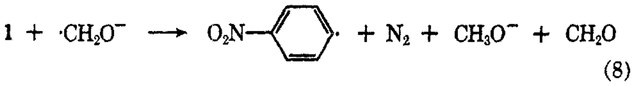
zoniation by one of the mechanisms discussed above, is conceivable. Another possibility is that the formaldehyde radical anion transfers an electron directly to **1**, as in eq 8. The combination of eq 2, 4, and 8 constitutes



(8)

a reasonable propagation cycle for a radical chain mechanism in methanol solution.

Experimental Section

Preparation of Arenediazonium Fluoroborates.—Benzenediazonium fluoroborate and its *o*-chloro, *m*-chloro, *p*-chloro, and *p*-nitro derivatives were synthesized by diazotization of the corresponding anilines in 38–40% HBF_4 with $NaNO_2$ below 0°.[25] The precipitated crude fluoroborates were collected and recrystallized from acetone and absolute ether to afford colorless powders or crystals. However, *p*-nitrobenzenediazonium fluoroborate was obtained as pale yellow crystals. Infrared absorption peaks (Nujol mulls) attributed to the $-N_2^+$ function were unsubstituted and *o*-chloro, 2290 cm^{-1}; *m*-chloro, 2280 cm^{-1}; *p*-chloro, 2300 cm^{-1}; *p*-nitro, 2310 cm^{-1}.

3,3′-Dichlorobiphenyl was prepared from the Ullmann reaction of 3-chloroiodobenzene with copper powder.[26] **3-Chlorobiphenyl** and **4-nitrobiphenyl** were synthesized by Gomberg–Bachmann reactions.[27]

Methyl *p*-Nitrophenylazo Ether.[23]—An aqueous solution of *p*-nitrobenzenediazonium chloride, prepared in the usual way from 13.8 g of *p*-nitroaniline, was added dropwise with vigorous stirring to 400 ml of cold (−10°) 20% aqueous NaOH. The mixture was then heated to 55°, and the golden yellow sodium *p*-nitrobenzeneisodiazotate was collected and dissolved in 500 ml of distilled water. This solution was slowly added to a solution of 17 g of $AgNO_3$ in 500 ml of distilled water; the resulting gray-white precipitate was collected, washed successively with water, ethanol, and ether, and air dried. This silver salt was suspended in a solution of 30 g of methyl iodide in 100 ml of absolute ether, and the suspension was stirred for 1 hr below 0° and then allowed to stand overnight in the refrigerator. The ether solution was filtered and evaporated, and the solid residue was recrystallized from petroleum ether with the use of charcoal. Pale yellow needles, mp 82–83° dec,[23] weighing 9.0 g (50% yield from *p*-nitroaniline), were obtained. This compound is stable for months if stored in the refrigerator under nitrogen. The ultraviolet spectral maximum (in 95% methanol) was at 277 mμ (log ε 4.10).

Reactions of Arenediazonium Fluoroborates and of 1 with Sodium Methoxide in Methanol.—To 10 ml of a 2 *M* or 0.1 *M* methanolic sodium methoxide solution containing a known amount of an internal standard for glpc analysis was added the fluoroborate (0.001 mol) at room temperature. The internal standards used were toluene (for estimation of benzene yields), *m*-nitrotoluene (for nitrobenzene), and bromobenzene (for chlorobenzene). The reactions were exothermic and rapid gas evolution was observed. After being heated at reflux for 5 min, the reaction mixtures were poured into 20 ml of chilled water; the mixture was extracted with pentane and the pentane extract was dried over anhydrous $MgSO_4$ and analyzed by glpc. The yields of reduction products obtained are listed in Table I or III.

The reduction products were also isolated from reaction mixtures by preparative glpc (column SE 30 silicon rubber or 10% Carbowax on Chromosolve P) and identified by comparison of infrared spectra with those of authentic specimens.

