ganate. It was mixed with 0.40 g. (0.0013 mole) of *dl*-α- or *dl*-β-1,2-diphenyl-1-aryl-2-aminoethanol and heated on the steam-bath until discoloration was complete (three to four hours). The mixture was acidified, the manganese dioxide reduced with sodium bisulfite, and the solution extracted with ether. The ether layer was in turn extracted with 10% sodium bicarbonate solution, which upon concentration and acidification yielded the acidic fragments. The ether layer was evaporated to dryness and the resulting ketones recrystallized from petroleum ether.

In an attempted oxidation with periodic acid[20] 96% of the starting material was recovered and traces of benzaldehyde could be identified as the 2,4-dinitrophenylhydrazone, m. p. 235–236°.

Summary

The course of the rearrangement with nitrous acid of certain unsymmetrically substituted triphenylethanolamines has been shown to be determined by the stereochemistry of the rearranging molecule.

A possible interpretation of this observation has been discussed and relative configurations have tentatively been assigned to the pairs of racemates studied.

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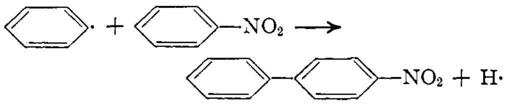
(20) R. Adams, Ed., "Organic Reactions," John Wiley and Sons, New York, N. Y., 1944, Chapt. VIII; Karrer and Hirohata, *Helv. Chim. Acta*, **16**, 495 (1933).

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY OF CORNELL UNIVERSITY]

The Mechanism of the Cyclization Reaction in the Decomposition of Diazonium Salts[1]

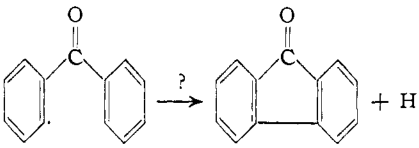
BY DELOS F. DETAR AND SENOL V. SAGMANLI

The work of Hey and Waters[2] has shown that a close relationship exists among the following three reactions which lead to the formation of biphenyl derivatives: (1) the decomposition of diazonium salts under alkaline conditions in the presence of an aromatic solvent by the method of Gomberg and Bachmann,[3] (2) the thermal decomposition of nitrosoacylanilides[4] in an aromatic solvent, and (3) the thermal decomposition of diacyl peroxides in an aromatic solvent. Hey and Waters have amassed a considerable body of evidence to indicate that free radicals are involved in all of these reactions. In order to account for the formation of symmetrical biaryls, they have postulated a reaction scheme which includes a radical substitution step.[2,5] Equation 1, for example, is postulated to be a common step in the decomposition in the presence of nitrobenzene of benzenediazohydroxide,[6a] nitrosoacetanilide,[4] or benzoyl peroxide.[6b] This step is formally analogous to the usual electrophilic substitution reactions such as the nitration of benzene[7] and it is also analogous to the less common nucleophilic substitution reactions such as the amination of pyridine.[8]



(1)

Direct evidence about the possibility of the radical substitution step (Eq. 1) in aromatic systems is not available, but indirect evidence discussed later suggests that radical substitution reactions are not of general occurrence. The purpose of the present program has been to obtain additional evidence about the occurrence of radical substitution by a study of systems which are especially favorable for this reaction. Because the possibility of closing a five- or a six-membered ring constitutes a considerable driving force in a chemical reaction,[9] a study of the products obtained from the reaction of a radical which can form a five- or a six-membered ring by radical substitution (Eq. 2) should give the desired information. The presence of the cyclized compound among the reaction products would con-



(2)

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(1) From a thesis presented by Senol V. Sagmanli to the Graduate School of Cornell University, June, 1949, in partial fulfillment of the requirements for the degree of Master of Science.

(2) (a) Hey and Waters, *Chem. Revs.*, **21**, 169 (1937); (b) Waters, "The Chemistry of Free Radicals," Oxford University Press, London, 1946, p. 148, p. 165.

(3) Bachmann and Hoffman, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 224.

(4) Grieve and Hey, *J. Chem. Soc.*, 1797 (1934).

