[Contribution from the Baker Laboratory of Chemistry of Cornell University and the Department of Chemistry of the University of South Carolina]

Intramolecular Reactions. II. The Mechanism of the Cyclization of Diazotized 2-Aminobenzophenones[1,2]

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The thermal decomposition of acidic aqueous solutions of 2-benzoylbenzenediazonium fluoborate leads to the formation of 64% yields of fluorenone (cyclization product) and 36% yields of 2-hydroxybenzophenone; 2-(4'-methylbenzoyl)-benzenediazonium fluoborate gives about the same results, and 2-(3'-nitrobenzoyl)-benzenediazonium fluoborate gives 33% of nitrofluorenones and 67% of 2-hydroxy-3'-nitrobenzophenone. The thermal decomposition is accurately summarized by a first-order rate expression, the methyl compound reacting somewhat more rapidly and the 3'-nitro compound less rapidly than the unsubstituted diazonium salt. These results together with other evidence indicate that the reaction mechanism is an ionic one, and that the *loss of the diazonium nitrogen as an* S_N1 *process*. Preliminary results are given for the reaction at higher *p*H levels in various buffers, the reaction being primarily, but not entirely, a free radical process under such conditions.

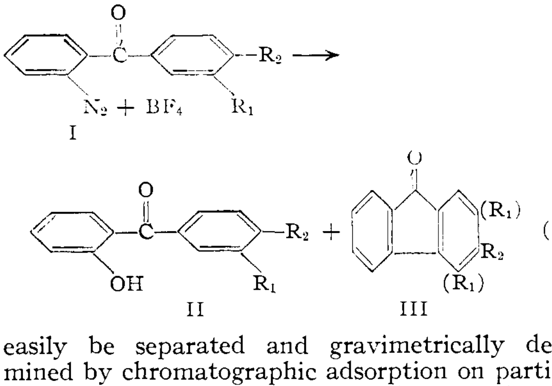
The intramolecular cyclization of diazonium compounds in such reactions as the Pschorr phenanthrene synthesis or the Graebe–Ullmann fluorenone synthesis[4] (eq. 1) has a superficial resemblance to the intermolecular biaryl synthesis developed by Gomberg and Bachmann.[5] A preliminary study of these cyclization reactions from the standpoint of reaction mechanism[1] showed, however, that the two types of reactions are actually quite different. The Gomberg–Bachmann reaction takes place under alkaline conditions and almost certainly involves free radical intermediates as was suggested long ago by Hey and Waters.[6] Perhaps the most convincing type of evidence for a homolytic cleavage of the carbon–nitrogen bond is the quantitative work[7] which has been completed recently showing the ortho–para directing influence and the activating influence of the nitro group, and the close parallel between the Gomberg–Bachmann reaction of benzenediazonium salts with nitrobenzene and alkali on the one hand and the reaction of dibenzoyl peroxide with nitrobenzene on the other. Further evidence for homolytic cleavage of the diazonium carbon–nitrogen bond under alkaline conditions is summarized elsewhere.[8]

The thermal decomposition of 2-benzoylbenzenediazonium salts in aqueous solution under acidic conditions leads to high yields of fluorenone (eq. 1), and by way of contrast only poor yields of fluorenone are obtained under alkaline conditions where an attempt was made to parallel the Gomberg–Bachmann conditions.[1,9] There is a considerable amount of evidence that diazonium salts undergo heterolytic cleavage of the carbon–nitrogen bond under acidic conditions, and the fluorenone synthesis thus seems to be an ionic process. It should be noted that many of the preparative cyclization reactions have been carried out in the presence of copper powder; the mechanism of this type of cyclization is still highly speculative.

We have undertaken a detailed study of the reactions of 2-benzoylbenzenediazonium salts for several reasons. For one thing, the over-all mechanism of the cyclization process needs to be placed on a more secure foundation. Furthermore, the ranges of reaction conditions under which ionic processes occur and of those under which free radical processes occur need to be defined. And finally, the details of the mechanisms need to be established with greater certainty; there is the question of S_N1 or aromatic S_N2 loss of nitrogen in the ionic process, and for the free radical process there is little evidence as to whether aryl radicals are produced and if so what they will do. The 2-benzoylbenzenediazonium salts afford a number of unique advantages for mechanism studies directed toward these ends, and the results reported herein constitute a start toward the above goals.

Results

Previous work has shown that the principal products of the thermal decomposition of 2-benzoylbenzenediazonium fluoborate (I, $R_1 = R_2 = H$) in aqueous solution are the normal replacement product, 2-hydroxybenzophenone (II), and the cyclization product, fluorenone (III). It was found that the fluorenone and the hydroxybenzophenone could easily be separated and gravimetrically determined by chromatographic adsorption on partially deactivated alumina followed by elution and weighing. Table I lists average yields of products



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[1] Part I: D. F. DeTar and S. V. Sagmanli, This Journal, **72**, 965 (1950).

[2] From the M. S. thesis of D. I. Relyea, Cornell Univ., 1953. Presented before the Division of Organic Chemistry at the 123rd Meeting of the American Chemical Society, Los Angeles, Calif., March, 1953.

[3] (a) University of South Carolina, Columbia, S. C.; (b) Rohm and Haas Research Assistant at the University of South Carolina.

[4] For bibliography see ref. 1. D. H. Hey and his students have recently carried out an extensive investigation of various cyclization reactions from the preparative standpoint; part VII, *J. Chem. Soc.*, 3 (1953).

