0.972	53	0.510	32(60)	5(9)	17(31)
NA^d	0.705	39	.561	23(60)	3(7)	13(33)
BP^e	0.970	79	.342	56(72)	2(2)	21(26)
BP^{e,f}	1.300	106	.326	80(76)	0	26(24)
BP^{e,f}	1.041	84	...	58(69)	4(5)	22(26)
BD^g	0.436	18	.816	12(61)	0	7(39)
BD^g	0.731	30	.698	16(55)	1(4)	12(41)

^{a} The following abbreviations are used: NB = nitrobiphenyl, NA = N-nitrosoacetanilide, BP = benzoyl peroxide, BD = benzenediazonium chloride + alkali. ^{b} Yields are based on the formation of one mole of nitrobiphenyls from one mole of N-nitrosoacetanilide, one mole of benzoyl peroxide, or one mole of benzenediazonium chloride. ^{c} The figures in parentheses give the ratio in which the isomers were formed. Thus in the first row 60% (0.583 g.) of the nitrobiphenyl fraction consisted of 2-nitrobiphenyl. The 0.583 g. represents a 32% yield based on the N-nitrosoacetanilide taken. ^{d} A solution of 1.50 g. of N-nitrosoacetanilide in 100 cc. of nitrobenzene allowed to stand for 48 hours at room temperature. ^{e} A solution of 1.50 g. of benzoyl peroxide in 100 cc. of nitrobenzene kept at 90–100° for more than 24 hours. ^{f} The greater than 100% yield of nitrobiphenyls was attributed to the presence of benzoic acid since no particular steps were taken to remove this material. Since benzoic acid has an extinction maximum at 230 mμ, it will tend to be measured as an enhanced yield of 2-nitrobiphenyl. In the third experiment carried out by Mr. Alex Hlynsky, the nitrobiphenyl fraction was extracted with alkali to ensure the removal of benzoic acid. ^{g} Aniline (1.15 g.) was diazotized (total of 5 cc. of water used) and stirred with 50 cc. of nitrobenzene at 5–10° while 5 cc. of 35% sodium hydroxide solution was added. In the first experiment the temperature was maintained at 0–5° with the result that some of the nitrobenzene solidified.

The similarity of the ratios of nitrobiphenyls formed in these three reactions provides additional evidence of the correctness of the free radical hypothesis, for other reactions of benzoyl peroxide and of diazonium compounds would lead one to expect a free radical process under the reaction conditions involved in biaryl formation.

The activating or deactivating influence of substituent groups in biaryl formation has been reported previously for a few examples, but some of these[21] do not distinguish well between an ionic and a free radical process. In the reaction of benzenediazonium chloride (1.00 mole) and alkali with an equimolar mixture of toluene and nitrobenzene, Grieve and Hey[13] were able to isolate 0.12 mole of nitrobiphenyls and only 0.032 mole of methylbiphenyls. This experiment is a significant one, even after making liberal allowance for a possibly incomplete recovery of biaryls, for in competitive electrophilic substitution reactions with benzene (which is less reactive than toluene) and nitrobenzene, it is the benzene which reacts to the virtual exclusion of the nitrobenzene. An example of such a reaction is the mononitration of benzene which can be carried out in 99.5% yield.[22]

We have carried out the thermal decomposition of N-nitrosoacetanilide in an equimolar mixture of benzene and chlorobenzene in order to determine whether the deactivating influence of the chloro group toward electrophilic substitution would pre-

---

(15) D. H. Hey, *J. Chem. Soc.*, 1966 (1934).

(16) W. Dietrick, *Helv. Chim. Acta*, **8**, 149 (1925).

(17) D. H. Hey and E. W. Walker, *J. Chem. Soc.*, 2213 (1948).

(18) J. W. Haworth, I. M. Heilbron and D. H. Hey, *ibid.*, 372 (1940).

(19) H. France, I. M. Heilbron and D. H. Hey, *ibid.*, 1364 (1938).

(20) D. H. Hey and W. A. Waters, *ibid.*, 882 (1948).

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

(22) Groggins, "Unit Processes in Organic Syntheses," 3rd ed., McGraw-Hill Book Company, Inc., New York, N.Y., 1947, p. 43.

vail here. Bird and Ingold, for example, found that benzene is nitrated thirty times as fast as chlorobenzene by nitric acid in acetic anhydride.[23] Our results show that the chloro group is more of an activating group than a deactivating one in the biaryl formation since more chlorobiphenyl was formed than biphenyl. This result is consistent with a free radical mechanism but is not in accord with an electrophilic substitution process.

