Substantiation of a Radical Mechanism or Mechanisms for Dediazoniation[1] in Alkaline Alcoholic Solvents[2]

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Reductions of benzenediazonium ion to benzene, of *m*-chlorobenzenediazonium ion to chlorobenzene, and of several other diazonium ions have been studied in methyl and *t*-butyl alcohols at various alkoxide concentrations, under various atmospheres, and in the presence of various cosolvents. A mechanism (or mechanisms) involving aryl-radical intermediates is indicated by (a) the adverse effect of oxygen gas on dediazoniation yields, (b) the obtaining of biphenyl derivatives in 50% benzene cosolvent, and (c) improvement of dediazoniation yields in *t*-butyl alcohol solution by adding cosolvents which are good hydrogen donors to radicals. No support is found for a nonradical, intramolecular mechanism suggested by Hantzsch. Some possible radical mechanisms are sketched. The decomposition of methyl *p*-nitrophenylazo ether (1) gives, in addition to nitrobenzene, appreciable yields of 4-nitrobiphenyl when benzene is a cosolvent. A radical mechanism is again indicated.

The decomposition of benzenediazonium salts in methanol solutions was intensively studied by DeTar and coworkers about 10 years ago.[4,5] In neutral or acidic methanol, the principal product was anisole, doubtless formed by an ionic mechanism. But in the presence of sodium acetate the yield of anisole was small, and the main products were benzene and biphenyl.

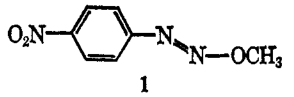
From the pattern of products formed, the pronounced effect of molecular oxygen on both products and reaction rates, and the kinetics both in the presence and absence of oxygen, DeTar reasoned that the reactions under alkaline conditions proceed largely by a radical mechanism. He discussed some possible mechanisms in detail.[4,5]

In this laboratory it has been observed that, contrary to indications in the literature,[6] reactions of diazonium salts with methanol solutions of sodium methoxide afford dediazoniation products in sufficiently good yields to be of preparative interest.[7] In the case of *o*-chlorobenzenediazonium fluoroborate, the mechanism of reaction depends on the sodium methoxide concentration.[8] With 2 *M* $NaOCH_3$ in CH_3OD, the product is >90% chlorobenzene-2-*d*, but when only 1 equiv of sodium methoxide is provided the chlorobenzene obtained is nearly deuterium free.

Similar observations have been made in regard to the reactions of *m*-chlorobenzenediazonium ion with sodium methoxide.[9] However, the results differ somewhat in degree; the product obtained in 2 *M* $NaOCH_3$ in CH_3OD (in the presence of air) is only 78% chlorobenzene-3-*d*.

The formation of deuteriochlorobenzenes in 2 *M* $NaOCH_3$ in CH_3OD indicates the intermediacy of chlorophenyl anions, whereas the formation of deuterium-free chlorobenzene when only 1 equiv of $NaOCH_3$ is provided suggests a mechanism involving chlorophenyl radicals as intermediates. The radical mechanism of DeTar and coworkers comes immediately to mind. However, although their evidence and arguments appeared for the most part to be valid, we hesitated to assign their interpretations directly to our reactions. In particular, the provision of sodium methoxide instead of sodium acetate as a base, even to the extent of only 1 molar equiv, might have allowed a new mechanism to come into play. A candidate for consideration was a mechanism proposed by Hantzsch more than 70 years ago.[10]

Hantzsch[10] observed that *p*-nitrobenzenediazonium sulfate reacted with methanolic sodium methoxide *im Kältegemisch* to form nitrobenzene in exceptional amounts plus a little methyl *p*-nitrophenylazo ether, presumably the *anti* stereoisomer (1). He postulated that the diazonium and methoxide ions coordinated to form a *syn* diazo ether, and that the *syn* diazo ether was unstable and decomposed intramolecularly to form nitrobenzene, formaldehyde, and molecular nitrogen. In modern terminology, the Hantzsch mechanism might be described as a 1,5-hydride shift with concerted fragmentation, as in eq 1. It is obviously compatible with the obtaining of ArH from reactions in CH_3OD solution.



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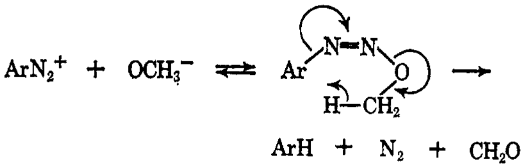

(1)

We therefore applied to reactions of diazonium ions with alkoxides in alcohols a number of tests for a radical mechanism. Were the Hantzsch mechanism the only one followed, no reactions uniquely characteristic of radicals should have been observed.

