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

Intramolecular Reactions. IV. Chain Transfer Reaction Involving an Aromatic Hydrogen Atom and Related Reactions of 2-(4'-Methylbenzoyl)-benzenediazonium Salts¹

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The reaction of 2-(4'-methylbenzoyl)-benzenediazonium salts with carbon tetrachloride in the presence of alkali leads to the formation of both 2-chloro-4'-methylbenzophenone and to the abnormal product 2-chloro-4-methylbenzophenone. This latter is attributed to the occurrence of an intramolecular chain transfer reaction involving an aromatic C–H bond (II \rightarrow III). Most of the replacement reactions of this diazonium salt led to the normal replacement products. The cuprous halide catalyzed decomposition of the diazonium salt in sulfuric acid leads to unusually high yields of the cyclization product, 3methylfluorenone, and shows promise of being of preparative value.

In a continuation of previous work on the mechanisms of the replacement of the diazonium group in 2-(4'-methylbenzoyl)-benzenediazonium salts (I) and related compounds,^{1,3} it was of especial interest to investigate the replacement of the diazonium nitrogen by halogen under conditions involving free radical intermediates in order to determine whether an o-benzoylphenyl radical can undergo an intramolecular chain transfer reaction $(II \rightarrow III)$. Since the expected product of the reaction of radical II with carbon tetrachloride is 2-chloro-4'-methylbenzophenone (IV),3d while radical III would lead to the isomeric 2-chloro-4methylbenzophenone (V), the presence of V would serve to demonstrate the occurrence of the chain transfer step. The products of the heterolytic cleavage of the C–N bond are known to be 3-methylfluorenone (65%) and 2-hydroxy-4'-methyl-benzophenone (35%),^{3b} and evidence has been presented to show that this cleavage is an SN1 type process so that an ionic intermediate would not be expected to give V. Further evidence about the mechanisms of the C-N bond cleavage already has been given.³



Preliminary experiments showed that the diazonium salt did react with a vigorously stirred mix-

(1) A preliminary report of part of this work has been made: D. I. Relyea and D. F. DeTar, THIS JOURNAL, 76, 1202 (1954).

(2) Rohm and Haas Co. Research Assistant, 1953.
(3) (a) D. F. DeTar and S. V. Sagmanli, THIS JOURNAL, 72, 965 (1950); (b) D. F. DeTar and D. I. Relyea, ibid., 76, 1680 (1954); (c) D. F. DeTar and Y.-W. Chu, *ibid.*, **76**, 1686 (1954); (d) D. F. DeTar and J. C. Howard, ibid., 77, 4393 (1955).

ture of carbon tetrachloride and sodium hydroxide to give a low yield of a mixture containing 3methylfluorenone and both of the chloromethylbenzophenones. A quantitative study was therefore carried out with a number of halogenated methanes and the results are summarized in Table I.

The only definitely established example of the intramolecular chain transfer step was that observed with the carbon tetrachloride reactions, although there appeared to be a small amount with the bromochloromethane reaction. In order for the chain transfer step to occur, it is necessary that the rate at which the radical abstracts a chlorine atom be sufficiently slow. Bromotrichloromethane appears to be much more reactive toward the halogen abstraction step,⁴ and the relatively high yield of pure 2-bromo-4'-methylbenzophenone and the absence of the isomeric 2-bromo-4-methylbenzophenone are therefore readily understandable.

The products obtained in these reactions provide a measure of the relative ease of abstraction of halogen and hydrogen atoms from some halogenated methane derivatives. Although there is a correlation between bond strength and rate of hydrogen abstraction in methyl radical reactions,⁵ such reactions all result in the formation of a single product, methane. The reactions reported in Table I involve abstraction of hydrogen and of three different halogens. They are therefore not directly comparable and will not necessarily correlate with the strength of the C-H or of the Chalogen bonds in the halogenated methanes. It can be seen that there is, however, a greater tendency to abstract the heavier halogen and that iodine is abstracted in preference to hydrogen even in methyl iodide.