(5) A variation of this mechanism has been proposed by Price, "Mechanisms of Reactions at Carbon-Carbon Double Bonds," Interscience Publishers, Inc., New York, N. Y., 1946, p. 53. Price postulates that the substitution is a two-step process. In general, evidence about the direct substitution step (Eq. 1) is also applicable to this variation.

(6) (a) Gomberg and Bachmann, THIS JOURNAL, **46**, 2339 (1924); (b) Hey, *J. Chem. Soc.*, 1966 (1934).

(7) (a) Gillespie and Millen, *Quart. Revs.*, **2**, 277 (1948); (b) *cf.* also Bartlett in Gilman, "Organic Chemistry," 2d ed., John Wiley and Sons, Inc., New York, N. Y., 1943, p. 205; (c) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 309.

(8) M. T. Leffler, "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 91; *cf.* ref. 7b, p. 211; Russell and Telibens, *Org. Syntheses*, **22**, 35 (1942).

(9) For example, although benzophenone in common with other benzene derivatives containing *m*-directing substituents is unreactive toward Friedel–Crafts substitution, nevertheless anthraquinones are readily formed from *o*-benzoylbenzoic acids by an internal Friedel–Crafts substitution into a ring containing the deactivating benzoyl group. The driving force which makes this reaction possible is the formation of the six-membered ring. The cyclization even occurs in the presence of two deactivating groups, for 2,4′-benzophenonedicarboxylic acid cyclizes to 2-anthraquinonecarboxylic acid.[10]

(10) Limpricht, *Ann.*, **309**, 96 (1899).

stitute evidence that radical substitution occurs under certain conditions, and the absence of the cyclized compound would show that radical substitution cannot be an important reaction.

Presumably radicals of the required type can be obtained by any of the three methods already mentioned. Diazonium compounds were chosen as the source of radicals in the present investigation. Evidence is presented in the discussion section that diazonium compounds react by a mechanism involving free radicals under alkaline conditions, but that they react by an ionic mechanism under acidic conditions.

The formation of cyclic products from diazonium compounds is a well-known reaction. Examples include the formation of variously substituted fluorenes, fluorenones, dibenzofurans[11] and phenanthrene derivatives,[12] the cyclization to phenanthrene derivatives being known as the Pschorr reaction. Practically all of these cyclizations have been carried out under strongly acidic conditions.

We have investigated the decomposition under a variety of conditions of a series of diazonium salts which can form cyclic products. The results summarized in Table I show that high yields of cyclic products are formed only under strongly acidic conditions. Decomposition in basic solution at a *p*H of about 9, conditions which should favor an internal Gomberg–Bachmann reaction, led to little or no cyclic product. The complex mixtures contained much polymeric material. These diazonium salts do undergo the typical Gomberg–Bachmann reaction with benzene and alkali to give 2-substituted biphenyls, and they undergo the coupling reaction in ammoniacal solutions in the presence of copper powder or cuprous oxide to give symmetrical biphenyl derivatives.[13]