Dediazoniation Yields in Methanol. Several substituted benzenediazonium fluoroborates were treated both with an equimolar amount of sodium methoxide in methanol and with 2 *M* methanolic sodium methoxide. In all cases there was vigorous gas evolution

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[1] "Dediazoniation" means replacement of a diazonio ($-N_2^+$) group by hydrogen. This process is sometimes loosely and inaccurately referred to as "deamination." "Dediazotization" means reversal of diazotization, $ArN_2^+ \rightarrow ArNH_2$.

[2] Research supported in part by the National Science Foundation.

[3] University of California at Santa Cruz, Santa Cruz, Calif.

[4] D. F. DeTar and M. N. Turetzky, *J. Amer. Chem. Soc.*, **77**, 1745 (1955); **78**, 3925, 3928 (1956).

[5] D. F. DeTar and T. Kosuge, *ibid.*, **80**, 6072 (1958).

[6] *Cf.* N. Kornblum, *Org. Reactions*, **2**, 277 (1944).

[7] J. F. Bunnett, T. G. Andrews, Jr., and J. K. Kim, unpublished observations.

[8] J. F. Bunnett, D. A. R. Happer, and H. Takayama, *Chem. Commun.*, 367 (1966); J. F. Bunnett and D. A. R. Happer, *J. Org. Chem.*, **32**, 2701 (1967).

[9] J. F. Bunnett and H. Takayama, unpublished observations.

[10] A. Hantzsch, *Ber.*, **27**, 2968 (1894).

upon mixing or immediately thereafter, at room temperature. Yields of dediazoniation products as determined by gas–liquid partition chromatography are listed in Table I. It is noteworthy that in every case a better yield was obtained in 2 *M* $NaOCH_3$.

TABLE I

YIELDS OF ArH FROM $ArN_2^+ BF_4^-$ + $NaOCH_3$ IN CH_3OH

Ar in ArN_2^+	Yield of ArH, % 1 equiv of $NaOCH_3$[a]	 2 *M* $NaOCH_3$[b]
C_6H_5–	62	81
p-$CH_3C_6H_4$–	72	74
o-ClC_6H_4–	70	81
m-ClC_6H_4–	63	77
p-ClC_6H_4–	74	82
p-$NO_2C_6H_4$–	73	81

[a] Substrate (0.001 mol) + $NaOCH_3$ (0.001 mol) in 10 ml of CH_3OH. [b] Substrate (0.001 mol) in 10 ml of 2 *M* $NaOCH_3$ in CH_3OH.

Dediazoniation Yields in Other Solvents.—It was expected that dediazoniation would occur less satisfactorily in *t*-butyl alcohol than in methanol, regardless of whether the Hantzsch or a radical mechanism prevailed. The concerted shifts shown in eq 1 require an α hydrogen in the alkoxy group. On the other hand, radicals are known to abstract hydrogen α to a hydroxy group far more readily than β hydrogens.[11]

Our expectation was borne out by experiments summarized in Table II. In *t*-butyl alcohol, yields of benzene from benzenediazonium ion and of chlorobenzene from *m*-chlorobenzenediazonium ion were all less than 24%, and often much less, depending somewhat on the base concentration and the atmosphere above the reaction mixture.

In most of the experiments of Table II, only the dediazoniation product was sought. However, in two experiments efforts were made to find biphenyl derivatives which might result from dimerization of aryl radicals. As indicated, these were obtained from both diazonium salts, though in low yield. In both cases, more than half of the aryl groups in the diazonium salts were incorporated into high molecular weight products of uncertain constitution.

If aryl radicals are generated in the *t*-butoxide–*t*-butyl alcohol system, the yield of dediazoniation product should increase on addition of solvent constituents which are good hydrogen donors to radicals. This requirement was satisfied by a number of experiments in Table II. The yield increased two- to threefold when methanol, cumene, or any of several aliphatic ethers constituted half of the solvent.

Most of the experiments of Table II were run in the usual air atmosphere of the laboratory. A few were run in a nitrogen atmosphere. The dediazoniation yields under nitrogen were somewhat depressed in one case where a comparison can be made and unaffected in the other.