Reactions of Arenediazonium Fluoroborates and of 1 with Potassium *t*-Butoxide in Diverse Solvent Systems.—To 10 ml of a solution of $K^+ (CH_3)_3CO^-$ in *t*-butyl alcohol, or to a mixture of 5 ml of such a solution and 5 ml of a cosolvent as listed in Table II or III, in the presence of an internal standard, was added 0.001 mol of the arenediazonium fluoroborate or **1** at room temperature. After gas evolution ceased, the reaction mixture was heated 5 min at reflux and poured into 20 ml of water. The mixture was extracted with pentane, and the pentane extracts were dried over anhydrous $MgSO_4$ and analyzed by glpc. The yields of dediazoniation products obtained are listed in Table II.

Estimation and Identification of Biphenyl Derivatives as Products.—Reactions were run much as described above, except that internal standards were usually not included. Reaction mixtures were poured into water and extracted with ether; the ether extracts were dried over anhydrous $MgSO_4$, concentrated by careful distillation in a Vigreaux column, and diluted to standard volume with ether. Aliquots (by microsyringe) were analyzed by glpc; product yields were estimated by comparison of peak areas with those from equal aliquots of standard solutions in ether of authentic samples. Product identities were confirmed by retention time analysis and by comparison of infrared spectra of samples isolated by glpc with those of authentic samples.

Registry No.—1, 16020-14-7.

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[25] A. Roe, *Org. Reactions*, **5**, 204 (1949); E. B. Starkey in "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N.Y., 1943, p 225.

[26] F. Ullmann, *Ann.*, **332**, 38 (1904).

[27] W. E. Bachmann and R. A. Hoffman, *Org. Reactions*, **2**, 224 (1944).

The Catalytic Decarbonylation of Aroyl to Aryl Iodides

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Chlorotris(triphenylphosphine)rhodium catalyzes the decarbonylation of aroyl to aryl iodides. In the case of *o*-halogenobenzoyl iodides, a special reaction mechanism appears to be operative.

The ease of preparation of aryl chlorides and bromides by decarbonylation of the corresponding aroyl halides,[1,2] with the help of chlorotris(triphenylphosphine)rhodium $RhCl(PPh_3)_3$ (I), raised the question whether the method was applicable to aroyl iodides. The latter have been studied surprisingly little. This is probably due to the fact that they are not easy to prepare and that they lack stability.

The aroyl iodides were prepared from the corresponding acyl chlorides and sodium iodide.[3] Although the yields usually did not exceed 50–60% (and in cases such as that of *p*-toluoyl and α-naphthoyl chloride are even below that range) and were not very reproducible, this method is easier than that of Staudinger and Anthes,[4] who used dry hydrogen iodide.

When the aroyl iodides were heated at 200–220° with a small quantity of the rhodium complex I at a pressure which permitted the immediate removal of the aryl iodides formed, the reaction lasted from 3 to 15 min. Contrary to the experience with the aroyl chlorides, the catalytic decarbonylation begins even

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[1] J. Blum, *Tetrahedron Lett.*, 1605 (1966).

[2] J. Blum, E. Oppenheimer, and E. D. Bergmann, *J. Amer. Chem. Soc.*, **89**, 2338 (1967).

[3] D. W. Theobald and S. C. Smith, *Chem. Ind.* (London), 1007 (1958).

[4] H. Staudinger and E. Anthes, *Ber.*, **46**, 1417 (1913).

