[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF SOUTH CAROLINA]

Intramolecular Reactions. V. Factors Affecting the Yield in Diazonium Cyclization Reactions[1]

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RECEIVED AUGUST 30, 1956

A quantitative study of the effect of a series of reaction conditions on the product yields in the diazonium cyclization reaction shows that there is a great deal of individuality among the various diazonium salts. For the diazonium salts derived from *cis*-2-aminostilbene, from 2-amino-*sym*-diphenylethane and from 2-amino-3′-nitrobenzophenone, the best conditions are those of Pschorr, the use of a copper powder catalyst in dilute sulfuric acid. However, 2-(4′-methylbenzoyl)-benzenediazonium bisulfate and *o*-phenoxybenzenediazonium fluoborate gave a considerable amount of reduction product in the presence of copper powder. For these compounds the use of moderately concentrated sulfuric acid gave the best results.

The diazonium salt derived from *cis*-2-aminostilbene gives excellent yields of phenanthrene when heated in an aqueous acidic solution containing a suspension of copper powder.[3] This phenanthrene synthesis is generally referred to as the Pschorr reaction. Many other examples of the diazonium cyclization reaction are known involving a variety of bridging groups.[1,4,5]

In the course of applying the cyclization reactions to the synthesis of products of known structure, various workers have developed a variety of experimental procedures. In a few cases quantitative studies or comparative studies of these procedures have been made. Examples are found in the previous papers of this series[1,3b,6] which contain quantitative data regarding the fluorenone and the phenanthrene cyclizations. There is also a report of several qualitative comparisons.[7] Other workers have made semi-quantitative studies of several reactions.[8,9]

We have been interested in a somewhat broader comparison of the efficiency of selected procedures, both from the stand-point of determining optimum reaction conditions and from the standpoint of obtaining qualitative information about the mechanisms of the cyclization process. The purpose of the present work was to test out a series of typical cyclization procedures on a representative series of diazonium salts.

Among the large variety of cyclization procedures that have been described previously, the following general classes may be recognized: (1) The diazonium salt is heated in dilute acidic solution. Diazotized 2-aminobenzophenone gives a 65% yield of fluorenone under these conditions,[6] but diazotized *cis*-2-aminostilbene gives only about 30% of phenanthrene, due to a side reaction leading to indazole.[3b] (2) The diazonium salt is heated in dilute acidic solution in the presence of copper powder. These are the usual conditions for the Pschorr phenanthrene synthesis. (3) The diazonium salt is heated in alkaline solution. This procedure has given good results in the synthesis of 2-hydroxyphenanthrene-9-carboxylic acid[10] and with 2-methoxyphenanthrene-9-carboxylic acid[11] but gives low yields in the fluorenone series and in several other series.[6,7] (4) An aqueous ethanolic solution of the diazonium salt is treated with copper powder, or an aqueous solution is treated with hypophosphorous acid.[3a] The first variant gave an 85% yield of 2,3-methylenedioxyphenanthrene-9-carboxylic acid,[12a] and the second gave a 70% yield of 4,6-dimethylphenanthrene-9-carboxylic acid,[12b] but in other than the phenanthrene series such methods appear to lead to extensive replacement of the diazonium group with hydrogen with a serious diminution of the yield of cyclic product. (5) Miscellaneous methods have been reported such as treatment of an acetone suspension of the crystalline diazonium fluoborate with copper powder,[8] formation of the triazene by reaction of the diazonium salt with dimethylamine followed by treatment of a suspension of the triazene in an organic solvent with gaseous hydrogen chloride[8] and preparation of and decomposition of the N-nitrosoacetylamide.[8,13] In none of the reported examples were the yields by these miscellaneous methods any more attractive than those obtained by the first four procedures.

Since a considerable amount of information was already available regarding the fluorenone synthesis,[6-9] 2-(4′-methylbenzoyl)-benzenediazonium bisulfate was selected for a survey of the cyclization conditions. These included the use of a wide range of sulfuric acid concentrations, with and without copper catalysts, and a few examples of the use of other media such as sodium hydroxide, aqueous alcohol and glacial acetic acid. From this work six reaction conditions were selected for further investigation with four other diazonium salts, so chosen as to be representative of the various types used in the cyclization reaction. The results of this comparative study are summarized in Table I. The individual runs which have been averaged in Table I

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(1) Part IV, D. F. DeTar and D. I. Relyea, THIS JOURNAL, **78**, 4302 (1956).