Though consistent with a radical mechanism, the experiments of Table II are not grounds for rejecting the Hantzsch mechanism. Except for the experiment with methanol present, the Hantzsch mechanism was precluded by the structures of the reactants. Perhaps an ordinarily less favored radical mechanism was thereby allowed to predominate.

A further problem is that the ethers employed as cosolvents in several experiments conceivably donate hydride ions to diazonium ions, forming aryldiimides.[12] Although phenyldiimide may itself be a radical source,[13,14] ionic mechanisms for its decomposition in basic media have been proposed,[13,14] and an intramolecular transformation to form benzene and nitrogen is possible.[13] Thus wholly nonradical mechanisms for reactions with the ethers are conceivable, but they are improbable because the concentration of free diazonium ions in the presence of an equal or greater amount of *t*-butoxide ion is probably very small.

Reactions in the Presence of Benzene.—Aryl radicals are known to arylate benzene, forming biphenyl derivatives.[11a] Therefore dediazoniation in a benzene-rich solution should afford biphenyl derivatives as well as the usual reduction products, but, if the whole reaction occurs by the Hantzsch mechanism, no biphenyl derivative should be formed.

In the event, reaction of *m*-chlorobenzenediazonium fluoroborate with 1 molar equiv of sodium methoxide in 50% benzene–50% methanol (v/v) under air gave 31% of 3-chlorobiphenyl[15] as well as 27% of chlorobenzene. This experiment shows that a major fraction of the reaction occurs by a radical mechanism.

The reaction of *m*-chlorobenzenediazonium fluoroborate with 1 equiv of potassium *t*-butoxide in 50% benzene–50% *t*-butyl alcohol was also investigated. The identified products were 3-chlorobiphenyl (20%), chlorobenzene (8%), and 3,3′-dichlorobiphenyl (1.2%). This experiment is further testimony that aryl radicals are generated in that system.

Reactions in the Presence of Oxygen.—In high concentrations, molecular oxygen often interferes with radical reactions. It may combine with radicals to interrupt a chain reaction sequence, or to form different ultimate products.

It was therefore expected that radical dediazoniation should be sensitive to oxygen in the system. In fact, reaction of *m*-chlorobenzenediazonium fluoroborate with an equimolar amount of sodium methoxide in methanol continuously bubbled with oxygen gas gave only 25% of chlorobenzene (26% in a duplicate run). This compares with 63% under air (Table I).[16]

On the other hand, dediazoniation *via* aryl anions, which is the predominate mode of reaction of *m*-chlorobenzenediazonium ion in 2 *M* $NaOCH_3$ (*vide supra*), should be less sensitive to oxygen. In fact, the yield of

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[11] (a) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp 480–482; (b) W. T. Dixon and R. O. C. Norman, *J. Chem. Soc.*, 3119 (1963).

[12] H. Meerwein, H. Allendörfer, P. Beekmann, F. Kunert, H. Morschel, F. Pawellek, and K. Wunderlich, *Angew. Chem.*, **70**, 211 (1958).

[13] S. G. Cohen and J. Nicholson, *J. Org. Chem.*, **30**, 1162 (1965).

[14] E. M. Kosower and P. C. Huang, *J. Amer. Chem. Soc.*, **87**, 4645 (1965); **89**, 3910 (1967).

[15] DeTar and Turetzky[4] reported that addition of benzene to the methanol solvent caused no increase in the yield of biphenyl from benzenediazonium ion in the presence of sodium acetate. This result was correctly interpreted as evidence that phenylation of benzene was not the origin of the biphenyl produced in their experiments. Actually, they provided not more than 1 benzene molecule per 110 molecules of methanol; appreciable phenylation of the benzene would have been observed only if benzene were much more reactive than methanol toward phenyl radicals. In contrast, our experiment provided 1 benzene molecule per 2.2 methanol molecules. There is no inconsistency between their observations and ours.

[16] Inasmuch as nitrogen is evolved copiously during reaction, runs "under air" are considerably flushed by autogenous nitrogen. Oxygen is thus made less available than would otherwise be the case.