TABLE I

FORMATION AND DECARBONYLATION OF AROYL IODIDES

		Formation of aroyl iodides						Yield of pure aryl iodides, %
		Reaction			Anal, %[b]			
No.	Aroyl iodide	Temp, °C	Time, hr	Bp,[a] °C (mm)	Calcd for I	Found for I	Decarbonylation products	
1	Benzoyl	60	2.5	135 (28)	[c]		Iodobenzene	62
2	*p*-Toluoyl	50	2	156 (27)	51.7	51.9	*p*-Iodotoluene	63
3	*o*-Chlorobenzoyl	35	0.75	168 (30)	47.7	47.7	*o*-Chloroiodobenzene	53
4	*p*-Chlorobenzoyl	35	1	165 (30)	47.7	47.2	*p*-Chloroiodobenzene	98
5	*p*-Bromobenzoyl	45	1	140 (6)	40.8	40.9	*p*-Bromoiodobenzene	82
6	*o*-Iodobenzoyl	45	0.3	149 (1)	71.0	71.0	*o*-Diiodobenzene	72
7	*m*-Iodobenzoyl	45	1	155 (3)	71.0	70.5	*m*-Diiodobenzene	64
8	3,4-Dichlorobenzoyl	65	1.5	170 (3)	43.2	43.3	3,4-Dichloroiodobenzene	98
9	Isophthaloyl	70	2	172 (2)	65.8	66.1	*m*-Diiodobenzene	65
10	α-Naphthoyl	60	1	146 (0.1)	45.0	45.5	α-Iodonaphthalene	60

[a] Boiling points of analytical samples. The crude aroyl iodides were usually distilled over a 5° range. The aroyl iodides 4–10 solidified at room temperature and showed unsharp melting points. However, no attempt was made to recrystallize these unstable and easily hydrolyzable compounds. [b] Analyses were made immediately after the acyl iodides were distilled. Already after several hours, low values of iodine were obtained. [c] Known compound, *cf.* ref 3.

below the temperature indicated above; *e.g.*, at 160° benzoyl iodide undergoes 2% decarbonylation in 15 min.

This increased ease of decarbonylation parallels the thermal decomposition of the aroyl halides. Benzoyl iodide decomposes thermally to iodobenzene at 500° (but not yet at 250°), while benzoyl bromide requires a temperature of 700°.[4] *m*-Ethylbenzoyl iodide decomposes to *m*-iodoethylbenzene at 300–400°, in the presence of catalytic quantities of palladium, platinum, or nickel.[5]

The preparation and catalytic decarbonylation of a number of aroyl iodides is summarized in Table I. The yields in the decarbonylation reaction are generally higher than 50%, *p*-halobenzoyl iodides giving particularly good yields. The iodides of dicarboxylic acids studied behave normally.

Some theoretical interest attaches to the observation that *o*-iodobenzoyl iodide gives a 72% yield of *o*-diiodobenzene, while *o*-iodobenzoyl chloride and bromide give only low and variable yields.[1] As suggested before,[1] these yields may be due to the formation of a benzyne-type compound which could polymerize; indeed, considerable amounts of polymeric material are obtained in these cases. The benzyne hypothesis is supported by our observation that the catalytic decarbonylation of the *o*-iodinated acid chloride and bromide in the presence of 0.5 mol of iodine gives a 30 and 47% yield, respectively, of *o*-diiodobenzene, accompanied by small quantities of the normal products, *o*-chloro- and *o*-bromoiodobenzene. Benzyne is known to react with elementary iodine to give *o*-diiodobenzene in good yield, which is not the case with bromine and iodine monochloride.[6]

The occurrence of benzyne in our reaction may suggest that *o*-iodobenzoyl halides do not decompose by the mechanism previously suggested,[2] but thermolytically. This is, however, not the case, as *o*-iodobenzoyl chloride, heated with iodine, but without the rhodium complex as catalyst, does not give *o*-diiodobenzene.

In order to obtain *o*-diiodobenzene, one has to start with an *o-iodo* compound: *o*-chlorobenzoyl iodide gives only *o*-chloroiodobenzene, even when its catalytic decarbonylation is carried out in the presence of iodine, and the yield is the same as in the absence of iodine, while *o*-iodobenzoyl chloride and bromide, as pointed out above, do give *o*-diiodobenzene when treated with the rhodium complex in the presence of iodine.

There exist, then, two alternative hypotheses to account for our observations.

(1) All *o*-halobenzoyl halides decompose *via benzyne.* This would mean that the mechanism of their reaction is different from that governing the behavior of the *meta* and *para* analogs. Our experiments seem to indicate that the elimination of *ortho* halogen other than iodine does either not occur or is very slow.