[5] W. E. Bachmann and R. A. Hoffman, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 224.

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

[7] D. R. Augood, D. H. Hey and G. H. Williams, *J. Chem. Soc.*, 44 (1953); 2094 (1952); D. H. Hey, A. Nechvatal and T. S. Robinson, *ibid.*, 2892 (1951); D. F. DeTar and H. J. Scheifele, This Journal, **73**, 1442 (1951).

[8] D. F. DeTar, *ibid.*, **73**, 1446 (1951).

[9] D. H. Hey and R. D. Mulley, *J. Chem. Soc.*, 2276 (1952).

TABLE I

PRODUCTS OF THE THERMAL DECOMPOSITION OF APPROXIMATELY 1-MMOLE SAMPLES OF DIAZONIUM SALTS IN 100 ML. OF 0.05 *M* SULFURIC ACID

	2-Hydroxybenzophenone			Fluorenone			Total yield	
Reacn. temp., °C.	Yield, %	Std. dev.[a] of avg.	No. of runs	Yield, %	Std. dev.[a] of avg.	No. of runs	%	95% conf. limits
Unsubstituted 2-benzoylbenzenediazonium fluoborate ($R_1 = R_2 = H$)[b]								
25	36.5	0.5	8	64.1	0.7	3	100.6	2.3
38	36.9	.8	3	62.4	.7	3	99.3	2.3
50	37.0	.8	3	62.6	.7	3	99.6	2.3
72	34.9	.9	2	67.9	.8	2	102.8	2.8
2-(4'-Methylbenzoyl)-benzenediazonium fluoborate ($R_1 = H$, $R_2 = CH_3$)[b]								
25	36.4	1.2	4	60.0	0.8	4	96.4	3.4
45	34.2	1.4	3	61.3	.9	3	95.7	3.9
65	33.6	1.4	3	60.0	.9	3	93.6	3.9
2-(3'-Nitrobenzoyl)-benzenediazonium fluoborate ($R_1 = NO_2$, $R_2 = H$)[b]								
25	65.8	1.6	3	31.6[c]	0.8	3	97.4	3.8
45	66.9	1.2	5	33.6[c]	.6	5	100.5	2.9
65	67.2	1.1	6	33.0[c]	.6	6	100.2	2.7

[a] Based on analysis of variance estimates of *s*, all estimates for a given compound being pooled for the purpose, since the between temperatures variance was in all cases nonsignificant; *s* is based on from 9 to 15 degrees of freedom. [b] Eq. 1. [c] Mixture of 2-nitrofluorenone and 4-nitrofluorenone; sinters 165°, m.p. 175–223°. 4-Nitrofluorenone has m.p. 174° and 2-nitrofluorenone has m.p. 222–223°. This mixture is thus estimated to contain roughly 60–70% of the 2-nitro isomer.

formed from 2-benzoylbenzenediazonium fluoborate, and from its 4'-methyl and its 3'-nitro derivatives upon thermal decomposition in dilute aqueous sulfuric acid at several temperatures. The following points may be noted: (1) The combined yields of hydroxybenzophenone and fluorenone account for nearly all of the diazonium salt. (2) The yields of these two products were insensitive to temperature. It was demonstrated statistically[10,11] by a variance analysis that there is no reason for suspecting any temperature effect as far as these data are concerned: the variations in yield in Table I are all well within the scope of random experimental error. Hey and Mulley[9] report a 58.5% yield of fluorenone and a 26.5% yield of 2-hydroxybenzophenone in a single run.

The absence of effect due to copper sulfate is shown in Table II. Copper powder, on the other hand, gives a significantly higher yield of fluorenone. The effectiveness of chloride ion and of bromide ion in competing for replacement of diazonium ion is shown in Table III. Although fluoborate salts were used in this work, it is believed that the particular anion used has relatively little effect. The rate of reaction of benzenediazonium ion in water is insensitive to the anion and the results obtained here show that the product yields are rather insensitive to the presence of chloride ions. Furthermore, the rates and products were independent of moderate variations in initial diazonium salt concentration (over a factor of about 2).

TABLE II

THE EFFECT OF COPPER POWDER AND CUPRIC SULFATE ON THE THERMAL DECOMPOSITION OF 1-MMOLE SAMPLES OF 2-BENZOYLBENZENEDIAZONIUM FLUOBORATE IN 100 ML. OF 0.05 *M* SULFURIC ACID

Catalyst	Fluorenone Avg. % yield[a]	2-Hydroxybenzophenone Avg. % yield[a]
0.1 g. Cu powder (45°)[b]	70.7	21.3
.01 *M* $CuSO_4$ (25°)	60.1	32.4
.01 *M* $CuSO_4$ (45°)	60.2	33.6

[a] All values are averages of two determinations; same precision as in Table I. [b] Hey and Mulley report a 52.5% yield of fluorenone and an 8% yield of 2-hydroxybenzophenone in a single determination using copper powder.[9]

TABLE III

PRODUCTS OF THE THERMAL DECOMPOSITION AT 45° OF 1-MMOLE SAMPLES OF 2-(4'-METHYLBENZOYL)-BENZENEDIAZONIUM FLUOBORATE IN 100 ML. OF 0.05 *M* SULFURIC ACID CONTAINING ADDED SODIUM CHLORIDE OR BROMIDE