(2) Taken from the M.S. thesis of T. E. Whiteley, University of South Carolina.

(3) (a) P. Ruggli and A. Staub, *Helv. Chim. Acta*, **20**, 37 (1937); (b) D. F. DeTar and Y. W. Chu, THIS JOURNAL, **76**, 1686 (1954); *cf.* R. Pschorr, *Ber.*, **29**, 496 (1896.)

(4) K. H. Saunders, "The Aromatic Diazo-Compounds and Their Technical Applications," 2d Ed., Longmans, Green and Co., New York, N. Y., 1949, p. 254.

(5) D. F. DeTar, "Organic Reactions," Vol. IX, John Wiley and Sons, Inc., New York, N. Y., in press.

(6) D. F. DeTar and D. I. Relya, THIS JOURNAL, **76**, 1680 (1954).

(7) D. F. DeTar and S. V. Sagmanli, *ibid.*, **72**, 965 (1950).

(8) D. H. Hey and J. M. Osbond, *J. Chem. Soc.*, 3164 (1949); D. H. Hey and R. D. Mulley, *ibid.*, 2276 (1952).

(9) A. J. Nunn, K. Schofield and R. S. Theobald, *ibid.*, 2797 (1952).

(10) R. Pschorr, *Ber.*, **39**, 3106 (1906).

(11) R. Pschorr, *ibid.*, **34**, 3998 (1901).

(12) (a) R. Konovalova, S. Yunussov, and A. Orekov, *Bull. Soc. Chim. France*, [5], **6**, 1479 (1939); (b) E. E. Lewis and R. C. Elderfield, *J. Org. Chem.*, **5**, 290 (1940).

(13) D. F. DeTar and C. S. Savat, THIS JOURNAL, **75**, 5117 (1953).

and a number of others which represent additional reaction conditions are given in Tables II and III.

TABLE I

EFFECT OF CONDITIONS ON YIELD IN THE DIAZONIUM CYCLIZATION REACTION[a]

Diazonium salt from	Reaction conditions 1 N H_2SO_4	1 N H_2SO_4 + Cu	1 N H_2SO_4 + CuCl	21 N H_2SO_4	21 N H_2SO_4 + Cu	21 N H_2SO_4 + CuCl
cis-2-Aminostilbene	36	94	94	46	60[b]	42
2-Amino-*sym*-diphenylethane	45	74	68	58	49	49
2-Amino-3′-nitrobenzophenone	40[b]	90	74[c]	53[b]	51	67
2-Aminodiphenyl ether	14[c]	20[d]	20[d]	27[c]	10[c,d]	17[c,d]
2-Amino-4′-methylbenzophenone	60	45[d]	46	74[e]	67	73[b]

[a] Entries are average percentage yield of cyclic product from crystalline diazonium salt, based on two runs unless otherwise indicated. The individual runs are presented in Tables II and III. Reaction temperatures from 25–90° or more all give the same product yield in the fluorenone series as can be seen from the data in Table II and from previous work. The averages for the yield of 3-methylfluorenone from diazotized 2-amino-4′-methylbenzophenone are for all runs under a given set of conditions regardless of temperature. For the first four compounds all cyclizations were carried out at 80°. The std. deviations given in Tables II and III were pooled: these are 3.8% for a single entry, 2.7% for averages of 2 (37 D.F.). Two averages which differ by 6% are significantly different at the 95% level. [b] Average of three values. [c] Single value. [d] Extensive reduction occurred. See Tables II and III. [e] Average of six values.

The reasons for the choice of the six reaction conditions listed in Table I are as follows: The use of dilute sulfuric acid, both with and without copper powder was, of course, mandatory, since these are the most commonly used cyclization conditions. The use of cuprous chloride was suggested by previous work.[1] There were also indications that the yields might be improved in more concentrated acid since the lower water concentration might reduce the yield of phenol and increase that of cyclic product. The 21 N acid was chosen as a suitable compromise, since 36 N acid led to diminished yields (Table II), apparently due to sulfonation. It also seemed desirable to test the effect of copper and cuprous chloride in the more concentrated acid. The low yields obtained with alkali and in aqueous ethanol indicated that there was little point in testing these conditions except perhaps with the phenanthrene synthesis.