(2) *o*-Iodobenzoyl chloride and bromide react first with the added iodine to form the aroyl iodide which then decomposes normally to *o*-diiodobenzene. Indeed, Goldman and Noyes[7] have postulated the equilibrium

$$2C_6H_5COBr + I_2 \rightleftharpoons 2C_6H_5COI + Br_2$$

Our experiments have shown that *without the rhodium complex* benzoyl bromide, *p*-chlorobenzoyl chloride and *o*-iodobenzoyl chloride can be distilled with iodine without any formation of the corresponding aroyl iodides. The situation changes, however, *when the rhodium complex is added* to these systems.

Even in the presence of the complex and iodine, benzoyl bromide and *p*-chlorobenzoyl chloride do not give iodobenzene and *p*-chloroiodobenzene, while *o*-chloro- and *o*-bromobenzoyl chloride behave somewhat similarly to *o*-iodobenzoyl chloride and bromide under these conditions and yield, in addition to the normal products (*o*-dichlorobenzene and *o*-bromochlorobenzene), small and varying quantities of *o*-chloro- and *o*-bromoiodobenzene, respectively, together with traces of the corresponding *meta* and *para* isomers and some polyhalogenobenzene derivatives.

We suggest that in the case of *o*-chloro- and *o*-bromobenzoyl chloride, the *o*-halogenated aryl iodides

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(5) E. B. McCall, private communication. See E. B. McCall and P. J. S. Bain, Monsanto Chemicals Ltd., British Patent 957,957 (1964); *Chem. Abstr.*, **61**, 5563 (1964).

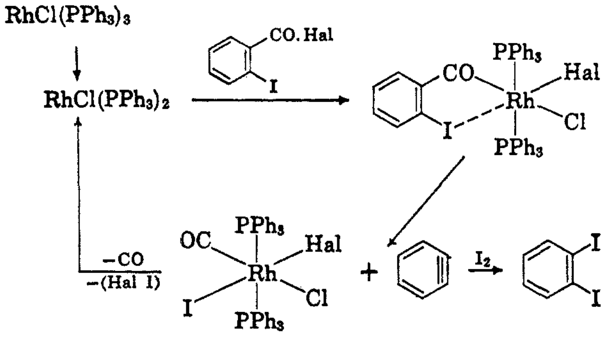
(6) L. Friedman and F. M. Lagullo, *Angew. Chem. Intern. Ed. Engl.*, **4**, 239 (1965).

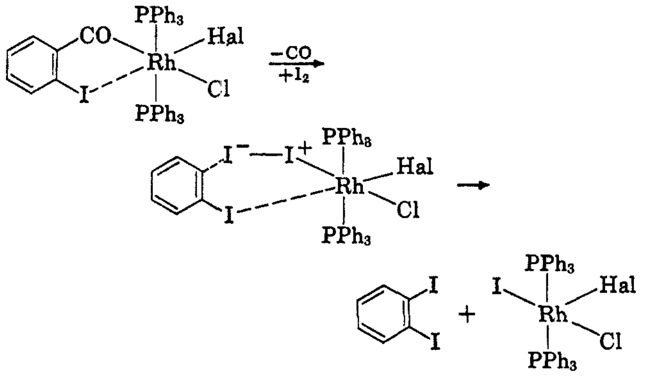
(7) A. Goldman and M. Noyes, *J. Amer. Chem. Soc.*, **79**, 5360 (1957).

are produced from iodotris(triphenylphosphine)rhodium[8,9] that is formed from the chloro compound and free iodine. The iodo derivative catalyzes the reaction described here exactly as the chloro compound. Furthermore, when an aroyl chloride, *e.g.*, α-naphthoyl chloride, is heated with an *equivalent* amount of the iodo complex, approximately equal amounts of α-chloro- and α-iodonaphthalene are formed.