TABLE I

PRODUCTS OBTAINED ON THE DECOMPOSITION OF DIAZONIUM SALTS WHICH CAN FORM CYCLIC PRODUCTS

Amine diazotized	Reaction conditions	Decomposition products[a]
2-Aminodiphenyl ether hydrochloride	50% H_2SO_4	45% pure dibenzofuran[bc]
	NH_4OH + CuOH	35% 2,2′-diphenoxyazobenzene[d]
	*p*H 9 (NaOH)	No steam-volatile material[e]
	NaOH + C_6H_6	25% 2-phenoxybiphenyl[e]
2-Aminobenzophenone	Dil. H_2SO_4	80% fluorenone[f]
	NH_4OH + Cu	10% fluorenone, 30% 2,2′-dibenzoylbiphenyl[e]
	NH_4OH + CuOH	10% fluorenone, 30% 2,2′-dibenzoylbiphenyl
	Acetate buffer	fluorenone, benzophenone
	NaOH	1% steam-volatile material[g]
	NaOH + C_6H_6	15% 2-benzoylbiphenyl[e]
2-Aminodiphenyl sulfide	Dil. H_2SO_4	15% dibenzothiophene, 2-hydroxydiphenyl sulfide[e]
	H_2SO_4 + Cu	25–35% dibenzothiophene[e]
	H_2SO_4 + $CuSO_4$	25% dibenzothiophene[e]
	*p*H 8–9 (NaOH)	10% dibenzothiophene
2-Aminodiphenyl sulfone	Dil. H_2SO_4	60% 2-hydroxydiphenyl sulfone[h]
	H_2SO_4 + Cu	30% mixture[i]
	H_2SO_4 + $CuSO_4$	45% 2-hydroxydiphenyl sulfone; 5% biphenylene sulfone
	NaOH	No biphenylene sulfone found
2-Amino-4′-methyldiphenyl sulfide	Dil. H_2SO_4	22% 3-methyldibenzothiophene[e]
	H_2SO_4 + Cu	23–40% 3-methyldibenzothiophene[e]
	NaOH	No steam-volatile material[e]
2-Amino-4′-methyldiphenyl sulfone	Dil. H_2SO_4	35% 2-hydroxy-4′-methyldiphenyl sulfone[e]
	H_2SO_4 + Cu	30% neutral mixture, 10% 2-hydroxy-4′-methyldiphenyl sulfone[e]
	NaOH	No isolable product

[a] The yields reported are based on partly purified material unless otherwise specified. [b] M. p. 84.5–85.5°. Duplicate experiments gave 42 and 48% yields. Graebe and Ullmann report a 30% yield of pure dibenzofuran.[11b] [c] Isolated by steam distillation. [d] Procedure of Atkinson,[14] product isolated by chromatographic adsorption on alumina using benzene as the solvent. Azo compounds are often formed in these coupling reactions; m. p. of product 169–170°; Haeussermann and Teichmann[15] report a m. p. of 168–169°. [e] See experimental section. [f] M. p. 78–82°. Ullmann and Mallett report a 90% yield.[11d] [g] Probably fluorenone. [h] M. p. 79–81°. A small amount of biphenylene sulfone was also obtained. [i] Biphenylene sulfone and diphenyl sulfone.

Discussion

The following factors indicate that the decomposition of diazonium salts under acidic conditions occurs by an ionic mechanism: (1) the decomposition of benzenediazonium chloride and its derivatives in aqueous acid solution follows first order kinetics over a wide range of concentrations of diazonium salt.[16] (2) Pray[16b] showed that the rate of decomposition of benzenediazonium chloride was almost completely unaffected by the presence of roughly 0.4 molar concentrations of a large number of salts including as anions chloride, bromide, nitrate, sulfate, formate, oxalate and thiocyanate. (3) Euler[16c] showed that benzenediazonium nitrate, bromide and sulfate in the complete absence of chloride ion decomposed at the same rate as benzenediazonium chloride. This evidence indicates that the diazonium ion is decomposing independently of the anions present. It would require the formation of either an $N_2\cdot^+$ radical or of an $H_2O\cdot^+$ radical if an aryl radical were to be formed in the decomposition, and it seems reasonable to suppose that the reaction is instead an ionic one[17]

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[11] (a) Fischer and Schmidt, *Ber.*, **27**, 2786 (1894); (b) Graebe and Ullmann, *ibid.*, **29**, 1876 (1896); (c) Huntress, Pfister and Pfister, THIS JOURNAL, **64**, 2845 (1942); (d) Ullmann and Mallet, *Ber.*, **31**, 1694 (1898); (e) Graebe and Ullmann, *Ann.*, **291**, 8 (1896); (f) Chardonnens and Würmli, *Helv. Chim. Acta*, **29**, 922 (1946).

[12] (a) Pschorr, *Ber.*, **29**, 496 (1896); (b) Pschorr, *ibid.*, **39**, 3106 (1906); (c) Pschorr, Seydel and Stöhrer, *ibid.*, **35**, 4400 (1902), p. 4408.