Although the above results indicate that biaryl formation occurs by a free radical mechanism, they give no indication of the details of the process. We consider the radical substitution hypothesis[3] inadequate for reasons discussed elsewhere.[4] A possible alternative hypothesis has also been presented,[4] but further discussion is not appropriate until more evidence has been accumulated.

In connection with the decomposition of N-nitrosoacetanilide we have examined briefly other products formed. The work of Kharasch and his coworkers[24a] and of others[24b] on the products of the thermal decomposition of acetyl peroxide has made it seem likely that the formation of acetoxyl radicals should result also in the formation of some carbon dioxide by decarboxylation of such radicals. Huisgen and Horeld,[24c] however, report (without experimental detail) that carbon dioxide is not evolved in the thermal decomposition of N-nitrosoacetanilide in aromatic solvents. We have confirmed this point by the measurements shown in Table V. The amount of carbon dioxide obtained from acetyl peroxide in nitrobenzene was also measured for comparison purposes. Inasmuch as the rate of decomposition of N-nitrosoacetanilide is very much faster than that of acetyl peroxide, decompositions of the nitroso compound are usually carried out at a relatively low temperature (25–50°). To eliminate the possibility that the greater decarboxylation of acetyl peroxide was due to a greater thermal instability of acetoxyl radicals at the higher temperatures usually employed for the peroxide decompositions (80–100°), both reactions were carried out at about the same temperature. The pronounced difference in the extent of decarboxylation shows clearly that the peroxide and the nitrosoamide (*via* benzenediazoacetate) cannot both be reacting entirely by a dissociation into acetoxyl radicals which then react only by decarboxylation or with solvent. It seems necessary to assume that the decarboxylation of acetyl peroxide is tied in with the cleavage step or else that one or both compounds are undergoing an induced (chain) decomposition.

TABLE V

DETERMINATION OF THE AMOUNT OF CARBON DIOXIDE EVOLVED FROM THE REACTION OF N-NITROSOACETANILIDE WITH AROMATIC SOLVENTS[a]

NA[b] Mmoles	Solvent[c]	Temp., °C.	CO_2, %
18.2	Nitrobenzene (200)	50	0.0
9.1	Nitrobenzene (80)	95[d]	0.7
[e]	Nitrobenzene (45)	95	75[f]
18.2	Benzene (10)	50	0.8
18.2	Benzene (89) + Chlorobenzene (102)	50	0.4

[a] For procedure used see experimental section. [b] NA = N-nitrosoacetanilide. [c] Amount of solvent (cc.) given in parentheses. [d] The N-nitrosoacetanilide was dissolved in 30 cc. of nitrobenzene and added gradually to 50 cc. of nitrobenzene maintained at 95°. [e] 4.87 mmoles of acetyl peroxide in 20 cc. of nitrobenzene added to 25 cc. of the same solvent maintained at 95°. This peroxide sample was very kindly furnished by R. A. Mundy of this Laboratory. [f] 7.31 mmoles.

That the acetoxyl group is converted largely to acetic acid was reported by Huisgen and Horeld. We have confirmed this not only by titration, but also by isolation and preparation of a derivative of the acetic acid.

Acknowledgment.—We wish to express our appreciation to the Rohm and Haas Company for a grant which made possible the completion of this work.

Experimental

Source of Reagents.—The N-nitrosoacetanilide was prepared by nitrosation of acetanilide with nitrosyl chloride according to the method of France, Heilbron and Hey.[25] The benzoyl peroxide was commercial (Eastman Kodak Co. white label). The reference samples of 2-, 3- and 4-nitrobiphenyl were prepared by the Gomberg–Bachmann reaction from the corresponding nitroanilines. They were purified by distillation and by recrystallization to constant m.p. and to constant extinction coefficient.

Procedure for Isolation of the Nitrobiphenyls.—The dark brown nitrobenzene solution resulting from the thermal decomposition reactions described in Table IV was subjected to steam distillation. The flask used was a 500-cc. long-necked round-bottom flask equipped with a Kjeldahl head to minimize mechanical carry-over of tarry residues. The nitrobenzene was obtained in the first liter of distillate, several fractions being collected near the end of the removal of the nitrobenzene. The nitrobiphenyls came over in the next four liters of distillate, but a total of nine liters was collected. The nitrobiphenyl fractions and the fractions containing the last few cc. of nitrobenzene were combined and extracted in portions with methylene chloride. To avoid contamination with stopcock lubricant, the extraction was carried out in a 5-l., 3-necked round-bottom flask equipped with an 1800 r.p.m. T-shaped centrifugal stirrer, and the lower methylene chloride layer was transferred by vacuum to a ground-joint (unlubricated) distillation assembly. The residue after removal of the methylene chloride was re-steam-distilled, 2.5 l. of distillate collected of which the last liter was clear and colorless. The difference in amount of steam required is due to the absence of tarry residues which seem to retard the distillation of the nitrobiphenyls. After extraction with methylene chloride and some concentration by distillation, the solution was dried over magnesium sulfate and the extracts evaporated to dryness. The composition of this mixed nitrobiphenyl fraction containing a trace of nitrobenzene was determined spectrophotometrically. Preliminary experiments with chromatographic separation on silica showed some separation of the isomers, but the experiments were not pursued further.