The diazonium salts listed in Table I are representative of those used in the various cyclization reactions in that the cyclization of diazotized *cis*-2-aminostilbene typifies the Pschorr phenanthrene synthesis, that of diazotized 2-amino-*sym*-diphenylethane is representative of the two-atom bridge series, including the aporphine types,[14] the two 2-aminobenzophenones represent respectively a type which gives good yields of fluorenone in acidic solution in the absence of catalysts and one which does not. The salt from 2-aminodiphenyl ether is intended as a representative of the ethers and possibly of the N-alkyldiphenylamines.

TABLE II

PRODUCTS FROM 2-(4′-METHYLBENZOYL)-BENZENEDIAZONIUM BISULFATE

Conditions	Fluorenone, %[a] Obsd.	2-Hydroxy-4′-methylbenzophenone, %[b] Obsd.	4-Methylbenzophenone, %[c] Obsd.	Av. total[d]
1 N H_2SO_4, reflux	59	32	0	
	62[e]	38	0	
	86[f,g,h]	14[g,h]	0	
Av.	61	35	0	96
10 N H_2SO_4, reflux	69	29	0	
21 N H_2SO_4, 60°	65	14	0	
	80	19	0	
21 N H_2SO_4, 90°	80[i]	..	0	
	76	20	0	
21 N H_2SO_4, reflux	72	18	0	
	78	17	0	
Av.	75[j]	18[j]	0	93
31 N H_2SO_4, 60°	25[h,k]	3	0	
	77[l]	12	0	
1 N H_2SO_4, Cu, R.T.	48	25	13	
R.T.	43	38	10	
reflux	79[e,h]	36[h]	3[h]	
Av.	46	33	12	91
21 N H_2SO_4, Cu, 80°	66	22	0	
	70	21	0	
Av.	68	22	0	88
1 N H_2SO_4, CuCl, R.T.	47	44	6	
	46	36	5	
	68[h]	21[h]	5[h]	
Av.	46	40	6	92
10 N H_2SO_4, CuCl, 80°	62	27	0	
21 N H_2SO_4, CuCl, 60°	73	20	0	
80°	72	13	0	
90°	75	20	0	
Av.	73	18	0	91
31 N H_2SO_4, CuCl, 60°	82	13	0	
	75	12	0	
Av.	78	12	0	90
36 N H_2SO_4, CuCl, 60° (2.5 hours)	49[m]	2	0	
1 N H_2SO_4, Cu, 50–50	7	5	91	
C_2H_5OH–H_2O, R.T.	4	10	88	
Av.	6	8	90	104
Glacial AcOH, 90°	62	..	0	
2 N, NaOH, Cu, 35°	29	38	20	
2 N, NaOH, Cu, reflux	29[e]	30	17	
Av.	29	34	18	81

[a] Std. dev. is 4.3 (absolute) (15 D.F.); based on deviations of yields of replicate runs from their average. All runs in the same medium are considered replicates, regardless of temp. Yields are based on crystalline diazonium salt. [b] Std. dev. 4.1 (14 D.F.). [c] Std. dev. 1.8 (4 D.F.). [d] Std. dev. 4.3% (14 D.F.). [e] Fluoborate salt used. [f] 1 g. run; others were 150–350 mg. [g] Separation incomplete. [h] Omitted in calcn. of std. dev. [i] Diazonium salt not isolated; diazotization mixture made up to indicated acid strength and heated. Yield is based on the amine. [j] Av. of preceding 6 runs (5 for hydroxy compound). [k] Run for several hours permitting loss by sulfonation. [l] Run for 2 hr. [m] Loss by sulfonation.

The most surprising feature of the results reported in Table I is the extreme individuality exhib-

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[14] G. Barger and G. Weitnauer, *Helv. Chim. Acta*, **22**, 1036 (1939).