	2-Hydroxy-4'-methylbenzophenone		2-X-4'-Methyl benzophenone		3-Methylfluorenone	
Added salt, *M*	Avg. %[a] yield	Std. dev.[b] of avg.	Avg. %[a] yield	Std. dev.[c] of avg.	Avg. %[a] yield	Std. dev.[c] of avg.
2.0 NaCl	28.2	0.2	..	...	..	...
4.0 NaCl	25.2	.2	..	...	..	...
6.2 NaCl	21.1	.2	14.2	0.8	60.3	0.8
6.2 NaBr	17.8	.2	27.7	1.2	51.3	1.2

[a] Based on three runs at each salt concentration. [b] Based on the twelve determinations carried out in this group; 8 D.F. [c] Based on both the 3-methylfluorenone and the 2-halo-4'-methylbenzophenone averages. These compounds were estimated by obtaining total wt. of the mixture and then obtaining the ratio by means of an accurate carbon analysis; 4 (Degrees of Freedom).

A few preliminary product studies have been carried out at higher *p*H levels with 2-benzoylbenzenediazonium fluoborate. At 25° and a *p*H of 8.6 (borate buffer) fluorenone yields of 22 and 24% were obtained; at a *p*H of 12.3 (phosphate buffer) not too reproducible fluorenone yields of 5, 28 and 27% were obtained. Hey and Mulley[9] report a 19.5% fluorenone yield in a single run in the presence of sodium hydroxide.

The rates of the reactions were determined manometrically, and are reported in Table IV. For a first-order reaction followed manometrically the pressure at any time is given by the expression

$$p = a + be^{-kt} \qquad (2)$$

with $a = p_\infty$ (scale reading) and $b = p_\infty - p_0$ (p_0 is manometer reading at zero time, and b is therefore a measure of the total amount of gas evolved). Most of the parameters reported in Table IV were obtained by a least squares procedure.[11] The error to be minimized is the scalar error in p, since the error in reading the manometer is independent of the liquid level.

Arrhenius parameters and heats and entropies of activation are summarized in Table V. The listed values of the parameters reproduce the rate con-

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(10) References to statistical terms and procedures are W. J. Youden, "Statistical Methods for Chemists," John Wiley and Sons, Inc., New York, N. Y., 1951; W. J. Dixon and F. J. Massey, "Introduction to Statistical Analysis," McGraw-Hill Book Co., Inc., New York, N. Y., 1951.

(11) W. Deming, "Statistical Adjustment of Data," John Wiley and Sons, Inc., New York, N. Y., 1948; L. J. Reed and E. J. Theriault, *J. Phys. Chem.*, **35**, 673, 950 (1931).

Table IV

Summary of Rate Constants for the Thermal Decomposition of the 2-Benzoylbenzenediazonium Fluoborates in 0.01 *M* Concentration in 0.05 *M* Aqueous Sulfuric Acid Solution

Temp., °C.	10^6k sec.$^{-1}$	10^6s_k	$-b$	s_b	Extent of reacn. for calcn., %	Yield[a] of N_2, %
2-Benzoylbenzenediazonium fluoborate						
24.86	4.718	0.038	318.21	0.55	11–94	100.6
24.86	4.977	.044	243.56	.41	19–86	92.6[b]
35.01	23.14	.12	358.25	.61	4–97	97.2
45.00	97.74	1.3	236.48	.82	12–97	75.2*
44.99	99.49	0.55	258.51	.45	10–97	75.5*
55.02	391.3	2.2	469.44	.43	21–89	94.7
2-(4′-Methylbenzoyl)-benzenediazonium fluoborate						
24.91	6.883	...	253.83	0.47	18–93	82.7*
24.92	6.573	0.031	343.28	.56	5–98	85.7*
34.66	30.32	.085	437.28	.32	14–94	90.6
45.00	131.4	.33	399.59	.28	7–94	98.3
45.00	134.9	6.8	467.39	.52	7–60	102.2
55.00	523.0	1.7	359.52	.36	6–97	96.3
2-(3′-Nitrobenzoyl)-benzenediazonium fluoborate						
35.01	8.19	(0.04)	273.78	0.19	(4–64)	86.6[b]
45.00	35.48	.092	430.00	.32	9–96	74.7*
55.14	140.3	(.5)	366.28	.29	(14–87)	96.5
55.14	141.3	(.6)		.35	(14–96)	96.4
65.64	541.4	(2.0)	330.75	.29	(8–90)	96.5
65.63	542.3	(1.5)	328.43	.20	(12–87)	98.5
2-(4′-Methoxybenzoyl)-benzenediazonium fluoborate						
45.00	158.0	0.88	328.13	0.15	8–99	97.6

[a] It was discovered part way through this work that one sample of commercial fluoboric acid gave impure fluoborates; subsequently all of the fluoboric acid used was prepared from reagent grade chemicals in "Polythene" bottles. The impurity seemed to have no significant effect on the rate, and these runs have therefore been included in Table IV and are marked with an asterisk. The diazonium fluoborates used in the product studies (Tables I–III) were all prepared from fluoboric acid of established purity. Standard deviation 1.4% (7 D.F.), 95% conf. limits 3.3%. [b] Accidental loss of nitrogen in these runs.