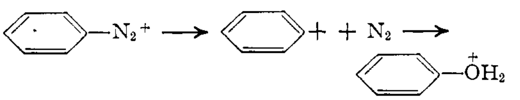
[13] (a) Vorländer and Meyer, *Ann.*, **320**, 122 (1902); (b) Atkinson, Morgan, Warren and Manning, THIS JOURNAL, **67**, 1513 (1945).

[14] Atkinson, Lawler, Heath, Kimball and Read, *ibid.*, **63**, 730 (1941), Method 2; *cf.* also ref. 13.

[15] Haeussermann and Teichmann, *Ber.*, **29**, 1446 (1896).

[16] (a) Cain and Nicoll, *J. Chem. Soc.*, **81**, 1412 (1902); **83**, 470 (1903); (b) Pray, *J. Phys. Chem.*, **30**, 1417 (1926); (c) Euler, *Ann.*, **325**, 292 (1902); (d) Crossley, Kienle and Benbrook, THIS JOURNAL, **62**, 1400 (1940); (e) Moelwyn-Hughes and Johnson, *Trans. Faraday Soc.*, **36**, 948 (1940).

[17] In this equation and in Eq. 4 we use the carbonium ion formulation for illustration of the principle involved in the reaction. The question as to whether the reaction is an S_N1 or an S_N2 attack of the diazonium cation by water is an open one.

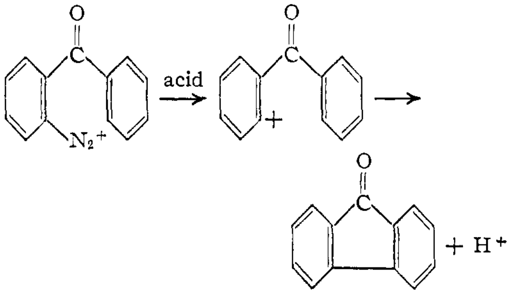


(3)

The products formed in the decomposition of diazonium salts under acidic conditions are consistent with an ionic mechanism. In aqueous solutions, for example, both phenol and chlorobenzene are formed, the amount of the latter increasing as the ratio of chloride ions to water molecules increases.[16d] The decomposition of benzenediazonium chloride in the presence of phenol at about 80°[18a] leads to the formation of *p*-hydroxybiphenyl (30% yield), some of the ortho isomer, and diphenyl ether (25% yield). In methanol the usual decomposition product is the methyl ether[18b] although alcoholic solvents often lead to replacement of the diazonium group by hydrogen, a reaction that appears to involve free radical intermediates.

Evidence that free radicals are involved in the decomposition of diazonium salts in basic solution and in the thermal decomposition of nitrosoacylanilides has been summarized by Waters.[2b] Other evidence of the presence of radicals is based on the fact that alkaline solutions of diazonium salts[19] and the nitrosoacylanilides[20] are both vinyl polymerization initiators.

The reactions reported in Table I are consistent with and lend considerable support to the hypothesis that two different mechanisms are involved in the decomposition of diazonium salts depending on the acidity of the medium. The cyclization reaction under acidic conditions appears to involve ionic intermediates and may be considered to be a sort of internal Friedel–Crafts reaction (Eq. 4). A survey of the literature indicates that the great majority of the cyclization reactions have been carried out in concentrated acid solution.[11] A few cyclizations have been carried out under alkaline conditions,[12e] but the diazonium salts involved were unusual in that they were stable enough to be recrystallized from boiling ethanol.



(4)

It seems customary to add copper powder in the Pschorr reaction[12] although many examples have been carried out without copper powder. We investigated this point briefly with the diazonium salts derived from the sulfur compounds as shown in Table I. Copper seems to increase the yield of cyclic product somewhat and to inhibit the replacement of the diazonium group by hydroxyl. Copper sulfate seems to have somewhat the same effect and has an advantage in that it does not lead to contamination of the desired cyclic product with reduced by-product formed by replacement of the diazonium group by hydrogen. We are able to offer no explanation for the effect of copper and its salts, but since the effect is not comparable with the effect obtained on changing the *p*H, the experiments involving copper will not be considered further at this time.