Determination of the Nitrobiphenyls and of Nitrobenzene.—Figure 1 shows the absorption spectra of these four compounds in isoöctane. The following wave lengths were chosen for the analysis; 221.5, 231.5, 244.0, 247.0, 252.0, 260.0, 290.0, 294.0. The method of Tunnicliff, Brattain and Zumwalt[26] was followed and the data treated by the usual least squares method. Known mixtures were analyzed by this procedure as shown in Table VI. The steam distillation was also checked in part as also shown in the above table. Since the nitrobiphenyls are not very soluble in isoöctane, it was found advisable to use methylene chlo-

---

[23] M. L. Bird and C. K. Ingold, *J. Chem. Soc.*, 918 (1938).

[24] (a) M. S. Kharasch, H. N. Friedlander and W. H. Urry, *J. Org. Chem.*, **14**, 91 (1949); M. S. Kharasch and M. T. Gladstone, THIS JOURNAL, **65**, 15 (1943). (b) Edwards and Mayo, *ibid.*, **72**, 1265 (1950). (c) R. Huisgen and G. Horeld, *Ann.*, **562**, 137 (1949).

[25] H. France, I. M. Heilbron and D. H. Hey, *J. Chem. Soc.*, 369 (1940).

[26] D. D. Tunnicliff, R. R. Brattain and L. R. Zumwalt, *Anal. Chem.*, **21**, 890 (1949).

ride to dissolve the fraction isolated by steam distillation and for making the preliminary dilution. The final dilution was made with isoöctane so that the solution measured contained exactly 2% of methylene chloride, as did the reference solvent. It was found that the extinction coefficients observed in the presence of this amount of methylene chloride were the same as those found in pure isoöctane.

TABLE VI

ANALYSIS OF KNOWN MIXTURES OF NITROBIPHENYLS

Isomer[a]	Concn. taken mg./l.[b]	Concn. found mg./l.	Ratio of isomers, %	
			Taken	Found
2-NB	4.44	4.41	41.2	40.4
3-NB	3.77	3.88	35.0	35.5
4-NB	2.56	2.63	23.8	24.1
Total	10.77	10.92	100	100
2-NB	4.44	4.59	38.7	39.3
3-NB	1.88	1.89	16.4	16.2
4-NB	5.12	5.19	44.8	44.5
Total	11.44	11.67	100	100
2-NB	2.55	2.65	25.9	26.7
3-NB	1.14	1.11	11.6	11.2
4-NB	2.83	2.84	28.8	28.6
$C_6H_5NO_2$	3.32	3.34	33.7	33.6
Total	9.84	9.94	100	100
2-NB[c]	4.46	4.40	35.5	36.1
3-NB	4.10	3.84	32.6	32.5
4-NB	4.00	3.84	31.8	31.5
$C_6H_5NO_2$	0.0	0.0	...	...
Total	12.56	12.18	100	100

[a] NB = nitrobiphenyl. [b] The figures in this column were calculated from the quantities actually taken, For the first three analyses, the test solution was made up by mixing dilute solutions of the pure known compounds. For the test of the steam distillation a sample consisting of 0.1115 g. of 2-nitrobiphenyl, 0.1025 g. of 3-nitrobiphenyl and 0.1000 g. of 4-nitrobiphenyl was used. [c] In this experiment the nitrobiphenyls (but no nitrobenzene) were carried through the steam distillation procedure; the recovery was about 97% as shown by the figures.