Table V

Activation Energies for the Thermal Decomposition of the 2-Benzoylbenzenediazonium Fluoborates, Based on the Rate Constants of Table IV

	Arrhenius Parameters[a]		Activated Complex Parameters[b]		
Diazonium salt	ln A	E	$\Delta S^{\ddagger}$	$\Delta H^{\ddagger}$	$s_{\ln k}$[c]
2-(4′-Methylbenzoyl)-benzenediazonium fluoborate	35.4740 ± 0.28	28,058 ± 170	9.91 ± 0.56	27,435 ± 170	0.023
2-Benzoylbenzenediazonium fluoborate	35.4784 ± .25	28,250 ± 155	9.91 ± .50	27,624 ± 155	.022
2-(3′-Nitrobenzoyl)-benzenediazonium fluoborate	34.6816 ± .06	28,368 ± 39	8.17 ± .12	27,723 ± 39	.005

[a] Least squares fit to the equation: $\ln k = \ln A - E/RT$, assuming no error in T. [b] Least squares fit to the equation: $\ln k = \ln (K/h) + \Delta S^{\ddagger}/R + \ln T - \Delta H^{\ddagger}/RT$; $\ln (K/h) = 23.73712$, $R = 1.9865$. The error limits shown are estimates of the standard deviation. [c] Estimate of the standard deviation of ln k (as calculated from either equation using the adjusted parameters); the percentage deviation of k is 100 times this number.

stants of Table IV with standard deviations of 2.3, 2.2 and 0.5% for the 4′-methyl, the unsubstituted, and the 3′-nitro compounds, respectively. The error limits of the parameters were calculated from the reciprocal matrix.[11] The parameters of the unsubstituted compound and the methyl compound are not significantly different, but the parameters for the nitro compound are significantly larger than those for the methyl compound. (It should, however, be noted that the rate constants of Table IV do differ significantly from one compound to another.)

A preliminary survey was made of the reaction rates in a series of buffer solutions. Two sets of experiments were carried out, one set with a benzene layer present (Gomberg–Bachmann conditions) and one set with just the aqueous phase. Although all of the reactions became two-phase (or multiphase) as reaction products began to precipitate the presence of the large mobile benzene phase increased the rates of all reactions run in the higher *p*H buffers. In the absence of an initial second phase the reactions gave quite good first-order plots (linear log $(p_\infty - p)$ against t) up through the *p*H 8.58 experiments. Those run at the higher *p*H values and those run in the presence of benzene gave S-shaped log $(p_\infty - p)$ plots.

A possible interpretation would be a retarded reaction of higher order than first. Approximate nitrogen yields are reported for these kinetic runs, but it is to be noted that all such yields are differential yields. There is evidence from work carried out with benzenediazonium salts in acetate buffers in methanol that oxygen takes part in some of these reactions at high *p*H levels, and an oxygen absorption of say 10% would appear as a nitrogen deficit of 20%.

Table VI

Approximate First-order Rate Constants and Nitrogen Yields for the Thermal Decomposition of 2-Benzoylbenzenediazonium Fluoborates in 0.01 *M* Concentration in 0.10 *M* Buffer Solutions at 25°[a]

	*p*H			
Salt	4.65	6.68	8.58	12.3
2-Benzoylbenzenediazonium fluoborate	7.5(75%) ...(..)	9.4 (55%) (46)(45)	20(37%) (1300)(51)	(60)(13%) (2800)(48)
4′-Methyl salt	7.0(76%) (9)(55)	9.7 (59%) (72)(41)	28 (37%) (1500)(39)	(95)(25%) (3100)(54)
3′-Nitro salt	...(41%) ...(..)	4.0 (41%) (170)(62)	160 (37%) (200)(48)	(2900)(25%) (>2000)(47)

[a] Top line of figures refers to reactions run in the plain buffer (100 ml.). The first number is the rate constant × 10^6 sec.$^{-1}$, the second number is the percentage of nitrogen formed. The lower line refers to reactions in the presence of a benzene phase (25 ml. of benzene, 75 ml. of buffer). Rate constants in parentheses are for reactions which are *not* first order; they serve only to give an idea of the order of magnitude of the rate. All of the rate constants were obtained from the half-lives found by plotting log $(p_\infty - p)$ against t. Nitrogen yields have an accuracy of something like ±15% relative.

Experimental[12,13]

2-Aminobenzophenone, 2-Amino-4′-methylbenzophenone and 2-Amino-4′-methoxybenzophenone.—These compounds were prepared by the method of DeTar[14] from the Friedel–Crafts reaction of the acid chloride of the tosyl derivative

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(12) All melting points are corrected.

(13) Analyses by Mrs. M. Libowitz, except those marked 13b, which were by Mrs. P. J. Bohrer.

(14) D. F. DeTar, *Org. Syntheses*, **32**, 8 (1952).

of anthranilic acid with benzene, toluene or anisole. The melting points were 105–106° and 94–95° for 2-aminobenzophenone and 2-amino-4′-methylbenzophenone, respectively, in exact agreement with the reported values.[14,15] The 2-amino-4′-methoxybenzophenone had a m.p. 76.2–76.8°, a value somewhat higher than that reported by Ullmann and Bleier[15]; it was therefore analyzed.

Anal. Calcd. for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.76; N, 6.17. Found: C, 73.53, 73.47; H, 5.59, 5.57; N, 6.20, 6.19.