TABLE II

REACTIONS OF $ArN_2^+ BF_4^-$ WITH $K^+ (CH_3)_3CO^-$ IN VARIOUS SOLVENTS[a]

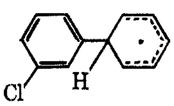
ArN_2^+	Molar ratio of $(CH_3)_3COK$ to ArN_2^+	Solvent (v/v)	Atmosphere	ArH yield, %[b]	Other products
$C_6H_5N_2^+$	1.0	$(CH_3)_3COH$	Air	18; 23[c]	Biphenyl (12%)[d]
	1.0	$(CH_3)_3COH$	N_2	12; 13	
	1.0	CH_3OH, 50% $(CH_3)_3COH$, 50%	Air	42	
	1.0	$(C_2H_5)_2O$, 50% $(CH_3)_3COH$, 50%	Air	46; 50	
	1.0	$(C_2H_5)_2O$, 50% $(CH_3)_3COH$, 50%	N_2	49; 49[e]	
	1.0	Dioxane, 50% $(CH_3)_3COH$, 50%	Air	38	
	1.0	$(CH_3OCH_2CH_2)_2O$, 50% $(CH_3)_3COH$, 50%	Air	48	
	1.0	$CH_2(OCH_3)_2$, 50% $(CH_3)_3COH$, 50%	Air	39	
	1.0	Cumene, 50% $(CH_3)_3COH$, 50%	N_2	27; 27	
	5.0	$(CH_3)_3COH$	Air	5	
	5.0	$(C_2H_5)_2O$, 50% $(CH_3)_3COH$, 50%	Air	19	
	10.0	$(CH_3)_3COH$	Air	4	
m-$ClC_6H_4N_2^+$	1.0	$(CH_3)_3COH$	Air	11; 14	3,3′-ClC_6H_4-C_6H_4Cl (2.3%)[d]
	5.0	$(C_2H_5)_2O$, 50% $(CH_3)_3COH$, 50%	Air	20	
	10.0	$(CH_3)_3COH$	Air	2; 2	

[a] Substrate (0.001 mol), $(CH_3)_3CO^- K^+$ as indicated, and 10 ml of indicated solvent in all experiments. [b] Duplicate entries represent duplicate runs. [c] A run with 18 mg of added H_2O gave 23% benzene. [d] Experiments for determination of biphenyl derivatives involved 0.01 mol of substrate and 0.01 mol of $(CH_3)_3CO^- K^+$ in 10 ml of *t*-butyl alcohol. [e] A run with 169 mg of added diphenylamine gave 46% benzene.

chlorobenzene from an oxygen-bubbled reaction was 77%, the same as under air.[16]

The effect of oxygen on reactions of *m*-chlorobenzenediazonium ion with 1 molar equiv of methoxide ion in 50% benzene–50% methanol was also investigated. With oxygen bubbling, 23% of chlorobenzene and 25% of 3-chlorobiphenyl were formed. Under air, the yields were 27 and 31%, respectively, as reported above. With nitrogen bubbling, yields of 40 and 23%, respectively, were obtained.

Thus the more oxygen in the system, the lower is the yield of chlorobenzene, much as in the absence of benzene. The effect of oxygen on the yield of 3-chlorobiphenyl is irregular and of smaller magnitude. In the latter case, oxygen can affect the yield in two ways. By intercepting aryl radicals and diverting them to oxygen compounds, it can diminish the yield. But by oxidizing *m*-chlorophenylcyclohexadienyl radicals (2)[17] to 3-chlorobiphenyl, in competition with their dimerization and other reactions, it can increase the yield.[18] The two effects nearly balance each other.



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Mechanisms of Dediazoniation.—Both the interference by molecular oxygen and the obtaining of a biphenyl derivative in the presence of benzene indicate radical intermediates in the reactions of diazonium salts with equimolar amounts of sodium methoxide in methanol. In *t*-butyl alcohol, the obtaining of a biphenyl derivative in the presence of benzene and the increase in dediazoniation yield on addition of good hydrogen donors also support a radical mechanism.

The Dediazoniation Mechanism in Methanol.—It is clear that the Hantzsch mechanism is not the only one in operation under the conditions investigated. However, it is not possible to dismiss the Hantzsch mechanism altogether. Although no evidence requiring it has been found, the possibility remains that a small fraction of dediazoniation in methanol occurs by the Hantzsch mechanism.

The next question is what kind of radical mechanism is followed. DeTar and Turetzky[4] proposed a chain mechanism for dediazoniation in acetate-buffered methanol. Its essential chain-propagating steps are illustrated in eq 2 and 3.

$$C_6H_5\cdot + CH_3OH \longrightarrow C_6H_6 + \cdot CH_2OH \qquad (2)$$

$$C_6H_5N_2^+ + \cdot CH_2OH \longrightarrow C_6H_5\cdot + N_2 + CH_2OH^+ \qquad (3)$$

Equation 3 involves electron transfer from the $\cdot CH_2OH$ radical to the diazonium ion with concerted homolysis of the C–N bond.