Table III

Products from the Diazonium Fluoborate of *cis*-2-Aminostilbene, from the Diazonium Fluoborate of 2-Amino-*sym*-diphenylethane, from 2-Phenoxybenzenediazonium Fluoborate and from 2-(3′-Nitrobenzoyl)-benzenediazonium Fluoborate

	cis-2-Aminostilbene	2-Amino-*sym*-diphenylethane				2-Phenoxybenzenediazonium fluoborate		2-(3′-Nitrobenzoyl)-benzenediazonium fluoborate		
Conditions[a]	Phenanthrene[b]	9,10-Dihydrophenanthrene[c]	2-Hydroxy-*sym*-diphenylethane[d]	*sym*-Diphenylethane[e]	Phenanthrene[f]	Dibenzofuran[g]	Diphenyl ether[h]	Mixture of 2- and 4-nitrofluorenone[i]	2-Hydroxy-3′-nitrobenzophenone[j]	3-Nitrobenzophenone[k]
1 *N* H_2SO_4	37	44	45	0	0	14	0	37	56	0
	35	45	44	0	0			37	50	0
								47	54	0
1 *N* H_2SO_4, Cu	95	78	6	6	2.4	24	26	89	4	2
	93	70	10	5	2.2	15	34	90	4	0
1 *N* H_2SO_4, CuCl	92	71	7	4	1.7	17	26	74	2	19
	96	65	2	5	0.7	23	18			
1 *N* H_2SO_4, Cu, H_3PO_2	97	..	..	..	..	..	..	..	..	..
10 *N* H_2SO_4, Cu	97	..	..	..	..	25	23	..	..	..
10 *N* H_2SO_4, CuCl	..	..	..	..	..	..	..	61	4	30
21 *N* H_2SO_4	46	59	34	0	0	27	0	54	42	0
	45	57	32	0	0			52	39	0
								53	40	0
21 *N* H_2SO_4, Cu	62	52	29	5	2.0	10	52	46	8	0
	61	46	25	6	2.1			56	7	4
	56									
21 *N* H_2SO_4, CuCl	40	50	39	0	0	17	31	65	20	0
	45	48	28	0	0			69	20	0

[a] Carried out on 100–400 mg. of diazonium salt in 25 ml. of solution at 80° until spot test on β-naphthol paper was negative (1 to 4 hr. except for uncatalyzed reactions of 2-phenoxybenzenediazonium salts which required 20–30 hr.). All entries are per cent yields based on crystalline diazonium salt. [b] Std. dev. 2.6 (7 D.F.). [c] 3.6 (6). [d] 4.4 (5). [e] 0.6 (3). [f] 0.3 (3). [g] 5 (2). [h] 6 (2). [i] 4.1 (7). [j] 1.9 (7). [k] 3.4 (2).

ited by the various salts. In view of this characteristic there is indeed some question as to how typical any given reaction may be.

With the diazonium salts derived from *cis*-2-aminostilbene, 2-amino-*sym*-diphenylethane and 2-amino-3′-nitrobenzophenone, the best results were obtained under the Pschorr conditions, copper powder in the presence of dilute sulfuric acid. With 2-(4′-methylbenzoyl)-benzenediazonium salts and 2-phenoxybenzenediazonium salts, the Pschorr conditions lead to appreciable reduction giving by-products which are difficult to remove. For these latter two salts the use of 21 *N* sulfuric acid alone gave the best results. In none of the cyclizations did cuprous chloride offer any advantage over the above conditions.

The reaction of the diazonium salts in the absence of catalysts probably involves S_N1 cleavage of the C–N bond,[6] and the higher yields of cyclic product at the higher acid concentrations can be explained on the basis that there are fewer water molecules to react to give the phenolic by-product.

The results in the presence of cuprous chloride and of copper powder are more difficult to explain in detail. There is a considerable variation in the effectiveness of these catalysts at the two acid levels. The high phenanthrene yield with copper powder, cuprous chloride or with hypophosphorous acid and copper powder does suggest that some sort of free radical process may be involved under these conditions.

Experimental

The preparation of the following compounds has already been described: 2-amino-4′-methylbenzophenone,[6,15] 2-amino-3′-nitrobenzophenone,[6] *cis*-2-nitrostilbene,[3b,16] 2-aminodiphenyl ether,[7,17] 2-(3′-nitrobenzoyl)-benzenediazonium fluoborate,[6,18] the diazonium fluoborate of *cis*-2-aminostilbene,[3b] 3-methylfluorenone,[6] 4-methylbenzophenone,[19] 2-hydroxy-4′-methylbenzophenone,[6] 2-chloro-4′-methylbenzophenone,[6] mixtures of 2- and 4-nitrofluorenone,[6] dibenzofuran,[7] diphenyl ether,[19] *sym*-diphenylethane.[19]

***cis*-2-Aminostilbene Hydrochloride.**—*cis*-2-Nitrostilbene was reduced with ferrous hydroxide,[3a,b] but the amine was converted to its hydrochloride with concd. aq. hydrochloric acid; m.p. 201–203°.