2-(3′-Nitrobenzoyl)-benzoic Acid.—To a solution of 22.6 g. (0.10 mole) of anhydrous *o*-benzoylbenzoic acid in 50 ml. of concd. sulfuric acid was added gradually a solution of 7.5 ml. (0.13 mole) of concd. nitric acid in 10 ml. of concd. sulfuric acid. The temperature was maintained at 40–50° during the addition and for one-half hour longer. The mixture was poured into ice and water and the oil which separated solidified in about an hour. The crude material was recrystallized using 50 ml. of glacial acetic acid, giving 16.6 g. (61%) of very pale yellow crystals, m.p. 156–172°. Upon further recrystallization from acetic acid a sample with m.p. of 186.2–187.5° was obtained.[16]

Anal. Calcd. for $C_{14}H_9NO_5$: neut. equiv., 271.2. Found: neut. equiv., 269.7, 269.4.

2-Amino-3′-nitrobenzophenone.—A mixture of 21.6 g. (0.080 mole) of 2-(3′-nitrobenzoyl)-benzoic acid and 40 ml. of thionyl chloride was refluxed for 40 minutes, the acid gradually dissolving. The hot solution was filtered, 50 ml. of dried hexane was added, and 20.3 g. (88%) of almost colorless acid chloride precipitated. A solution of 14.5 g. (0.050 mole) of the acid chloride was prepared by warming with 225 ml. of dried acetone. The solution was cooled to 20° and 3.5 g. (0.050 mole) of sodium azide in 10 ml. of water was added, followed by another 50 cc. of water; then after 30 minutes another 500 cc. of water was added gradually to precipitate the azide, 13.7 g. (92%). Upon purification by solution in chloroform and precipitation with hexane a colorless sample was obtained, m.p. 106° (gas evol.).

Anal. Calcd. for $C_{14}H_8N_4O_4$: C, 56.76; H, 2.72; N, 18.91. Found[13b]: C, 56.44; H, 3.12; N, 19.17.

The crude dried azide was refluxed with 75 ml. of dried toluene for about half an hour, the solution cooled to 35° and extracted with a 50% by volume solution of concd. sulfuric acid in water also cooled to 35°. The sulfuric acid layer was separated and added to an ice–concd. ammonium hydroxide (250 ml.) mixture. Filtration gave 7.50 g. (67%) of crude 2-amino-3′-nitrobenzophenone, m.p. 92–93°. Recrystallization from 150 ml. of ethanol gave a 75% recovery in the first crop, m.p. 93.5–94.5°.

Anal. Calcd. for $C_{13}H_{10}N_2O_3$: C, 64.46; H, 4.16; N, 11.57. Found[13b]: C, 64.76; H, 4.71; N, 11.68.

2-Benzoylbenzenediazonium Fluoborate.—Ten grams (0.05 mole) of 2-aminobenzophenone was dissolved in 35 ml. of hot concentrated (12 *M*) hydrochloric acid. The solution was chilled, and the slurry of amine salt diazotized with a solution of 3.5 g. of sodium nitrite in 10 ml. of water over a period of about ten minutes. The mixture was allowed to remain in the ice-bath for another 15 minutes, and then filtered. To the yellow solution was added 75 ml. of the fluoboric acid solution described below. The yellow precipitate on filtration, washing with methanol, then ether, and drying weighed 8.8 g. (60%).

Anal. Calcd. for $C_{13}H_9N_2OBF_4$: C, 52.74; H, 3.06; N, 9.52. Found: C, 52.39, 52.43; H, 2.92, 2.95; N, 9.58, 9.57.

2-(4′-Methylbenzoyl)-benzenediazonium fluoborate was prepared in like manner in 56% yield.

Anal. Calcd. for $C_{14}H_{11}N_2OBF_4$: C, 54.23; H, 3.58; N, 9.04. Found: C, 54.15; H, 3.50; N, 9.07.

2-(4′-Methoxybenzoyl)-benzenediazonium fluoborate was obtained in 70% yield.

Anal. Calcd. for $C_{14}H_{11}N_2O_2BF_4$: C, 51.57; H, 3.38; N, 8.59. Found: C, 51.54, 51.21; H, 3.38, 3.42; N, 8.60.

2-(3′-Nitrobenzoyl)-benzenediazonium fluoborate was obtained in 90% yield.

Anal. Calcd. for $C_{13}H_8N_3O_3BF_4$: C, 45.78; H, 2.36; N, 12.32. Found: C, 45.48, 45.58; H, 2.32, 2.35; N, 12.30, 12.32.

2-Hydroxybenzophenone.—This compound was prepared by the Friedel–Crafts method utilizing 2-methoxybenzoyl chloride.[17] Demethylation occurred during the reaction, and the yield of distilled product was 40%. After chromatography on Grade 4 alumina[18a] with a 50% benzene–50% pentane solvent a 30% over-all yield of colorless crystals, m.p. 38.5–39.0°, was obtained.

2-Hydroxy-4′-methylbenzophenone was prepared in 47% (distilled) yield in analogous fashion. After chromatographic purification the m.p. was 61.0–62.0°.[17]

2-Hydroxy-3′-nitrobenzophenone.—This compound was isolated from decomposition of the corresponding diazonium fluoborate, and isolated by chromatographic means as discussed below; m.p. 96–97°.

Anal. Calcd. for $C_{13}H_9NO_4$: C, 64.20; H, 3.73; N, 5.76. Found: C, 64.11; H, 3.71; N, 5.88.

