41. *Studies in the Diphenyl Series. Part V. The Preparation of Asymmetrical Diaryl Derivatives.*

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Diazonium salts stabilised by naphthalene-1-sulphonic acid, naphthalene-1 : 5-disulphonic acid, or zinc chloride have been decomposed in hydrocarbon and nitrobenzene suspensions in a manner analogous to the existing procedures for sodium benzenediazotate and nitrosoacetanilide. The greater reactivity of nitrobenzene, compared with benzene, with respect to sodium benzenediazotate as found by Grieve and Hey (J., 1934, 1797) has been confirmed for the stabilised diazonium salts. Decompositions of the stabilised salts by fused sodium acetate in conjunction with acetic anhydride or glacial acetic acid have afforded yields of diaryls amounting in some cases to 70%. The last-named processes appear to be far superior to the alkaline decomposition of diazotates.

Of the various methods studied in recent years for the preparation of asymmetrical diaryls from diazo-compounds, the reactions of hydrocarbons and derivatives with alkali diazotates (Gomberg and co-workers, *J. Amer. Chem. Soc.*, 1924, **46**, 2339; 1926, **48**, 1372) and with nitrosoacetanilide and analogous compounds (see Grieve and Hey, J., **1934**, 1797 *et seq.*, for their own work and for a bibliography of the subject) appeared to offer a basis for variations in procedure which would afford serviceable yields.

The decomposition of stabilised diazonium salts with hydrocarbons and certain benzene and naphthalene derivatives is now described. Three types of stabilised diazonium salt were used, *viz.*, with naphthalene-1-sulphonic and -1 : 5-disulphonic acid and with zinc chloride, and their reactions were studied in benzene, toluene, naphthalene, nitrobenzene and acetic acid. The agents used for promoting reactivity were solid sodium and potassium hydroxides, anhydrous sodium carbonate, alcoholic potassium hydroxide, glacial acetic acid, acetic anhydride, and the last two each with fused sodium acetate.

The dry, finely powdered, stabilised salt was mixed with the dry medium at 0—5° and slowly treated with the reagent for promoting the reaction. In the case of alcoholic potassium hydroxide the rate of decomposition was usually rapid and evolution of nitrogen was complete in 3—4 hours, but with acetic acid and its variants the temperature was 18—40° and the minimum period for completion of the major part of the reaction was 24 hours. In all cases the mixture was heated finally at suitable temperatures, usually on the boiling water-bath, to complete the reaction. The diaryl derivative was then extracted by a suitable procedure and by steam-distillation where practicable.

The yields were variable : (1) In benzene suspensions, solid sodium and potassium hydroxides gave only moderate results and better success was obtained with alcoholic potassium hydroxide. (2) Anhydrous sodium carbonate is a much better decomposition reagent than caustic alkali. (3) Decompositions in toluene were practically unsuccessful, whereas with nitrobenzene excellent yields were always obtained (Grieve and Hey, *loc. cit.*, found that the reaction of sodium benzenediazotate with an equimolecular mixture of toluene and nitrobenzene, both in excess, gave about four times as much nitrodiphenyl as of methyldiphenyl). Nitrobenzene is also much more reactive than benzene, and experiments with naphthalene were unsuccessful. (4) Grieve and Hey's generalisation (*loc. cit.*) that a phenyl group invariably enters an aromatic nucleus C_6H_5R in the para- and/or ortho-position with respect to R has been confirmed and extended to nitrophenyl groups, and in no case has a symmetrical diaryl been found in a reaction unless the stabilised salt was suspended in the appropriate medium for the purpose; *e.g.*, *p*-nitrobenzenediazonium salt with nitrobenzene. (5) Yields up to 70% were obtained when acetic anhydride or glacial acetic acid was used in conjunction with fused sodium acetate. This again is in accord with the superior decomposition of nitrosoacetanilide with benzene compared with the corresponding decomposition of sodium benzenediazotate (Grieve and Hey, *loc. cit.*). (6) Reactions in molten 1-nitronaphthalene gave poor yields of products containing azo-compound. (7) Some chloro-derivative was always obtained from the decompositions of diazonium salts stabilised with zinc chloride.

EXPERIMENTAL.