In our opinion, a modified version of the DeTar–Turetzky mechanism is more probable in basic solutions. In place of eq 3, we suggest eq 4 and 5.

$$\cdot CH_2OH + CH_3O^- \rightleftarrows \cdot CH_2O^- + CH_3OH \qquad (4)$$

$$\cdot CH_2O^- + C_6H_5N_2^+ \longrightarrow C_6H_5\cdot + N_2 + CH_2O \qquad (5)$$

Equation 4 is a proton (or hydrogen atom) transfer reaction which transforms the hydroxymethyl radical into its conjugate base, which may be viewed alternatively as the radical anion that would result from addition of an electron to formaldehyde. Equation 5 involves electron transfer and C–N bond homolysis, and is analogous to eq 3. We have no evidence as to

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[17] D. F. DeTar and R. A. J. Long, *J. Amer. Chem. Soc.*, **80**, 4742 (1958).

[18] E. L. Eliel, S. Meyerson, Z. Welvart, and S. H. Wilen, *ibid.*, **82**, 2936 (1960).

TABLE III

DECOMPOSITION OF METHYL *p*-NITROPHENYLAZO ETHER IN VARIOUS MEDIA

Solvent	Base concn, *M*	Reaction time, min	Yield of $C_6H_5NO_2$, %	Yield of *p*-$O_2NC_6H_4C_6H_5$, %
CH_3OH	Nil	10	76	
CH_3OH	CH_3ONa, 0.1 M	5	83	
CH_3OH	CH_3ONa, 2.0 M	5	85	
$(CH_3)_3COH$	Nil	10	12	
$(CH_3)_3COH$	$(CH_3)_3COK$, 0.5 M	10	38	
$(CH_3)_3COH$	$(CH_3)_3COK$, 1.0 M	10	43	
CH_3OH, 50%; benzene, 50%	Nil	10	18	26
$(CH_3)_3COH$, 50%; benzene, 50%	Nil	15	6	13
$(CH_3)_3COH$, 50%; benzene, 50%	$(CH_3)_3COK$, 0.5 M	10	17	36
Benzene	Nil	15	3	37
$(C_2H_5)_2O$	$(CH_3)_3COK$, 0.1 M	5	61	
Hexane	Pyridine, 0.1 M	90	8[a]	

[a] Much of **1** appeared to remain unreacted.

whether electron transfer may be concerted with C–N homolysis, or whether alternatively the phenylazo radical ($C_6H_5N_2\cdot$) may be a transitory intermediate.

In view of indications that α-hydroxyalkyl radicals ($R_2\dot{C}$–OH) are stronger acids than their parent alcohols (R_2CHOH),[19] eq 4 probably lies appreciably to the right in basic methanol solutions. The formaldehyde radical anion (eq 5) is surely a better electron donor to a diazonium ion than is the hydroxymethyl radical (eq 3). Electron transfer from $\cdot CH_2O^-$ to aryl iodides is implicated as a key step in the radical-induced deiodination of aryl iodides in alkaline methanol.[20]

A radical chain mechanism involving eq 2, 4, and 5 as the chain-propagating cycle would be strongly favored by an increase in the basicity of the medium because eq 4 would be shifted to the right. However, with chlorine-substituted benzenediazonium ions, very high methoxide ion concentrations perhaps suppress the radical-chain mechanism by converting nearly all the diazonium salt into a covalent diazo ether, which should be less prone to accept electrons from $\cdot CH_2O^-$. Alternative ionic mechanisms would thereby be allowed to operate.[21]

Much less probable as a radical mechanism for dediazoniation in methanol is one fashioned after the Rüchardt–Merz mechanism for the Bachmann–Gomberg reaction.[22] The modified mechanism (except for termination steps) is as shown in eq 6. This mechanism requires water in eq 6a, or the generation of diazotate ($ArN{=}NO^-$) ions by some other means. However, we have found in other work[9] that the rate of decomposition of *o*-chlorobenzenediazonium ion in 0.1 *M* $NaOCH_3$ is augmented only to the extent of about 50% on addition of 4.5% (v/v) of water to the otherwise anhydrous medium.