An ionic cyclization reaction such as that of Eq. 4 might be influenced by the presence of activating or deactivating groups in the ring which does not contain the diazonium group. The low yield of cyclization product obtained with the sulfones appears to be an example of this effect, the sulfonyl group exerting a greater deactivation than the carbonyl group. The 4′-methyl derivatives of the sulfur compounds were investigated for the activating influence of the methyl group, but the methyl group did not produce much increase in the yield of cyclic product. The work of Ruggli and Staub[21] on the reactions of the diazonium salts derived from *cis*-2-aminostilbene and from 2-aminodiphenylethane shows that steric factors may be important. The structure of the former diazonium salt is such that cyclization can occur with little change in the configuration of the molecule and cyclization occurs under all conditions tried, even in the presence of sodium hypophosphite. The latter diazonium salt cyclizes to 9,10-dihydrophenanthrene in lower yields even under favorable conditions, a result which may be attributed to the less rigid configuration with the greater chance for side reactions to occur in the interval between loss of nitrogen and rotation to a configuration suitable for cyclization.

The failure of the diazonium salts to cyclize under alkaline conditions where an internal Gomberg–Bachmann reaction is possible and the fact that these same salts undergo the regular Gomberg–Bachmann reaction with benzene to form 2-phenoxybiphenyl and 2-benzoylbiphenyl indicate clearly that the radical substitution reaction illustrated by Eq. 2 cannot account for the formation of the cyclic products. There is the further implication that this radical substitution step (Eq. 1) is not usually involved in the other examples of biphenyl formation.

These conclusions have a certain amount of support from the work of others. Wieland, Schapiro and Metzger[22] tried unsuccessfully to isolate aniline from the products of the decomposition of benzoyl peroxide in nitrobenzene.

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[18] (a) Hirsch, *Ber.*, **23**, 3705 (1890); (b) Beeson, *Am. Chem. J.*, **16**, 235 (1894).

[19] Price and Durham, THIS JOURNAL, **64**, 2508 (1942).

[20] Blomquist, Johnson and Sykes, *ibid.*, **65**, 2446 (1943).

[21] Ruggli and Staub, *Helv. Chim. Acta*, **20**, 37 (1937).

[22] Wieland, Schapiro and Metzger, *Ann.*, **513**, 93 (1934), p. 105.

Aniline might be expected as a product if hydrogen atoms had been produced. They also studied the decomposition of hydrocinnamoyl peroxide in benzene, a reaction which gave a 70% yield of 1,4-diphenylbutane and presumably little or no diphenylethane, the expected radical substitution product. Finally, one might expect the radical substitution reaction to be endothermic to the extent of about 10 kcal.[23] or so.

On the basis of recent work on typical free radical reactions such as the olefin oxidations[25] it appears possible that the biaryl formation involves a repeating sequence such as the one given in Eq. 5. A similar sequence can be written for nitrosoacylanilide decompositions, and for the Gomberg–Bachmann reaction, but in the latter case the structure of the starting product—whether diazohydroxide, diazoanhydride, or something else—is not known. Equation 5 implies that almost all of the biaryl

$$\begin{aligned} &C_6H_5COO\cdot + C_6H_5NO_2 \longrightarrow C_6H_5COOH + \cdot C_6H_4NO_2 \\ &\cdot C_6H_4NO_2 + (C_6H_5COO)_2 \longrightarrow \\ &\qquad C_6H_5C_6H_4NO_2 + CO_2 + C_6H_5COO\cdot \qquad (5) \end{aligned}$$

formed in these reactions is the result of the induced decomposition of the peroxide, nitrosoacylanilide or diazoanhydride. Assuming that the data obtained by Nozaki and Bartlett[26] for the induced decomposition of benzoyl peroxide can be extrapolated to solutions of one molar concentration, it can be estimated that about one-half of the peroxide will be decomposed by the induced mechanism. This is more than adequate to account for the usual 20–25% yields of biaryl obtained in these reactions.