Preparation of the Stabilised Diazonium Salts.—The amine (0·1 g.-mol.) was diazotised at 0° in a mixture of hydrochloric acid (24 c.c., *d* 1·16) and water (150 c.c.) and treated with finely powdered naphthalene-1-sulphonic acid (0·1 g.-mol.), naphthalene-1 : 5-disulphonic acid (0·2 g.-mol.), or anhydrous zinc chloride (0·1 g.-mol.). Some stabilised diazonium salt separated immediately, but the mixture was stirred for about 1 hour to complete the precipitation. Aniline and α- and β-naphthylamines did not give serviceable naphthalenediazonium monosulphonates, since they separated as uncrystallisable oils.

Decompositions of the Stabilised Diazonium Salts.—(a) *From diazotised aniline and naphthalene-*1 : 5-*disulphonic acid in benzene suspension.* The dry salt (10 g.), well agitated with benzene (30 g.), was treated slowly at room temperature with the decomposing reagent (3 g.); after 48 hours, the mixture was heated at 80° until nitrogen ceased to be evolved. The results were as follows :

Decomposing reagent.	Yield of diphenyl, g.	%.	Remarks.
Solid sodium hydroxide	0·4	10·2	Grieve and Hey obtained a 19% yield from sodium benzenediazotate by Gomberg's method.
Solid potassium hydroxide	0·4	10·2	
Anhydrous potassium carbonate	0·3	7·6	

(b) *From diazotised aniline stabilised with zinc chloride in benzene solution.* Method as for (a), with 10 g. of stabilised salt and reaction period of 24 hours :

Decomposition reagent.	Yield of diphenyl, g.	%
Ethyl-alcoholic potassium hydroxide (15 c.c. of 30% solution)	1·3	14·6
Solid sodium hydroxide (3 g.)	0·25	2·8
Anhydrous sodium carbonate (3 g.)	0·80	9·0
Acetic anhydride (1 g.) and fused sodium acetate (3 g.)	1·8	20·2
Glacial acetic acid (1 g.) and fused sodium acetate (3 g.)	1·1	12·3

Acetic acid, acetic anhydride, and fused sodium acetate when used alone gave results very inferior to those afforded by the combination of either of the first two with the last.

(c) *From diazotised α-naphthylamine and naphthalene*-1 : 5-*disulphonic acid in a mixture of glacial acetic acid and anhydrous sodium acetate.* The stabilised salt (10 g.) was thoroughly mixed at room temperature with a solution of naphthalene (3 g.) in glacial acetic acid (30 g.) and anhydrous sodium acetate (3 g.), kept for 20 hours, and then heated for 1 hour at 80° until bubbles of nitrogen ceased to appear. The mixture was diluted with water and steam-distilled; naphthalene (3·3 g.) and α-naphthol (1·1 g.) were obtained, but no dinaphthyl could be detected.

(d) *With anhydrous sodium carbonate as decomposition reagent.* The stabilised diazonium salt (10 g.) was suspended (*a*) in benzene (30 g.), (*b*) in nitrobenzene (30 g.), and decomposed with anhydrous sodium carbonate (3 g.). After 24 hours the mixture was heated at 80° to complete the reaction.

		Products.					
			Yield,			Yield,	
Amine.	Stabiliser.	(a).	g.	%.	(b).	g.	%.
Aniline	Naphthalene-1 : 5-disulphonic acid	Diphenyl	0·7	17·0	4-Nitrodiphenyl	1·38	35·1
o-Nitroaniline	Naphthalene-1-sulphonic acid	2-Nitrodiphenyl	1·95	35·2			
m-Nitroaniline	Naphthalene-1-sulphonic acid	3-Nitrodiphenyl	3·02	54·4	3 : 4′-Dinitrodiphenyl	3·4	48·7
p-Nitroaniline	Naphthalene-1-sulphonic acid	4-Nitrodiphenyl	3·24	58·2	4 : 4′-Dinitrodiphenyl	3·0	42·6
α-Naphthylamine	Naphthalene-1 : 5-disulphonic acid	Phenyl-α-naphthyl	0·7	15·2	No result		
β-Naphthylamine	Naphthalene-1 : 5-disulphonic acid	No result.			No result		

(e) *With fused sodium acetate* (3 *g.*) *and glacial acetic acid* (1 *g.*) :