The results obtained in these experiments and those reported previously for the replacement of a diazonium group which was a blocking group in an optically active biphenyl^{3d} serve to emphasize the rapidity of the halogen abstraction step. With the 2-(4'-methylbenzoyl)-benzenediazonium salts this halogen abstraction competes favorably with both

$R \cdot + CCl_4 \longrightarrow RCl + \cdot CCl_3$

the intramolecular chain transfer reaction and with cyclization of the radical to 3-methylfluorenone,³ while with the 2-(2'-nitro-6'-methylphenyl)-benzenediazonium salts (and with the corresponding

(5) A. F. Trotman-Dickenson, Quart. Revs., 7, 198 (1953).

⁽⁴⁾ M. S. Kharasch, E. V. Jensen and W. H. Urry, ibid., 69, 1100 (1947)

TABLE I
PRODUCTS OF THE REACTION OF 2-(4'-METHYLBENZOYL)-BENZENEDIAZONIUM SALTS WITH HALOGENATED METHANES AND
Aoueous Alkali

Wt. of	F.	Leaction medium	n medium					
salt, g.	phase, ml.	Aqueous phaseb	2,4'-C1MB	2,4-C1MB	2,4'-BrMB	2,4'-IMB	3MF	4MB
0.75B°	100 CCl4	100 ml. 0.1 <i>M</i> NaH ₂ PO ₄ -Na ₂ HPO ₄ , <i>p</i> H 7.2	7(29)	3(12)		· · · · ·	16(55)	1(4)
0.75B	100 CC14	100 ml. 0.1 <i>M</i> Na ₂ HPO ₄ -Na ₃ PO ₄ , <i>p</i> H 12.3	6.5(37)	1.6(9)			8(40)	3(14)
1.00F	10 CCl ₃ Br	30 ml. 0.3 M NaOH, pH 13			66(100)			
1.00B	100 CHCl ₂ Br	100 ml. 0.1 <i>M</i> Na ₂ HPO ₄ -Na ₃ PO ₄ , <i>p</i> H 12.3	Absent ^d	Absent ^d	62(88)	• • • • •	14(12)	
1.00B	100 CH ₂ ClBr	100 ml. 0.1 <i>M</i> Na ₂ HPO ₄ -Na ₃ PO ₄ , <i>p</i> H 12.3	$Absent^d$	Absent ^d	⁴ 14(26) ^e		15(21)	35(48)
1.00F	$10 \ \mathrm{CH_2I_2}$	30 ml. 0.3 N NaOH, pH 13				57(100)		Absent ^d
1.00B	30 CH ₃ I	75 ml. 0.7 M NaOH, p H > 13				54(100)		Absent ^d
				4 .1 14		0.4/ D	10D ' 01	

^a 2,4'-ClMB is 2-chloro-4'-methylbenzophenone; 2,4-ClMB is 2-chloro-4-methylbenzophenone, 2,4'-BrMB is 2-bromo-4'methylbenzophenone, 2,4'-IMB is 2-iodo-4'-methylbenzophenone, 3MF is 3-methylfluorenone, 4MB is 4-methylbenzophenone. The first number is the percentage yield based on the diazonium salt; the number in parentheses is the relative amount of the component present in the first chromatographic band. ^b The 0.1 *M* designation means that each buffer component is present in 0.1 *M* concn. ^e B signifies bisulfate; F, Fluoborate. ^d Based on absence of one or more characteristic peaks. ^e There appears to be about 2.4(5) of the 2-bromo-4-methylbenzophenone present.

peroxide) the halogen abstraction even competes with the internal rotation of the biaryl rings which leads to racemization.