Reaction of N-Nitrosoacetanilide with Benzene.—Preliminary experiments showed that biphenyl and azobenzene dissolved in benzene are not adsorbed on columns of silica or alumina. A 3.00-g. (18.2 mmoles) sample of N-nitrosoacetanilide in 10 cc. of benzene was kept at 45° for a few hours. The benzene solution was washed with bicarbonate to remove acetic acid, dried over magnesium sulfate, then poured through a column of F-20 alumina.[27] Most of the tarry by-products were retained on the column and the biphenyl-azobenzene mixture was obtained in the first fraction (1.4 g., 9 mmoles). In the next fractions 0.1 g. of material was obtained. This gave crystals, m.p. 210–211.5° cor. on sublimation and was probably *p*-terphenyl, m.p. 213° cor.[28]

From another decomposition of 90 mmoles of N-nitrosoacetanilide in 400 cc. of benzene at room temperature other products were identified. Distillation of the benzene and titration of an aliquot showed the presence of 72.5 meq. of acetic acid (benzene and acetic acid form an azeotrope). By vacuum distillation and chromatography 6.95 g. (45 mmoles) of a mixture of azobenzene and biphenyl was obtained; the completeness of the recovery was not ascertained, however. Analysis for nitrogen showed the presence of about 1% indicating the presence of about 6% of azobenzene in the mixture. A sample of azobenzene was isolated by extraction with concd. sulfuric acid, the azobenzene precipitated by addition to water; after recrystallization it was obtained in the form of orange crystals, m.p. 64–67°. The reported m.p. of azobenzene is 68°.[29]

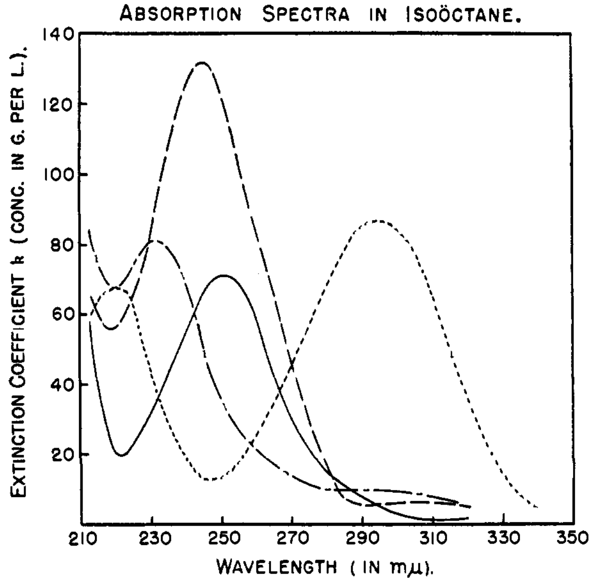

Fig. 1.——, $C_6H_5NO_2$; — —, *m*-$C_{12}H_9NO_2$; --------, *p*-$C_{12}H_9NO_2$; —-—, *o*-$C_{12}H_9NO_2$

Reaction of N-Nitrosoacetanilide with a Mixture of Benzene and Chlorobenzene.—N-Nitrosoacetanilide (20 g., 120 mmoles) was allowed to decompose in a mixture of 810 cc. (8 moles) of chlorobenzene and 720 cc. (8 moles) of benzene at room temperature overnight. Distillation of the solvent gave 103.2 meq. of acid in the first liter of distillate and 0.5 meq. of acid in the next 500 cc. of distillate. The acetic acid was isolated by extraction with potassium hydroxide, evaporation to dryness, and distillation of the resulting potassium acetate with 85% phosphoric acid. This gave a colorless liquid (about 5 cc.), b.p. 108–118°, which in turn was converted to acetanilide, m.p. 112–114°. Distillation of the residue under reduced pressure and chromatographic separation gave 11.4 g. of a mixture of azobenzene, biphenyl and chlorobiphenyl. A nitrogen analysis indicated the presence of a maximum of 6% azobenzene and chloroazobenzene, and a chlorine analysis indicated the presence of about 70% of chlorobiphenyl. To summarize there were obtained the following: 4 mmoles, 3% of azo compounds; 21 mmoles, 17% of biphenyl; and 40 mmoles, 35% of chlorobiphenyls.

Determination of Carbon Dioxide.—The thermal decomposition of the nitrosoamide was carried out in a flask equipped with a reflux condenser, a dropping funnel, and with an inlet for high purity nitrogen. The exit gases from the top of the condenser passed through a trap cooled with solid carbon dioxide, a tube containing Drierite (calcium sulfate), and then into an absorption bulb containing Ascarite (sodium hydroxide on asbestos).

ITHACA, N. Y. RECEIVED JULY 6, 1950

---

[27] Chromatographic grade obtained from the Aluminum Ore Company.

[28] W. E. Bachman and W. T. Clarke, THIS JOURNAL, **49**, 2093 (1929).

[29] I. M. Heilbron, "Dictionary of Organic Compounds," Vol. I, Oxford University Press, 1934, p. 117.