2-Amino-*sym*-diphenylethane Hydrochloride.—*cis*-2-Nitrostilbene (3.68 g.) was hydrogenated in methanolic solution (180 ml.) with 0.36 g. of 10% palladium-on-charcoal. Dry hydrogen chloride was passed through an ether solution of the amine to give 3.8 g. of 2-amino-*sym*-diphenylethane hydrochloride, m.p. 189–190°.[3a] The absence of the strong peak at 796 cm.$^{-1}$ characteristic of *cis*-2-aminostilbene shows that reduction was complete.

2-Phenoxybenzenediazonium Fluoborate.—2-Aminodiphenyl ether was diazotized in hydrochloric acid and the fluoborate salt precipitated with fluoboric acid (82% yield). **The diazonium fluoborate of 2-amino-*sym*-diphenylethane** was similarly prepared in 50% yield.

2-(4′-Methylbenzoyl)-benzenediazonium Bisulfate.[6]—2-Amino-4′-methylbenzophenone (1.0 g.) was dissolved in 12 ml. of glacial acetic acid, 2 ml. of methanol and 1 ml. of concd.

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(15) H. J. Scheifele and D. F. DeTar, *Org. Syntheses*, **32**, 8 (1952).

(16) Using the decarboxylation procedure of D. F. DeTar and L. A. Carpino, This Journal, **78**, 475 (1956).

(17) F. Ullmann, *Ber.*, **29**, 1881 (1896).

(18) The salt was purified by solution in dimethylformamide and reprecipitation with ether.

(19) Commercial sample.

sulfuric acid. It was diazotized at 0° with 0.6 ml. of freshly distilled *n*-butyl nitrite. Ether was added until the mixture became turbid and, on rubbing, the diazonium salt crystallized. It was purified by solution in glacial acetic acid and precipitation with ether; yield 80%.

3-Nitrobenzophenone.[20]—This was prepared by the Friedel–Crafts reaction from *m*-nitrobenzoyl chloride; colorless crystals, m.p. 93.5–94.0°, after vacuum sublimation and recrystallization from ethanol. The reported m.p. is 94–95°.

Phenanthrene.—This was a colorless sample, m.p. 96–97°, prepared by Mr. Julian Pruitt.[21]

2-Hydroxy-3′-nitrobenzophenone.—This compound was isolated from the decomposition of 2-(3′-nitrobenzoyl)-benzenediazonium salts; m.p. 95.5–96.5°, reported m.p. 96–97°.[6]

2-Hydroxy-*sym*-diphenylethane. This was isolated by chromatography from decomposition mixtures; m.p. 81–82°, reported m.p. 83.5°.[22]

Gattermann Copper Powder.[23]—Zinc dust was added to a saturated aqueous solution of copper sulfate until the blue color began to fade. The copper powder was washed by decantation and allowed to stand in dilute hydrochloric acid until hydrogen no longer was evolved. It was then washed until chloride ion was absent in the wash water, filtered, washed with ethanol, with ether and dried *in vacuo*. The catalyst was freshly prepared for each run.

Cuprous Chloride.[24]—This also was freshly prepared for each run in 2-g. quantities by heating 20 ml. of a solution containing 312 g. of copper sulfate pentahydrate and 81 g. of sodium chloride per liter while adding 8 ml. of a second solution containing 138 g. of sodium bisulfite and 88 g. of sodium hydroxide per liter. The precipitated cuprous chloride was washed by decantation using freshly boiled water, then centrifuged and used without drying.

Kochi Cuprous Chloride Solution.[25]—To 15 ml. of acetone (purified with permanganate) was added 5 ml. of water, 0.6 g. of lithium chloride and 1.2 g. of cupric chloride dihydrate. Nitrogen was bubbled through to remove oxygen, and the mixture was then refluxed for 24 hr. The small amount of solid material was disregarded.

Procedure for Decomposition of the Diazonium Salts.—The same general technique was followed with all the reactions. A 150–350 mg. sample of the diazonium salts was mixed with 25 ml. of the reaction medium in a 125-ml. erlenmeyer flask and allowed to stand, or heated, with occasional shaking until the spot test on filter paper moistened with sodium β-naphthoxide solution was no longer red. In the runs with copper or cuprous chloride approximately 2-g. amounts of these catalysts were used.