In many chemical reactions the possibility of closing a five-membered or a six-membered ring leads to enhanced reactivity due to a particularly favorable steric arrangement of the reacting centers. A simple example is the great ease of the intramolecular formation of succinic anhydride from succinic acid as compared with the difficulty of the intermolecular formation of acetic anhydride from acetic acid. It is therefore to be expected that the substitution of an aryl free radical into an aromatic ring should be an especially favorable reaction for the o-benzoylphenyl type of free radical (II, III). The fact that this radical does not cyclize particularly well therefore requires some sort of explanation. It has been noted that the ionic cleavage of the C-N bond of the 2-(4'-methylbenzoyl)-benzenediazonium ion (I) leads to a considerable amount of reaction with water to form 2-hydroxy-4'-methylbenzophenone (35%) in addition to the intramolecular ring closure. It has been suggested that the results can be explained on the basis of the formation of a highly reactive and relatively non-selective carbonium ion interme-diate.^{3b} The comparative failure of the cyclization with the *o*-benzoylphenyl type of radical may also be attributed to the very high reactivity of the radical toward various alternative reactions.

The results of the reaction of the 2-(4'-methylbenzoyl)-benzenediazonium salts (I) with cuprous halides are summarized in Table II and those of the reaction with iodide solutions in Table III. None of these reactions leads to any of the abnormal type of replacement product V; the suggestion¹ that such a product was present in some of these reactions was based on a misinterpretation of a peak at 10.69 μ . This peak was later found due to 4-methylbenzophenone (Table V) formed in small amounts in the Sandmeyer bromine replacement reaction and in larger amounts in the iodide runs at high ρ H.

TABLE II

PRODUCTS OF THE REACTION OF 2-(4'-METHYLBENZOYL)-BENZENEDIAZONIUM SALTS WITH CUPROUS HALIDES

In all runs 3.2 mmoles of the crystalline diazonium salt and 4 mmoles of the cuprous halide (CuX) were used

C.		2-Halo-4'-	Product y	ields, %a
prous halide	Reaction conditions	benzo- phenone	3-Methyl- fluorenone	benzo- phenone
CuCl	HC1, 60° ^b	92(100)°		
CuBr	HBr, 60° ^b	$84(97)^{c}$		2(3)
CuCl ^d	H ₂ O, 60° ^e		52(66)	27(33)
CuBr^d	H ₂ O, 60°		52(68)	24(32)
CuId	H₂O, 60°		61(71)	25(29)
CuCl	H₂O, 5–30°		44(67)	22(33)
CuBr	H₂O, 5–30°		53(69)	24(31)
CuI	H ₂ O, 5–30°		54(82)	12(18)
CuC1	H ₂ SO ₄ , [′] 60°		86(91)	9(9)
CuBr	H ₂ SO ₄ , ^f 60 °		94(93)	6(6)
CuI	$H_{2}SO_{4}, f 60^{\circ}$		83(87)	13(13)

^a The first number represents the actual yield, based on diazonium salt, the number in parentheses the relative yield of the product in the first chromatographic adsorption band. ^b Coned. aq. hydrohalic acid used to dissolve the cuprous halide; in all other runs a suspension of the cuprous halide was used. ^c None of the 2-halo-4-methylbenzophenone was present. ^d The diazonium fluoborate was used in these runs, the bisulfate was used in all other runs. ^e Reaction time 1 hr. for all 60° runs, 6 to 12 hr. for the runs at the lower temperature. ^f 10 M.

The reactions in the presence of precipitated cuprous halide take place somewhat faster than those in homogeneous aqueous solution. These might be free radical reactions under such conditions that the radical II has no particularly favorable intermolecular reaction path, but the point deserves additional study. One most interesting feature is the relatively high yield of cyclization product formed in sulfuric acid with a solid cuprous halide catalyst present.

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TABLE III

PRODUCTS OF THE REACTION OF 2-(4'-METHYLBENZOYL)-BENZENEDIAZONIUM SALTS WITH AQUEOUS POTASSIUM LODIDE

		Product yields, %a				
pН	Reaction medium	2-Iodo-4'- methyl- benzo- phenone	3- Methyl- fluore- none	4- Methyl- benzo- phenone		
2	25 ml, $0.7~M$ KI	83(100)				
4.7	100 ml. 0.05 M KI, 0.1					
	M acetate ^b	99(1 00)				
7.2	100 ml. 0.7 M KI, 0.1 M					
	phosphate	74(100)				
9.2	25 ml. 0.7 M KI, 0.4 M					
	borate ^d	13(62)	7(20)	6(18)		
13	25 ml. 0.7 M KI, 0.7 M					
	KOH	6(40)	4(15)	11(45)		