2-Chloro-4′-methylbenzophenone.—This was prepared by the Friedel–Crafts reaction; m.p. 98.5–99.5°.[19]

Fluorenone.—Eastman Kodak Co. fluorenone was distilled and recrystallized from a benzene–pentane mixture; m.p. 82.5–83.0°.

3-Methylfluorenone.—This was obtained from the diazonium salt and purified by chromatography and by crystallization from a benzene–pentane mixture; m.p. 66.0–66.5°.[20]

2-Nitrofluorenone.—This was prepared by nitrating fluorene, the nitrofluorenone mixture then being oxidized by sodium dichromate in acetic acid. Recrystallization from acetic acid and from ethyl acetate gave a product with m.p. 222–224°.[21]

Fluoboric Acid.—In the course of the preparation of the diazonium fluoborates it was discovered that one sample gave diazonium salts of only 75–80% purity and, further, that the fluoboric acid gave a precipitate (silica?) upon addition of hydrochloric acid. Fluoboric acid was therefore prepared by adding 43 g. of reagent grade boric acid gradually to 230 g. of reagent grade 48% hydrofluoric acid in a 500-cc. Polythene bottle over a period of two hours, the temperature being maintained below 25°. After another hour the fluoboric acid was decanted from a little solid into another Polythene bottle.

Buffer Solutions.—*p*H 1.0, 2.81 ml. of 95% sulfuric acid; *p*H 4.65, 5.72 ml. of glacial acetic acid and 13.6 g. of sodium acetate trihydrate; *p*H 6.68, 17.42 g. of dipotassium phosphate and 13.61 g. of monopotassium phosphate; *p*H 8.58, 12.37 g. of boric acid and 2.66 g. of sodium hydroxide; *p*H 12.3, 14.2 g. of disodium phosphate and 38.0 g. of trisodium phosphate dodecahydrate: all quantities added to sufficient water to give one liter of solution.

Quantitative Product Isolation.—It was found that the fluorenones were easily separated from the 2-hydroxybenzophenones on Grade 4 alumina[18a] (Alcoa F-20 Alumina with 12 g. of water added per 100 g. of alumina) using a 50% by volume solution of benzene in pentane. *R* values[18b] for the fluorenones and the methylhalobenzophenones were about 0.5, and for the hydroxybenzophenones about 0.15.

For the product studies approximately 1 mmole of the diazonium salt was allowed to undergo thermal decomposition in 100 ml. of aqueous solution for a period of at least ten half-lives. The suspended reaction products were extracted with one 15-ml. and three 10-ml. portions of methylene chloride, the solvent evaporated and the residue weighed as a check. The residue was taken up in 5–10 ml. of benzene and placed on a column of alumina 1.7 cm. by 12 cm. The benzene–pentane solvent was then run through the column and 40 cc. of percolate collected in a tared 50-ml. beaker. The hydroxybenzophenone was then stripped from the column by a solution of 13% (by volume) of methanol in chloroform. The two 50-ml. beakers were placed in a desiccator and a slow stream of dry, dust-free air aspirated through the desiccator until the solvents had evap-

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(15) F. Ullmann and H. Bleier, *Ber.*, **35**, 4278 (1902).

(16) J. Ranier, *Monatsh.*, **29**, 177 (1908).

(17) F. Ullmann and I. Goldberg, *Ber.*, **35**, 2812 (1902).

(18) (a) H. Brockmann and H. Schodder, *ibid.*, **74**, 73 (1941); (b) P. H. Monaghan, H. A. Suter and A. L. LeRosen, *Anal. Chem.*, **22**, 811 (1950).

(19) W. P. Cohen, *Rec. trav. chim.*, **38**, 117 (1918).

(20) F. Ullmann and E. Mallet, *Ber.*, **31**, 1694 (1898).

(21) W. F. Kuhn, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 447.

orated. Evaporation was facilitated by warming the desiccators so that the internal temperature was 30–40°. This was accomplished by wrapping around the outside a rubber tube through which a gentle flow of steam was passed.

The procedure was standardized by making up known mixtures of the fluorenone and the corresponding hydroxybenzophenone. The results are presented in Table VII. No correction was applied to the fluorenone values, but the appropriate average correction listed in Table VII was applied to all hydroxybenzophenone values.

Rate Determinations.—The rate of nitrogen evolution was followed manometrically in an apparatus described elsewhere.[22a] It is similar to the apparatus described by Moelwyn-Hughes and Johnson[22b] and is a large scale version of the Barcroft–Warburg apparatus. Total nitrogen yields were obtained from the apparatus dimensions and the appropriate formula described elsewhere.[22a] The amount of oxygen present varied from one run to the next, since the flasks were flushed for varying periods of time with nitrogen prior to reaction.

For the statistical adjustment ten p–t values were selected at random (but with a view to giving a fairly wide and even distribution of pressure readings). The adjusted values of a, b and c generally gave standard deviations of 0.5 mm. or less for pressures ranging from 0 to 350 mm. or more. The reaction range covered was usually about 10–95%, and the deviations between calculated and observed pressures were entirely random over the whole range. The reactions are thus described by a first-order expression with a high degree of precision. Standard deviations of the rate constants were calculated from the reciprocal matrix.[11] For those lines of data containing items in parentheses, the rate constants were obtained by averaging five or more values determined by the Roseveare[22c] procedure. The rate constants were checked over the reaction range specified by obtaining for each time the value of e^{-kt}; a and b are then linear in p and e^{-kt} and were obtained for two points. The standard deviation was estimated from $\{\Sigma(p_\infty - p_{\text{calcd.}})^2/8\}^{1/2}$, and is not a minimum value since a least squares adjustment was not carried out. It might be mentioned that these particular data are of considerably higher precision than the other data because of improvements in experimental techniques. For these runs the standard deviation of the rate constants was obtained by an empirical method based on s_p, $-b$, and extent of reaction, a method which reproduced fairly well the least squares s_k values for the runs so analyzed.