Although it might be pointed out that the efficient operation of the sequence shown in Eq. 5 would mean that relatively few radicals of the type required in Eq. 2 are present in these diazonium salt decompositions, this same argument would also require as a corollary that the radical substitution step be much less favored than the sequence of Eq. 5.

Experimental[27]

Starting Materials and Reference Compounds.—These are summarized in Table II. The reported procedures were followed except where otherwise indicated.

Decomposition of the Diazonium Salts Derived from 2-Aminodiphenyl Ether.—(A) Decomposition in alkaline solution. The amine hydrochloride was dissolved in hydrochloric acid and diazotized with the equivalent amount of sodium nitrite. To this solution was added 5 *N* sodium hydroxide solution drop by drop until the *p*H was about 9. A brown solid separated. The temperature was maintained at 5–10° during the addition of alkali, and the reaction mixture allowed to remain overnight at room temperature. There was no steam-volatile material, and the 0.86 g. residue did not readily yield any crystalline material.

Table II

Preparation of Starting Materials and Reference Compounds

Compound	Obsd. m. p., °C.	Reported m. p., °C.	Ref.
2-Aminodiphenyl ether hydrochloride[a]	154.5–155	154	28
2-Aminobenzophenone	104	103	29
2-Aminodiphenyl sulfide[b]	41–42	43	30
2-Amino-4′-methyldiphenyl sulfide[a]	46–47	48.5–49	30a
2-Aminodiphenyl sulfone[b]	119.5–121	122	30a, 31
2-Amino-4′-methyldiphenyl sulfone[b]	120–121	120–121	30a, 32
Dibenzofuran	86–85	87	33
2,2′-Diphenoxybiphenyl	101–102	100–101	34, 35
2-Phenoxybiphenyl	49–50	49.5	36
2,2′-Dibenzoylbiphenyl	166.5–168	165–167	37
2-Benzoylbiphenyl	87–88	86–87	38

[a] Catalytic reduction of nitro compound with hydrogen and Raney nickel.[30a] [b] Reduced with iron and trace of hydrochloric acid in dilute ethanol. The catalytic reduction is the better method.

(B) **Decomposition in Alkaline Solution in Presence of Benzene.**—The amine hydrochloride (4.4 g.) was diazotized in 13 cc. of water by use of 1.1 cc. of 18 *M* sulfuric acid and 1.4 g. of sodium nitrite. The diazonium salt solution was stirred with 25 cc. of benzene at about 5° while 5 *N* sodium hydroxide was run in until the *p*H was 8–9. After standing overnight without further cooling the mixture was steam distilled. Evaporation of the benzene gave 1.2 g. (25%) of a nearly colorless crystalline solid, m. p. 39–45°, which on recrystallization from methanol gave colorless needles, m. p. 48–49.5°. The mixed m. p. with authentic 2-phenoxybiphenyl was 48.5–50°.

Decomposition of the Diazonium Salts Derived from 2-Aminobenzophenone. (A) Decomposition with Copper Powder in Ammonium Hydroxide.—The amine (1 g.) was diazotized in hydrochloric acid and the solution of diazonium salt added to a stirred suspension of 2 g. of copper powder in 20 cc. of 7.5 *M* ammonium hydroxide. Stirring was continued for one hour at room temperature, then the mixture was steam distilled. The distillate contained 0.11 g. (10%) of fluorenone, m. p. 79–81°. Ether extraction of the non-volatile residue gave 0.25 g. (30%) of a brown crystalline solid, m. p. 164–167°. Recrystallization from ethanol gave colorless needles, m. p 167–168°; mixed m. p. with authentic 2,2′-dibenzoylbiphenyl 168–169°.