Isolation and Identification of Reaction Products from 2-(4′-Methylbenzoyl)-benzenediazonium Salts.—The cooled reaction mixture was extracted with five 15-ml. portions of methylene chloride.[26] The solution was evaporated, the residue dissolved in 5 ml. of benzene and introduced onto a column of alumina, 19 × 100 mm., of approximately grade 4.[27] A 50-50 mixture of benzene and pentane was then passed through the column and the first 40 ml. of solvent collected in a tared beaker (fraction 1). A further 40 ml. was collected but usually contained only a few mg. of dissolved material. A solution of 13% methanol in chloroform was then passed through the column and 40 ml. collected (fraction 2). In some runs, especially those in the presence of copper or of cuprous chloride, there was a small dark yellow band which remained on the column after the methanol–chloroform treatment. Solvents were removed at room temperature by evaporation using a desiccator equipped for continuous passage of a slow stream of dry dust-free air. The recovery of material from the chromatographic separation was usually 90–100%.

The decompositions carried out in sulfuric acid of various concentrations and at various temperatures gave a chromatographic first fraction which was almost pure 3-methylfluorenone as determined by m.p. (typically 64–66° as compared with 66.0–66.5° for the pure 3-methylfluorenone) and by the identity of the infrared spectra with those of the pure material. The chromatographic second fraction was checked in a few cases and proved to be pure 2-hydroxy-4′-methylbenzophenone, m.p. 60.5–61.5°.

The decompositions carried out in the presence of copper or of cuprous chloride gave a first fraction which was an oil-coated solid. The infrared curve had all the peaks present in 3-methylfluorenone–4-methylbenzophenone mixtures and no others. Since both of these products are expected, no attempt was made to separate them for further identification. The absence of 2-chloro-4′-methylbenzophenone was shown by the infrared curves.

The runs in 85 and 96% sulfuric acid gave low yields of extractable material; the aqueous layer was yellow. These results suggest that sulfonation was occurring at these acid concentrations.

The identity of the products present in the first chromatographic fraction was checked for all runs except for a few replicate runs carried out in the absence of catalysts.

The results of the product studies are summarized in Table II. In addition to these results, it was found that the reaction of 2-(4′-methylbenzoyl)-benzenediazonium bisulfate with the Kochi cuprous chloride solution in acetone gave 98.3 and 99.0% of 2-chloro-4′-methylbenzophenone.

Reaction Products from 2-(3′-Nitrobenzoyl)-benzenediazonium Salts.—The procedure was the same as the above except for use of grade 2 alumina as adsorbent and methylene chloride as eluent. The mixture of 2- and 4-nitrofluorenones was identified on the basis of the identity of the infrared peaks with those present in samples previously obtained. The proportions of isomers varied somewhat from one set of reaction conditions to another, but this point was not investigated. The 2-hydroxy-3′-nitrobenzophenone was also identified on the basis of its infrared curve.

The spectra of the first chromatographic fraction derived from certain runs in the presence of copper or of cuprous chloride had the peaks characteristic of 3-nitrobenzophenone in addition to those of the nitrofluorenone mixture.

The results of these runs are summarized in Table III.

Reaction Products from *o*-Phenoxybenzenediazonium Salts.—The reaction product from this diazonium salt was a black tar, and a large portion of the reaction mixture consisted of unidentified highly colored products. The dibenzofuran and the diphenyl ether were obtained in the first 40 ml. of benzene eluent using grade 1 alumina. They were identified and determined quantitatively by means of their infrared spectra. The results are summarized in Table III.

Reaction Products from the Diazonium Fluoborate of *cis*-2-Aminostilbene.—Since benzaldehyde was present in some of the runs in the absence of catalysts, the reaction mixture was treated with a small amount of hydrogen peroxide or of potassium persulfate in order to oxidize it to benzoic acid. The chromatographic separation was carried out with grade 4 alumina using benzene as the eluent. The progress could be followed by observing the column with long wave length ultraviolet light; the phenanthrene, the indazole and an unidentified strongly adsorbed component were all fluorescent. The first fraction in all runs consisted of phenanthrene; *cis*-stilbene was absent, for there was no adsorption at 700 or at 780 cm.$^{-1}$ which are strong peaks for *cis*-stilbene. The results are summarized in Table III.