^a There is no evidence for the presence of 2-iodo-4-methylbenzophenone in any of the runs. The first number refers to the yield based on the diazonium salt, the number in parentheses to the relative yield based on product isolated. In all runs 0.5 g, of the diazonium fluoborate was used unless otherwise specified. $^{b}0.1 M$ each in acetic acid and in sodium acetate. This is a kinetic run that also contained 0.1 g. of iodine; 0.2 g. of diazonium salt. $^{\circ}0.1 M$ NaH₂PO₄ and 0.1 M Na₂HPO₄. $^{d}0.1 M$ KBO₃ and 0.1 M HBO₃.

Experimenta16

Reagents .- The preparation of 2-amino-4'-methylbenzophenone utilized the Friedel-Crafts reaction between toluene and the acid chloride of p-toluenesulfonylanthranilic acid.⁷ The preparations of 2-chloro-4'-methylbenzophenone and 2-(4'-methylbenzoyl)-benzenediazonium fluoborate and the chromatographic technique for isolating reaction products have been described.3b

2-(4'-Methylbenzoyl)-benzenediazonium Bisulfate.- $-T_0$ a stirred mixture of 50 ml. of concn. sulfuric aid and 4.2 g. (0.020 mole) of 2-amino-4'-methylbenzophenone was added 2.40 ml. (0.021 mole) of redistilled n-butyl nitrite, the temperature being maintained at 0-5°. After 10 minutes, ether (about 60 ml.) was added to the point of permanent turbidity and crystallization initiated by rubbing. Another 40 ml. of ether was added and the yellow diazonium salt filtered, yield 4.15 g. (67%). Addition of too much ether caused precipitation of a dark-colored oil and gave a sample of diazonium salt which deteriorated rapidly. A pure sample could be kept in a desiccator for about two weeks at room temperature without serious decomposition. One sample showed an interesting effect of light in that it was bright yellow when first obtained, slowly became orange on standing in the dark and changed to yellow again on exposure to light.

2-Bromo-4'-methylbenzophenone.—The Friedel-Crafts method gave a 65% yield, b.p. 180-200° at 5-8 mm., m.p. 89-90°; Heidenreich⁸ reports a m.p. of 92-93°.
2-Iodo-4'-methylbenzophenone.—A mixture of 13.3 g.

(0.050 mole) of 2-iodobenzoyl chloride, 100 ml. of toluene and 15.0 g, of anhydrous aluminum chloride was maintained at 45° for 6 hr. The 2-iodo-4'-methylbenzophenone has a b.p. 158-162° at 0.6 mm. and on recrystallization from eth-anol has a m.p. of 52.5-53.0°, yield of 22% of pure ketone.

Anal. Calcd. for $C_{14}H_{11}OI$: C, 52.19; H, 3.44; I, 39.39. Found: C, 52.50, 52.21; H, 3.41, 3.17; I, 38.95, 39.60 (two different analytical samples).

-2-Chloro-4-methylani-2-Chloro-4-methylbenzophenone.line hydrochloride was prepared in 16% yield by an acetylation-chlorination (with chlorine)-deacetylation procedure analogous to a bromination procedure.³ The amino group was converted to the cyano group by the Sandmeyer

ville, Tenn. (7) H. J. Scheifele and D. F. DeTar, Org. Syntheses, **32**, 8 (1952). (8) A. Heidenreich, Ber., 27, 1452 (1894).

method in 31% yield¹⁰; the partly purified material was a light orange solid, m.p. $51-55^{\circ}$ (reported m.p. $61-62^{\circ}$).¹¹ The 2-chloro-4-methylbenzonitrile was hydrolyzed with 75% sulfuric acid at 150° for 3 hr. to give an 82% yield of 2-chloro-4-methylbenzoic acid, m.p. $152-156^{\circ}$, reported m.p. $155.0-155.5^{\circ}$.¹¹ The acid (0.038 mole), 150 ml. of benzene and 9 g. (0.043 mole) of phosphorus pentachloride were heated at $50-60^{\circ}$ for 30 minutes, cooled to room temperature chloride. and 17 g. (0.13 mole) of anhydrous aluminum chloride added. The reaction was carried out at room temperature for 2 hr., at 80° for 2 hr. and at room temperature overnight. yield, b.p. 170–171° at 0.3 mm., colorless needles from ethanol, m.p. $51-52^{\circ}$. The 2-chloro-4-methylbenzophenone was obtained in a 46%