(B) **Decomposition in Alkaline Solution in Presence of Benzene.**—The amine (3 g.) was diazotized in the presence of sulfuric acid, filtered and stirred with 25 cc. of benzene at 5° while 5 *N* sodium hydroxide was added to a *p*H of 9. After standing overnight at room temperature, the reaction mixture was steam distilled. Evaporation of the benzene gave 0.63 g. of a yellow oil which crystallized in

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(23) The energy of the reaction $C_6H_5\cdot + C_6H_6 \rightarrow C_6H_5C_6H_5 + H\cdot$ cannot be calculated at present. The energy of the reaction $C_2H_5\cdot + C_2H_6 \rightarrow C_4H_{10} + H\cdot$ and of $C_2H_5\cdot + CH_2{=}CH_2 \rightarrow C_2H_5CH{=}CH_2 + H\cdot$ may be estimated as + 18 and + 15 kcal., respectively, using the data quoted by Steacie.[24] The C–C bond appears to be uniformly weaker than the C–H bond, so that these results probably apply to the phenyl radical also. Data are not available for calculating the energy involved in Price's mechanism.[5]

(24) Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Corporation, New York, N. Y., 1946, p. 78.

(25) Bolland, *Quart. Revs.*, **3**, 1 (1949).

(26) Nozaki and Bartlett, This Journal, **68**, 1686 (1946).

(27) All melting points are corrected. Microanalyses by Mrs. P. J. Bohrer.

(28) Jones and Cook, This Journal, **38**, 1534 (1916).

(29) Lothrop and Goodwin, *ibid.*, **65**, 363 (1943).

(30) (a) Gilman and Broadbent, *ibid.*, **69**, 2053 (1947); (b) Cullinane and Davis, *Rec. trav. chim.*, **55**, 881 (1936).

(31) Ullmann and Pasdermadjian, *Ber.*, **34**, 1150 (1901).

(32) Halberkann, *ibid.*, **55**, 3074 (1922).

(33) Cullinane, *J. Chem. Soc.*, 2267 (1930).

(34) Kleiderer and Adams, This Journal, **55**, 4219 (1933), p. 4225.

(35) Lesslie and Turner, *J. Chem. Soc.*, 281 (1932).

(36) Lüttringhaus and Sääf, *Ann.*, **542**, 241 (1939).

(37) Werner and Grob, *Ber.*, **37**, 2887 (1904).

(38) Bradsher, This Journal, **66**, 45 (1944).

part to give a solid. Repeated recrystallization of the material gave a few mg. of almost colorless crystals, m. p. 82–85°; mixed m. p. with authentic 2-benzoylbiphenyl 85–86.5°. The product and the authentic 2-benzoylbiphenyl were recrystallized from acetic acid on a microscope slide. Both specimens formed characteristic thin hexagons with two angles of about 92° and four of about 133°. In another experiment the reaction mixture was vacuum distilled. Only about one-fourth of the material was volatile up to 350° at 0.005 mm. pressure. The presence of some fluorenone was established by means of the ultraviolet absorption spectrum.

Decomposition of the Diazonium Salts Derived from 2-Aminodiphenyl Sulfide. (A) Decomposition in Acid Solution.—The orange-colored diazonium bisulfate was decomposed in dilute sulfuric acid by heating to about 90° for a few minutes. Steam distillation gave a 13% yield of dibenzothiophene, m. p. 89–94°, which was raised to 96–97°[39] on recrystallization from ethanol. The alkaline-soluble fraction amounted to 30%, and was identified by oxidation to 2-hydroxydiphenyl sulfone, m. p. 81–82°. Heppenstall and Smiles[40] report the melting point of the hydrate of 2-hydroxydiphenyl sulfone as 82°. Another experiment using 50% sulfuric acid gave a 16% yield of dibenzothiophene, m. p. 92–96°, and a 55% yield of alkaline soluble material.

(B) Decomposition in Acid Solution in the Presence of Copper Powder.—Duplicates of the above experiments except for the addition of copper powder (2 to 5 g. for a 1-g. sample of amine) led to somewhat different results. The yields of crude dibenzothiophene were 34 and 25% (m. p. 84–96°), respectively, and the yields of alkaline-soluble material were much lower, about 15%. The dibenzothiophene was contaminated somewhat with an oil which is probably the reduction product, diphenyl sulfide. The aqueous decomposition solution contained dissolved copper salts.