Reaction Products from the Diazonium Fluoborate of 2-Amino-*sym*-diphenylethane.—The extractions were carried out with ether. The chromatographic separation utilized grade 2 alumina with benzene as eluent. Since a reference sample of 9,10-dihydrophenanthrene was not available, the first chromatographic fractions from runs in sulfuric acid (in the absence of catalysts) were used. The infrared spectra of these fractions showed that *sym*-diphenylethane and phenanthrene were both absent. 9,10-Dihydrophenanthrene has been prepared previously by the diazonium cyclization reaction.

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(20) R. Geigy and W. Koenigs, *Ber.*, **18**, 2401 (1885).

(21) (a) W. E. Bachmann, THIS JOURNAL, **57**, 555 (1935); (b) A. Jeanes and R. Adams, *ibid.*, **59**, 2608 (1937).

(22) R. Stoermer, *Ber.*, **36**, 3982 (1903).

(23) C. Gattermann, *ibid.*, **23**, 1219 (1890).

(24) C. S. Marvel and S. M. McElvain, "Organic Syntheses," Coll. Vol. I, 2d Ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 170.

(25) J. K. Kochi, THIS JOURNAL, **77**, 5274 (1955).

(26) In runs in which copper or cuprous chloride was present the procedure was somewhat different: the reaction mixture was stirred with 15 ml. of methylene chloride and filtered. The catalyst was rinsed with four 10-ml. portions of methylene chloride, and the filtrate was extracted with three 10-ml. portions.

(27) H. Brockmann and H. Schodder, *Ber.*, **74**, 73 (1941); E. Lederer and M. Lederer, "Chromatography," Elsevier Publishing Co., New York, N. Y., 1954, p. 22.

The infrared spectra of reactions run in the presence of copper had peaks at 810 and 733 cm.$^{-1}$ that were not accounted for by the 9,10-dihydrophenanthrene or by *sym*-diphenylethane. Phenanthrene has characteristic peaks at these positions. The presence of phenanthrene was verified by the appearance of characteristic ultraviolet peaks at 3295, 3375 and 3455 Å. The rather concentrated sample required cut off at 3200 Å. The phenanthrene concentration as estimated by the base-line technique agreed excellently with that estimated from the infrared curve. That the phenanthrene originated from the diazonium salt of 2-amino-*sym*-diphenylethane and not from that of *cis*-2-aminostilbene present as an impurity was established by the observation that phenanthrene was not produced in all runs.

Quantitative Spectrophotometric Analyses.—Infrared spectra were obtained in carbon disulfide solution in a fixed cell 0.106 mm. thick using a Perkin-Elmer model 21 spectrophotometer equipped with sodium chloride optics. For quantitative work, concentrations were adjusted to give peaks between 15 and 85% transmittance. The curve of the pure solvent was used to obtain the 100% transmission line, and a strong solvent absorption peak was used to give the 0% absorption value. Ultraviolet spectra were obtained with a Cary model 14 spectrophotometer using solvent in the reference beam. The absorbance curve of solvent *vs.* solvent was run after each solution.

A representative calibration analysis of known 3-methylfluorenone and 4-methylbenzophenone mixtures is given in Table IV. The results obtained with mixtures of the other compounds are comparable.

TABLE IV

INFRARED ANALYSIS OF KNOWN MIXTURES OF 3-METHYLFLUORENONE AND 4-METHYLBENZOPHENONE[a]

3-Methylfluorenone taken, %[b]	4-Methylbenzophenone taken, %	3-Methylfluorenone found, %[c]	4-Methylbenzophenone found, %[d]
1.001	0.428	0.939	0.432
1.014	1.044	.984	1.066
0.985	1.438	.989	1.422
.916	0.094	.993	0.086
.351	.356	.404	.351
1.777	.157	1.726	.156

[a] Using the 3-methylfluorenone peaks at 1723 and 765 cm.$^{-1}$ and the 4-methylbenzophenone peaks at 1668 and 1276 cm.$^{-1}$. [b] Concn. in wt. % in CS_2. [c] Std. dev. 0.063. [d] Std. dev. 0.015.

An ultraviolet spectrophotometric assay was made of several samples of 2-(4'-methylbenzoyl)-benzenediazonium bisulfate and showed that the preparation of pure samples of this diazonium salt was readily reproducible.