Anal. Caled. for $C_{14}H_{11}OC1$: C, 72.89; H, 4.81; Cl, 15.37. Found: C, 72.67, 72.29; H, 4.64, 4.56; Cl, 15.42, 15.28 (two different samples).

2-Bromo-4-methylbenzonitrile.—2-Bromo-4-methylaniline was obtained in 66% yield from technical grade p-toluidine.9 Since the Sandmeyer procedure gave only fair results, a study was made of the effect of reaction variables on the yield. The diazotization was carried out by the alter-nate addition of the amine and a concentrated solution of sodium nitrite to the stirred mineral acid; the reaction flask was surrounded by an ice-bath. The diazonium salt solution was then added to the cuprous cyanide complex solution under the conditions given in Table IV. The product was extracted with ether, the ether extract washed and dried, the ether removed and the residue distilled. The result with the last run is typical: 48 g, (11%) of material, b.p. $51-59^{\circ}$ at 0.7-0.9 mm, identified as *m*-bromotoluene; 165 g. (32%) b.p. $91-97^{\circ}$ at 0.7-0.9 mm. identified as 2-bromo-4-methylbenzonitrile; 138 g. of residue (32%), assuming it to have the approximate composition of the biphenyl dimer).

2-Bromo-4-methylbenzophenone.—Hydrolysis of 2-bromo-4-methylbenzonitrile gave a 72% yield of 2-bromo-4-methylbenzoic acid, m.p. 150–151°, reported m.p. 147°.¹² This was converted to 2-bromo-4-methylbenzophenone. The 2-bromo-4-methylbenzophenone, b.p. 171–172° at 3 mm., did not crystallize.

Anal. Calcd. for $C_{14}H_{11}OBr$: C, 61.11; H, 4.03; Br, 29.05. Found: C, 61.93, 61.46; H, 4.52, 4.13; Br, 28.39. 28.82 (two different samples).

Rosemund-von Braun Reaction of 2-Bromo-4-methylben**zophenone** with Cuprous Cyanide.¹³—The product obtained from reaction at 150–200° with 0–0.25 ml. of pyridine per mmole of 2-bromo-4-methylbenzophenone using a 20-40%excess of cuprous cyanide was mainly 2-methyl-10-imino-9,10-anthraquinone, which after crystallization from 50:50 toluene-*n*-heptane had a m.p. of 90.5–91.5° (colorless needles).

Anal. Caled. for $C_{15}H_{11}NO$: C, 81.43; H, 5.01; N, 6.33. Found: C, 81.48, 80.93; H, 5.38, 5.30; N, 6.05. 6.29 (two different samples).

The evidence for the structure is based upon the analysis, the structure of the probable intermediate 2-cyano-4-meth-ylbenzophenone and upon hydrolysis with 75% sulfuric acid at 150° for 3 hr. to 2-methyl-9,10-anthraquinone, m.p. 173-175°. The infrared spectra indicated that the inine was different from 2-cyano-4-methylbenzophenone, although 4-methylbenzophenone-2-carboxylic acid is cyclized to 2-methyl-9,10-anthraquinone under the above hydrolysis conditions. Authentic samples of 2-methyl-9,10-anthraquinone14 were prepared from both 4-methylbenzophenone-2carboxylic acid and from 4'-methylbenzophenone-2-carboxylic acid by cyclization in concentrated sulfuric acid.

4-Methylbenzophenone-2-carboxylic Acid.—Treatment of 2-bromo-4-methylbenzophenone with a 25% excess of cuprous cyanide in 0.5 ml. of pyridine per minole at 130° for 30 minutes led to a product mixture which contained a nitrile (infrared spectra). This crude reaction mixture was hydrolyzed with 15% potassium hydroxide in 80% ethanol under reflux for 8 hr. The almost colorless crystalline 4-

(14) L. Gresly, Ann., 234, 239 (1886).