Table VII

Precision of the Chromatographic Procedure for Product Determination

Product determined	Range of wts. investigated, mg.	Avg.[a] cor., mg.	Std.[b] dev.	No. of detns.
Fluorenone	46–169	0.6	2.5	15
2-Hydroxybenzophenone	24–88	6.8	3.5	15
3-Methylfluorenone	73–109	0.3	1.3	6
4′-Methyl-2-hydroxybenzophenone	27–112	4.7	1.4	6
2- and 4-nitrofluorenone (mix.)[d]	37–105	2.1	3.1	6
3′-Nitro-2-hydroxybenzophenone	71–124	[c]	3.5	7

[a] Avg. corr. = avg. of (wt. taken − wt. found). [b] Per determination. [c] Calcd. cor. in mg. = $2.24 + 0.079x$ where x is the observed weight of the 3′-nitro-2-hydroxybenzophenone. [d] From the diazonium salt.

Discussion

The yields of the fluorenones and of the 2-hydroxybenzophenones reported in Table I demonstrate conclusively that the mechanism of the fluorenone cyclization and of hydroxybenzophenone formation involve a heterolytic C–N cleavage. With a nitro group present, the right-hand ring is deactivated toward electrophilic substitution and the yield of cyclic product is less than for the unsubstituted and methyl substituted compounds. For a homolytic ring closure just the opposite results are to be expected. The above conclusion is supported also by the facts that the diazonium salts are quantitatively accounted for, that the kinetic results are precisely fitted by a first-order expression, and that the rates are unaffected by variation in the oxygen content of the reaction mixtures. The conclusion also is in agreement with previously presented evidence[1,8] that diazonium salts usually undergo thermal decomposition by a heterolytic mechanism in acidic aqueous solution. There is always the question for compounds which can react by more than one mechanism as to whether conditions can be found such that one mechanism occurs quantitatively. It may be tentatively estimated that these reactions are 95% or more heterolytic on the reasonable supposition that the uncontrolled variation in amount of oxygen present would have resulted in 50–100% or more variation in rates and in products of any homolytic part of the process. In this connection it should be mentioned that the rate of the thermal decomposition of 2-(4′-methylbenzoyl)-benzenediazonium fluoborate at 25° in 0.05 M sulfuric acid in the presence of a benzene phase was 6.89×10^{-6} sec.$^{-1}$, identical with the rates given in Table IV for the reaction carried out in the absence of a benzene-phase in spite of the fact that benzene had a marked accelerating effect on the free radical processes at higher pH levels.

The effect of substituents on the fluorenone yield was surprisingly small, but this result is a reasonable one if the loss of nitrogen is an S_N1 process, the carbonium ion resulting being so reactive that it is not very selective. An analogy is to be found in a comparison of the migration aptitudes for the pinacol rearrangement and for the Demjanov rearrangement[23] of β,β'-diarylethylamines, ArAr′-$C^{14}HCH_2NH_2$, to stilbenes, ArC^{14}H=CHAr′ on treatment with nitrous acid. In the former reaction a methyl or a methoxyl substituent greatly facilitates the migration of the tolyl or the anisyl ring compared with migration of the phenyl ring, and this reaction thus constitutes an example of the type of electronic effect observed in many reactions. But in the Demjanov reaction the migration is almost statistical and thus rather insensitive to substituents. There is a considerable amount of evidence that aliphatic amines react with nitrous acid to give a diazonium intermediate that promptly undergoes S_N1 loss of nitrogen. The Demjanov results are thus consistent with a process involving a highly reactive and non-selective carbonium ion intermediate.

The effect of the electron-releasing methyl group and the electron-attracting nitro group on the rate of cleavage of the C–N diazonium bond is not entirely clear from Table IV because the effects on the hydroxylation process and on the ring closure reactions are not readily distinguishable. The two rates

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(22) (a) D. F. DeTar and M. N. Turetzky, in preparation; (b) E. A. Moelwyn-Hughes and P. Johnson, *Trans. Faraday Soc.*, **36**, 948 (1940); (c) W. R. Roseveare, This Journal, **53**, 1651 (1931).