(C) Decomposition in Acid Solution Containing Copper Sulfate.—The results were substantially the same as with copper powder: a 25% yield of dibenzothiophene and about 10% of alkaline-soluble oil.

Decomposition of the Diazonium Salts Derived from 2-Amino-4′-methyldiphenyl Sulfide. (A) Decomposition in Acidic Solution.—The solution of diazonium salt obtained from 2.2 g. of the amine with sulfuric acid was heated to boiling. Steam distillation gave 0.59 g. of an oil of which 0.14 g. was alkali-soluble.

(B) Decomposition in Acidic Solution in the Presence of Copper Powder.—From 1.1 g. of amine there was obtained on steam distillation 0.38 g. (40%) of an almost colorless crystalline product, m. p. 82–85°. On recrystallization from ethyl alcohol, colorless needles of 3-methyldibenzothiophene, m. p. 85–86°, were obtained.

Anal. Calcd. for $C_{13}H_{10}S$: C, 78.75; H, 5.08. Found: C, 78.8, 78.4; H, 4.8, 4.8.

A duplicate run gave a 23% yield of crude product, m. p. 81–84°.

(C) Decomposition in Alkaline Solution.—By the same procedure used with 2-aminodiphenyl sulfide above, 1.1 g. of the amine gave no steam-volatile material and only about 0.02 g. of alkaline-soluble material.

Decomposition of the Diazonium Salts Derived from 2-Amino-4′-methyldiphenyl Sulfone. (A) Decomposition in Acidic Solution.—This gave 0.76 g. of 2-hydroxy-4′-methyldiphenyl sulfone, m. p. 124–125°. Rittler[41] reports a m. p. of 125–126°.

(B) Decomposition in Acidic Solution in Presence of Copper Powder.—The diazonium salt solution derived from 1.09 g. of the amine gave 0.32 g. of volatile neutral material. Recrystallizations from benzene gave about 0.03 g. of 3-methylbiphenylene sulfone, m. p. 201–201.5°.

Anal. Calcd. for $C_{13}H_{10}O_2S$: C, 67.80; H, 4.38. Found: C, 67.8; H, 4.9.

The presence of phenyl *p*-tolyl sulfone was indicated by the considerable solubility of and the low m. p. (98–108°) of successive crops of crystals obtained from the mother liquor. Separation of the phenyl-*p*-tolyl sulfone in pure form was not feasible, but its presence was definitely established by microscopic examination of a few handpicked crystals. Rhombic-shaped crystals of two characteristic forms were obtained on crystallization from acetic acid on the microscope slide. One form had an obtuse angle of 112° and showed no extinction, the other had an obtuse angle of 95° and an extinction angle of 40°. 3-Methylbiphenylene sulfone crystallizes as needles with an extinction angle of 19°.

Summary

1. Evidence has been accumulated to indicate that the decomposition of diazonium salts in acidic media goes by way of a "carbonium ion" intermediate in contrast to the decomposition in alkaline media which occurs by way of free radical intermediates.

2. The decomposition of the diazonium salt derived from 2-aminobenzophenone in acidic media led to the formation of the cyclization product, fluorenone in 80% yield, but the decomposition in alkaline media led to the formation of only traces of fluorenone. Other diazonium salts gave similar results.

3. These results show that a radical substitution step is not involved in the cyclization reactions studied and suggest that a radical substitution step is not involved in other examples of biaryl formation.

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[39] Graebe, *Ann.*, **174**, 177 (1874).

[40] Heppenstall and Smiles, *J. Chem. Soc.*, 899 (1938).

[41] Rittler, German Patent 555,409; *Chem. Zentr.*, **103**, II, 1692 (1932). Both the 2-hydroxy-4′-methyldiphenylsulfone and the corresponding 4-hydroxy-4′-methyldiphenyl sulfone were obtained by action of *p*-toluenesulfonyl chloride on phenol. The abstract reports a m. p. of 138° for the former and 125–126° for the latter isomer. Since our compound was obtained from an amine of proved structure, it appears that the reported melting points are inverted.