⁽⁶⁾ All melting points are corrected; boiling points are uncorrected. The microanalyses were carried out by Galbraith Laboratories, Knox-

⁽⁹⁾ J. R. Johnson and L. T. Sandborn, "Organic Syntheses," Coll. Vol. I, 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 111.

⁽¹⁰⁾ H. T. Clarke and R. R. Read, "Organic Syntheses," Coll. Vol.

I, 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 514. (11) A. Claus and N. Davidsen, J. prakt. Chem., [2] 39, 491 (1889). (12) A. Claus and H. Kunath, ibid., [2] 39, 485 (1889).

⁽¹³⁾ Cf. M. S. Newman, Org. Syntheses, 21, 89 (1941); J. E. Callen, C. A. Dornfeld and G. H. Coleman, ibid., 28, 34 (1948).

	TABLE IV	
SUMMARY OF THE CUPROUS CYANIDI	DISPLACEMENT REACTIONS CARRIED OUT C	ON DIAZOTIZED 2-BROMO-4-METHYLANILINE

				Marked of	Deserves	Isolated	yield, %
Amine used, mole s	Mineral acid equiv.ª	Sodium nitrite, moles ^{a,b}	Cuprous cyanide, moles ^a	neutraliza- tion ^c	layer, ml.	4-methyl- benzonitrile	3-Bromo- toluened
0.131	0.67^{e} (5.10)	0.133(1.02)	0.16(1.22)	Α	300	35	
1.08	3.00^{e} (2.78)	1.10(1.02)	1.33(1.23)	Α	1000	11	
0.200	0.50° (2.50)	0.203(1.02)	0.20(1.00)	Α		4	
0.941	5.00^{f} (5.31)	1.00(1.06)	1.25(1.33)	Α	1500	21	9
0.807	5.00^{f} (6.20)	0.857(1.06)	1.00(1.24)	В		26	7
0.807	5.00^{f} (6.20)	0.857(1.06)	3.00(1.24)	В		28	
0.500	2.50^{f} (5.00)	0.550(1.10)	0.84(1.68)	С		38	
0.365	$0.80^{f,g}(2.19)$	0.380(1.04)	1.25(3.42)	С		47	
1.00	$2.50^{f,g}(2.50)$	1.05(1.05)	1.25(1.25)	С		38	14
2.42	$3.00^{f,h}(1.24)$	2.68(1.04)	5.00(2.07)	D		25	
1.37	3.00^{f} (2.19)	1.50 (1.04)	3.00(2.19)	D		21	
2.63	$6.00^{f,h}(2.42)$	2.81(1.04)	4,25(1.57)	D		32	11

^a The figure in parentheses is the molar ratio of the material to the amine. ^b Merck and Co. reagent grade, minimum assay 97%. ^c A = 20-30% excess sodium carbonate added to the cuprous cyanide complex solution before the addition of the diazo solution; B = 20-30% excess sodium hydroxide added to the cuprous cyanide complex solution before the addition of the diazo solution; C = half of the theoretical quantity of 20% sodium hydroxide solution added to the diazo solution and more 20% sodium hydroxide solution; D = diazo solution added directly to cuprous cyanide complex solution whose approximate neutrality was maintained by the simultaneous addition of 20% sodium hydroxide solution. ^d Small amount of material isolated but not weighed for the cases for which no yield is reported. ^e 48% hydrobromic acid. ^f 97% sulfuric acid. ^e 1.00 mole of acetic acid added to the sulfuric acid used in diazotization. ^h 3.00 moles of acetic acid added to the sulfuric acid used in diazotization.