COLUMBIA, S. C.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Base-promoted Dehydrohalogenation of *cis*- and *trans*-2-Chlorocycloalkyl Aryl Sulfones[1]

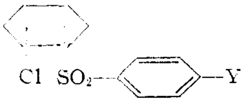
BY HARLAN L. GOERING, DOUGLAS I. RELYEA AND KING L. HOWE[2]

RECEIVED JUNE 29, 1956

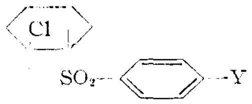
The base-promoted dehydrochlorination of *cis*-(I) and *trans*-2-chlorocyclohexyl aryl sulfones (II), and *cis*-(III) and *trans*-2-chlorocyclopentyl aryl sulfones (IV) in "80%" ethanol has been investigated. Rate constants and activation energies were determined for the least reactive of the four series of compounds, the *trans*-2-chlorocyclohexyl aryl sulfones. The other three series of compounds are too reactive to follow by the sampling technique used in the present work. For these compounds approximate relative reactivities were determined. In each of the four series of chlorocycloalkyl aryl sulfones I–IV, electron-withdrawing substituents in the aryl moiety increase the rate of dehydrochlorination. The following rate sequence for corresponding *p*-substituted 2-chlorocycloalkyl aryl sulfones was observed: *cis*-2-chlorocyclopentyl > *cis*-2-chlorocyclohexyl > *trans*-2-chlorocyclopentyl > *trans*-2-chlorocyclohexyl. The rate of elimination for *trans*-2-chlorocyclohexyl phenyl sulfone is essentially the same as that for *trans*-2-tosyloxycyclohexyl phenyl sulfone. The *trans*-2-chlorosulfones II and IV undergo *cis* elimination, evidently by a two-step process involving abstraction of the C_1-hydrogen followed by conversion of the resulting anion to the elimination product. The first step is rate determining and irreversible under the present conditions (*i.e.*, 80% ethanol containing 0.004 to 0.03 *M* sodium hydroxide). Presumably the *cis*-chlorosulfones I and III undergo a concerted *trans* dehydrohalogenation.

Introduction

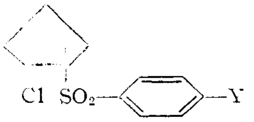
In connection with a study[3,4] of the stereochemistry of radical additions, several *cis*-(I) and *trans*-2-chlorocyclohexyl aryl sulfones (II) and *cis*-(III) and *trans*-2-chlorocyclopentyl aryl sulfones (IV) were prepared. This paper describes the base-promoted dehydrochlorination of these four series of compounds in "80%"[5] ethanol. The effect of the *β*-sulfone group on the rate of dehydrohalogenation was of interest for comparison with the effect of *β*-halogen atoms observed in an earlier study.[6] The behavior of the *trans*-2-chlorocycloalkyl aryl sulfones was also of particular interest because of the recent observation by Bordwell and co-workers[7] that in similar systems the *β*-sulfone group activates the *β*-hydrogen so that *cis* elimination occurs rather than a concerted *trans* elimination.



Ia, Y = H
Ib, Y = CH_3
Ic, Y = Cl



IIa, Y = H
IIb, Y = CH_3
IIc, Y = Cl
IId, Y = NO_2



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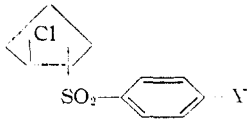
IIIc, Y = Cl



IVa, Y = H
IVb, Y = CH_3
IVc, Y = Cl
IVd, Y = NO_2

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(1) This work was supported by the United States Air Force through the Office of Scientific Research of the Air Research and Development Command under contract No. AF 18(600) 1037.

(2) Socony-Mobil Fellow, 1955–1956.

(3) H. L. Goering, D. I. Relyea and D. W. Larsen, THIS JOURNAL, **78**, 348 (1956).

(4) K. L. Howe and D. I. Relyea, unpublished results.

(5) The solvent was prepared by mixing four volumes of pure ethanol and one volume of water at 25°.

(6) H. L. Goering and H. H. Espy, THIS JOURNAL, **78**, 1454 (1956).

(7) (a) J. Weinstock, R. G. Pearson and F. G. Bordwell, *ibid.*, **76**, 4748 (1954); **78**, 3468, 3473 (1956); (b) F. G. Bordwell and R. J.