If, then, benzyne is an intermediate in any of these reactions, it would only be formed from the *o*-iodo halides, and for the decarbonylation reaction, a new pathway could be suggested in addition to the one previously proposed[2,10] (Scheme I). However, attempts to identify the halogen molecule (Hal I) by a mass spectrometric method gave no unequivocal results; thus the indicated pathway for the decomposition of the hexacoordinated rhodium compound is not proven.[11]

Scheme I





Experimental Section

Preparation of Aroyl Iodides.—A mixture of 0.1 mol of an aroyl chloride and 0.2 mol of powdered sodium iodide was stirred, with either heating or external cooling, so as to keep the internal temperature at the level indicated in Table I. At the end of the period prescribed in the table, the reaction mixture was extracted with warm hexane or carbon tetrachloride, and the inorganic salts were filtered off. The dark organic solution was shaken with mercury until colorless, filtered, and concentrated. The residue was distilled under diminished pressure and the colorless aroyl iodides so obtained were stored in brown ampoules; however, darkening occurred even so with most of these compounds after a few hours. Before use, the iodides were treated again with mercury and redistilled *in vacuo*. The analytical samples were fractionated shortly before the combustion analysis.

Decarbonylation of Aroyl to Aryl Iodides.—A quantity of 2–10 g of freshly distilled aroyl iodide and 50–100 mg of the rhodium complex (I) were placed in a Claisen flask connected to a vacuum system. The mixture was heated with a free flame, while a suitable vacuum was applied so as to permit distillation of the aryl iodide formed between 175 and 250° within approximately 5 min. Occasionally some iodine was liberated during the decarbonylation. The crude distillate was washed with sodium bisulfite solution and aqueous alkali, neutralized, dried in the usual manner, and redistilled. Identification of the aryl iodides was accomplished by vpc comparison with authentic samples of aryl iodides, prepared by unambiguous routes. The columns used for the chromatography where (a) 20% SE-30 silicon rubber on 30–60 mesh Chromosorb W, (b) Carbowax 20M on 30–60 mesh Chromosorb W. The latter column reacts with aroyl iodides which thus do not appear in the chromatogram.

***o*-Iodobenzoyl Bromide.**—A mixture of 11 g of *o*-iodobenzoic acid and 14 g of phosphorus tribromide was refluxed for 15 min. The dark liquid was decanted while still hot from the solid phase and combined with a hexane extract of the latter. The solvent and excess of the reagent were removed *in vacuo* and the resulting oil was distilled at 138° (2 mm) giving 13.5 g (98%) of a pale yellow product that solidified at room temperature. *Anal.* Calcd for C_7H_4BrIO: Br, 25.7. Found: Br, 26.0.

***o*-Diiodobenzene from *o*-Iodobenzoyl Chloride and Bromide.**—A mixture of 2.66 g of *o*-iodobenzoyl chloride, 1.27 g of iodine, and 0.1 g of the rhodium complex (I) was placed in a Claisen flask preheated at 200° and subjected to distillation (to 280°) during 10 min. The dark distillate was treated with 10% aqueous sodium hydroxide solution and sodium bisulfite solution, and the product (1.2 g) analyzed by gas chromatography. It consisted to the extent of 82% of *o*-diiodobenzene. The yield of pure *o*-diiodobenzene was thus 30%.

In a similar way, 1.55 g of *o*-iodobenzoyl bromide and 0.1 g of I were heated with 0.64 g of iodine, leading to 47% of *o*-diiodobenzene. In neither experiment, was *m*- or *p*-diiodobenzene formed.

Registry No.—*o*-Iodobenzoyl bromide, 16156-39-1; **2,** 16156-40-4; **3,** 16156-41-5; **4,** 6439-74-3; **5,** 16156-43-7; **6,** 16156-44-8; **7,** 16156-45-9; **7,** 16156-46-0; **9,** 16156-47-1; **10,** 16156-48-2.

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[8] D. N. Lawson, J. A. Osborn, J. F. Young, and G. Wilkinson, *J. Chem. Soc., Sect A*, 1711 (1966).

[9] M. A. Bennett and P. A. Longstaff, *Chem. Ind.* (London), 846 (1965).

[10] *Cf.* also the recent paper by M. C. Baird, J. T. Mague, J. Osborn, and G. Wilkinson, *J. Chem. Soc., Sect. A*, 1347 (1967).

[11] One of the referees has suggested an alternative to the above scheme which is equally compatible with the available evidence.