Amine.	Stabiliser.	Reactant.	Product.	Yield, g.	%
Aniline	Naphthalene-1 : 5-disulphonic acid	Nitrobenzene (30 g.)	4-Nitrodiphenyl	1·7	33·0
o-Nitroaniline	Naphthalene-1-sulphonic acid	Nitrobenzene (30 g.)	2 : 4′-Dinitrodiphenyl	2·0	30·0
m-Nitroaniline	Naphthalene-1-sulphonic acid	Nitrobenzene (30 g.)	3 : 4′-Dinitrodiphenyl	3·6	54·0
p-Nitroaniline	Naphthalene-1-sulphonic acid	Nitrobenzene (30 g.)	4 : 4′-Dinitrodiphenyl	4·6	69·0
α-Naphthylamine	Naphthalene-1 : 5-disulphonic acid	Nitrobenzene (30 g.)	1-Nitro-4-phenylnaphthalene	2·2	38·8
α-Naphthylamine	Naphthalene-1 : 5-disulphonic acid	Benzene (30 g.)	Phenyl-α-naphthyl	0·8	17·3
β-Naphthylamine	Naphthalene-1 : 5-disulphonic acid	Benzene or nitrobenzene	Mixtures containing azo-compounds		

(f) *With fused sodium acetate* (4 *g.*) *and acetic anhydride* (1 *c.c.*) :

Amine.	Stabiliser.	Reactant.	Product.	Yield, g.	%
Aniline	Naphthalene-1 : 5-disulphonic acid	Benzene (30 g.)	Diphenyl	1·8	46·6
m-Nitroaniline	Naphthalene-1-sulphonic acid	Benzene	3-Nitrodiphenyl	3·1	55·6
m-Nitroaniline	Naphthalene-1-sulphonic acid	Nitrobenzene (30 g.)	3 : 4′-Dinitrodiphenyl	3·8	54·0
p-Nitroaniline	Naphthalene-1-sulphonic acid	Benzene	4-Nitrodiphenyl	3·2	57·4
α-Naphthylamine	Naphthalene-1 : 5-disulphonic acid	Benzene	Phenyl-α-naphthyl	1·4	30·3
α-Naphthylamine	Naphthalene-1 : 5-disulphonic acid	Nitrobenzene	Mixtures containing azo-compounds		
β-Naphthylamine	Naphthalene-1 : 5-disulphonic acid	Benzene			

(g) *From diazotised amines stabilised with zinc chloride in benzene suspension with fused sodium acetate* (5 *g.*) *and glacial acetic acid* (1 *g.*). Salt taken, 10 g.; benzene, 30 g.

		Yield,	
Amine.	Product.	g.	%.
Aniline	Diphenyl	1·6	17·6
p-Nitroaniline	4-Nitrodiphenyl	3·4	37·2
p-Chloroaniline	4-Chlorodiphenyl	3·1	34·2
p-Anisidine	4-Methoxydiphenyl	2·3	26·5

Chlorobenzene (0·7 g.) and *p*-chloronitrobenzene (0·8 g.) were respectively obtained in the experiments above from aniline and *p*-nitroaniline.

(h) *From diazotised* p-*nitroaniline and three stabilisers in benzene suspension.* 10 G. of salt, 30 g. of benzene, (*a*) 15 c.c. of 30% ethyl-alcoholic potassium hydroxide, (*b*) fused sodium acetate (3 g.) and acetic anhydride (1 g.) :

	Decomposition	Yield of 4-nitrodiphenyl,	
Stabiliser.	reagent.	g.	%.
Naphthalene-1-sulphonic acid	(a)	1·4	25·1
Naphthalene-1-sulphonic acid	(b)	2·8	50·4
Naphthalene-1 : 5-disulphonic acid	(a)	1·8	39·6
Naphthalene-1 : 5-disulphonic acid	(b)	3·2	70·2
Zinc chloride	(a)	1·5	16·4
Zinc chloride	(b)	2·4	26·3

(i) Diazotised aniline, stabilised with zinc chloride or naphthalene-1 : 5-disulphonic acid (10 g. of each salt taken) and decomposed in toluene (30 g.) suspension with fused sodium acetate (3 g.) and acetic anhydride (1 g.), gave no diaryl, but with anhydrous sodium carbonate (4 g.) 4-methyldiphenyl (0·12 g.) was obtained.

The following compounds are new: 3 : 4'-*Dinitrodiphenyl*, crystallises from 80% acetic acid in pale yellow needles, m. p. 137° (Found : N, 11·6. $C_{12}H_8O_4N_2$ requires N, 11·5%). 1-*Nitro-4-phenylnaphthalene*, crystallises from 80% acetic acid in yellow clusters, m. p. 151° (Found : N, 5·8. $C_{12}H_8O_4N_2$ requires N, 5·6%).

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