 TABLE V

 Absorption Constants Used for Infrared Analysis^a

			Wa	ve length, mic	0 11 5		
Compound	5.81	6.00	10.69	10.78	10.79	10.80	10.88
2-Chloro-4'-methylbenzophenone	1.10	4.37	4.95	29.8			2.76
2-Chloro-4-methylbenzophenone	1.03	1.39	31.2	8.33			2.35
2-Bromo-4'-methylbenzophenone	0.59	6.32	7.73		22.6		2.22
2-Bromo-4-methylbenzophenone	4.98	10.5	22.5		12.6		5.54
2-Iodo-4'-methylbenzophenone			2.55			21.8	2.09
4-Methylbenzophenone	0.62	60.4	16.0	6.3	6.1	6.88	16.5
3-Methylfluorenone	41.1	1.7	1.0	1.0	1.0	2.70	26.7

^a These constants refer to carbon disulfide solutions in a 0.195 mm. path sodium chloride cell. Absorption constant = $(100/c) \log T_0/T$ with c the concn. in g./100 g. soln. and T_0 and T the percentage transmission of solvent and of solution, respectively.

methylbenzophenone-2-carboxylic acid had a m.p. of $143-146^{\circ}$ (61% yield from 2-bromo-4-methylbenzophenone).

Anal. Calcd. for $C_{15}H_{12}O_3$: C, 74.99; H, 5.03. Found: C, 74.97, 74.87; H, 5.12, 5.07 (two different samples).

4'-Methylbenzophenone-2-carboxylic acid has a m.p. of 138–139°; the reported m.p. is 139–140°.¹⁵ The m.p. of a mixture of 4-methylbenzophenone-2-carboxylic acid and 4'-methylbenzophenone-2-carboxylic acid is 111–12°.

methylbenzophenone-2-carboxylic acid is $111-127^{\circ}$. The Reaction of 2-(4'-Methylbenzoyl)-benzenediazonium Salts with Cuprous Halides.—The cuprous halides were prepared by the reaction of hot solutions of sodium bisulfite and of cupric sulfate and sodium halide.¹⁶ The precipitate was centrifuged and washed with water and was used as a suspension in water or in sulfuric acid, or it was dissolved in an excess of hydrohalic acid. The products were isolated by extraction of the reaction mixture with three 10-ml. portions of chloroform. The solvent was removed and a benzene solution of the residue introduced onto a 2 × 15 cm. column of Brockmann grade 4 alumina. A 50:50 benzenepentane mixture was run through and the first band collected. This contained the various benzophenones and the 3-methylfluorenone. The composition was determined by a quantitative infrared spectrophotometric technique using carbon disulfide solutions. The results are summarized in Table II.

The Reaction of 2-(4'-Methylbenzoyl)-benzenediazonium Salts with Halogenated Methanes and Alkali.—The dry crystalline diazonium salt was added to a vigorously stirred mixture of the halogenated methane and of aqueous alkaline

(16) C. S. Marvel and S. M. McElvain, "Organic Syntheses," Coll, Vol. I, 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 170. medium. Stirring was continued for about 12 hr. The fluoborate dissolved only slowly in the ice-cold reaction mixture, but the bisulfate dissolved readily. The products were isolated by chromatography as described above. The results are summarized in Table I. A mixture containing 2chloro-4'-methylbenzophenone, 2-chloro-4-methylbenzophenone, 3-methylfluorenone and 4-methylbenzophenone in the proportions given in Table I matched the product curve peak for peak.

Spectrophotometric Analysis of Reaction Products.— Quantitative solutions in carbon disulfide were prepared using the transfer tube of DeTar and Gold.¹⁷ The same cell was used for all measurements. The wave lengths for the analyses and the absorption constants are summarized in Table V. Typical analyses of known mixtures are given in Table VI. In these analyses the total calculated weight of products agreed with the weight taken within a standard deviation of 4%.

	TABLE	VI		
SPECTROPHOTOMETR	IC ANALYS	SIS OF KN	own Miz	TURES
	Mixt	ure l	Mixt	iire 2
Component	Amount taken, g.	found	Amount taken, g.	Amount found
2-Chloro-4'-methyl-				
benzophenone	1.27	1.23	1.23	1.23
2-Chloro-4-methyl-				
benzophenone	0.87	0.86	0.87	0.89
3-Methylfluorenone	2.88	2.91	2.34	2.37
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