$$ArN_2^+ + H_2O + 2RO^- \rightleftharpoons ArN{=}NO^- + 2ROH \qquad (6a)$$

$$ArN_2^+ + ArN{=}N{-}O^- \rightleftharpoons ArN{=}NON{=}NAr \qquad (6b)$$

$$ArN{=}NON{=}N{-}Ar \longrightarrow Ar\cdot + N_2 + ArN{=}NO\cdot \qquad (6c)$$

$$Ar\cdot + CH_3OH \longrightarrow ArH + \cdot CH_2OH \qquad (6d)$$

$$\cdot CH_2OH + CH_3O^- \rightleftharpoons \cdot CH_2O^- + CH_3OH \qquad (6e)$$

$$\cdot CH_2O^- + ArN{=}NO\cdot \longrightarrow CH_2O + ArN{=}NO^- \qquad (6f)$$

A third type of radical mechanism has been mentioned above: hydride ion capture by the diazonium ion from some suitable donor and radical decomposition of the resulting aryldiimide.

The Dediazoniation Mechanism in *t*-Butyl Alcohol.—In this solvent, eq 7a and 7b are a conceivable alternative to eq 6a. Both E1 and E2 mechanisms for eq 7b are conceivable. In view of the impossibility of a sequence such as steps 2, 4, and 5 in *t*-butyl alcohol, and of the feasibility of the sequence of steps 7a, 7b, 6b, and 6c, the latter deserves serious consideration. However, it is not evident what steps follow generation of the aryl radical. The fact that dediazoniation yields are poor in *t*-butyl alcohol solution, and that large amounts of high molecular weight by-products are formed, is consistent with this and other mechanisms involving aryl radical intermediates.

$$ArN_2^+ + (CH_3)_3CO^- \rightleftharpoons ArN{=}NOC(CH_3)_3 \qquad (7a)$$

$$ArN{=}NOC(CH_3)_3 + (CH_3)_3CO^- \longrightarrow ArN{=}NO^- + (CH_3)_2C{=}CH_2 + (CH_3)_3COH \qquad (7b)$$

Reduction of Methyl *p*-Nitrophenylazo Ether (1).—Compound **1**, mp 82–83°, was synthesized by methylation of silver *p*-nitrobenzeneisodiazotate.[23] It was decomposed by heating it in a number of solvents, with or without added bases. Results are displayed in Table III. In no case was there noticeable gas evolution until the solution was heated. In general, the heated reaction mixtures were dark red.

High yields of nitrobenzene were obtained in methanol, either without added base or at low or high sodium methoxide concentration.[24] In *t*-butyl alcohol, yields of nitrobenzene were lower, but they increased with an increase in *t*-butoxide ion concentration.

When benzene was present as a cosolvent with either alcohol, *p*-nitrobiphenyl was obtained in substantial amount. In *t*-butyl alcohol–benzene mixtures, the yield of *p*-nitrobiphenyl was increased by addition of 0.5 *M* potassium *t*-butoxide.

The evidence available thus indicates radical mechanism(s) for these reactions of **1**. Dissociation of **1** to form *p*-nitrobenzenediazonium ion, followed by dedia-

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[19] G. Porter and F. Wilkinson, *Trans. Faraday Soc.*, **57**, 1686 (1961); W. V. Sherman, *J. Amer. Chem. Soc.*, **89**, 1302 (1967).

[20] J. F. Bunnett and C. C. Wamser, *ibid.*, **89**, 6712 (1967).

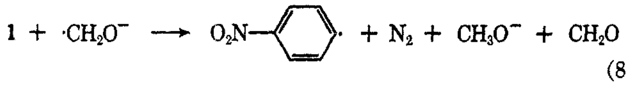
[21] An interesting possibility is that the original DeTar–Turetzky mechanism involving steps 2 and 3 does indeed operate in neutral and acidic media,[5] in which very little $\cdot CH_2OH$ would be converted into $\cdot CH_2O^-$, providing that electron-attracting substituents are present to facilitate electron transfer and providing that the medium is oxygen free. (Oxygen might capture radicals needed for chain propagation.) In the presence of oxygen, the radical mechanism might be sufficiently repressed to let the ionic mechanism which forms anisole derivatives predominate.

[22] C. Rüchart and E. Merz, *Tetrahedron Lett.*, 2431 (1964).

[23] H. v. Pechmann and L. Frobenius, *Ber.*, **27**, 672 (1894).

[24] Reactions of **1** with methanol and with sodium methoxide in methanol have also been studied by W. D. Gurowitz (Ph.D. Thesis, Purdue University, Lafayette, Ind., 1958).

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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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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