(23) L. S. Ciereszko and J. G. Burr, *ibid.*, **74**, 5431 (1952).

can, however, be separated easily by use of the data of Table I, since the reactions are all first order; the equation is

$$k_{\mathrm{MOH}}/k_{\mathrm{UOH}} = (k_{\mathrm{M}}/k_{\mathrm{U}})(Y_{\mathrm{MOH}}/Y_{\mathrm{UOH}}) = 1.33 \text{ (at } 35°) \quad (3)$$

The ratio of the rate constant for the formation of 2-hydroxy-4′-methylbenzophenone (k_{MOH}) to that for formation of unsubstituted 2-hydroxybenzophenone (k_{UOH}) is given by the product of the ratio of total rates of disappearance of the 4′-methyl salt (k_{M}) and the unsubstituted salt (k_{U}) and the ratio of the relative yields of the hydroxybenzophenones in their respective reactions ($Y_{\mathrm{MOH}} = 35/96$, $Y_{\mathrm{UOH}} = 36/100$). The value of $k_{\mathrm{MOH}}/k_{\mathrm{UOH}}$ for the 3′-nitro compound relative to unsubstituted 2-benzoylbenzenediazonium fluoborate is 0.65. Thus the methyl group increases the rate at which the diazonium group is replaced by water and the nitro group decreases it so that these compounds are similar to other diazonium salts in that electron-releasing groups facilitate replacement and electron-attracting groups hinder it. This type of effect is the expected one for an S_N1 process: the opposite effect is expected for an aromatic S_N2 process.

The results of the reactions carried out in the presence of high concentrations of sodium chloride and of sodium bromide (Table III) also are better explained on the basis of an S_N1 loss of nitrogen than by the aromatic S_N2 process. For an S_N2 process a high concentration of chloride ion might be expected to lead to two results: (1) a decrease in the fluorenone yield due to competition of the nucleophilic chloride ion with the ring as nucleophilic agent; (2) a decrease in the 4′-methyl-2-hydroxybenzophenone yield. Since chloride ion is about 1000 times as effective a nucleophilic agent as water,[24] in the 6.2 *M* sodium chloride solution less than 0.5% of the hydroxy compound should be produced by the aromatic S_N2 process. For the S_N1 process the yield of fluorenone should remain roughly the same whether or not chloride ion is present, and the relative yields of 2-hydroxy-4′-methylbenzophenone and of 2-chloro-4′-methylbenzophenone should approximate the relative concentrations of water molecules and chloride ions (assuming little or no selectivity in reaction of the carbonium ion). In the 6.2 *M* sodium chloride solution as a whole the ratio of water molecules to chloride ions is about 18. If the solvating power of sodium ion (about 4 water molecules per ion) is taken into account,[25] the ratio of "free" water molecules to chloride ions is about 9. The latter figure would give a minimum yield of chloro compound of about 5%. But it is obvious that the positive charge on the diazonium ion will cause the chloride ion concentration to be higher in the vicinity of the diazonium group than in the bulk of the solution, since ion–ion forces are stronger than ion–dipole forces. The yields reported in Table III for the sodium chloride reactions are thus in good qualitative agreement with the predictions made for the S_N1 mechanism and completely wrong for the aromatic S_N2 mechanism. By a similar argument as applied to the bromide reactions the relatively high yield of 2-bromobenzophenone and the lowering of the fluorenone yield both suggest that some aromatic S_N2 process may be occurring with the more nucleophilic bromide ion (about 7 times more nucleophilic than chloride).

It is of passing interest to note that the qualitatively observed higher yield of 2′-nitrofluorenone than of 4′-nitrofluorenone can also be explained for the postulated very fast and non-selective reaction of the carbonium ion. The direction of the dipole of the nitro group is such as to give a repulsion between the dipole and the positive charge of the diazonium group. Although the two benzene rings are undoubtedly somewhat out of plane because of steric repulsions of the ortho groups, it is likely that they are more nearly in the plane of the C—(C=O)—C atoms than perpendicular to this plane because of resonance considerations. The slightly preferred orientation of the nitrophenyl ring is therefore the one with the position para to the nitro group nearest the diazonium group.

That the S_N1 loss of nitrogen from diazonium salts is of fairly general occurrence has been suggested by Lewis and Hinds.[26]

For the reactions at higher *p*H levels, both the kinetics (Table VI) and the fluorenone determination indicate that the mechanism is more complex than the one taking place in acid solution. The reactions are faster, the kinetics complex, the rates are markedly increased by the presence of a benzene layer, and seem to be somewhat retarded by oxygen. These results all suggest that a free radical process is involved to some extent, but the rate of the ionic process (as observed under acidic conditions) is high enough so that the reaction is expected to be partly ionic in mechanism. At a *p*H of 8.58 most of the fluorenone produced can be accounted for on the hypothesis that it is formed by an accompanying ionic reaction of the same rate as that observed at a *p*H of 1. The hypothesis is reasonable since the ionic reactions of diazonium salts are not much affected by the presence of moderate concentrations of various ions. The observed first-order rate constant is analyzed into two parts

$$k_{\mathrm{obsd}} = k_{\mathrm{ionic}} + k_{\mathrm{other}}$$

or

$$20 \times 10^{-6} = 4.8 \times 10^{-6} + k_{\mathrm{other}}$$

The expected percentage fluorenone yield from the ionic process is therefore (4.8/20) (0.64) = 15%, and the yield of fluorenone from other processes is therefore (23 − 15) (20/15.2) = 11%. The somewhat more extensive preliminary results reported here thus substantiate the earlier conclusion that the ionic process gives much better yields of fluorenone than do the free radical processes taking place under alkaline conditions. It has not yet been adequately demonstrated that any of the fluorenone necessarily results from a free radical process, but such a conclusion is certainly a possible one.

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[24] C. G. Swain and C. B. Scott, THIS JOURNAL, **75**, 141 (1953).

[25] We are indebted to Dr. O. D. Bonner for pointing this out.

[26] E. S. Lewis and W. H. Hinds, THIS JOURNAL, **74**, 304 (1952).