154. Decomposition of Aryldiazonium Ions in Homogenous Solutions
Part II: Arylations with Benzenediazonium Ions and *p*-Nitrobenzenediazonium Ions in Dimethyl Sulfoxide¹)

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Dedicated to Professor *P. D. Bartlett*, Harvard University, for his 65th birthday

(22 II 72)

Summary. When *p*-nitrobenzenediazonium tetrafluoroborate is decomposed in the presence of dimethyl sulfoxide/benzene or dimethyl sulfoxide/nitrobenzene systems under nitrogen, the respective biphenyl derivatives are obtained in good yield. With benzenediazonium tetrafluoroborate in the same systems the yields are low. The influence of oxygen, iodine, iodobenzene and N, N-diphenylhydroxylamine on the products of the reactions were determined. The by-products, isomer distribution with nitrobenzene as a substrate, and the partial and total rate factors were also determined. From the above data it can be shown that the reaction with *p*-nitrobenzenediazonium salt is a homolytic process and that with the unsubstituted benzenediazonium salt is essentially a heterolytic reaction. The problem of the mechanism of the radical forming steps (electron transfer or adduct formation) and the mechanistic relationship to other modes of arylation (aroylperoxide, classical two-phase *Gomberg-Bachmann* reaction, catalysis by transition metal ions, nitrite ions, etc. electron transfer properties of DMSO) are discussed.

1. Introduction. – The mechanism of the thermal decomposition of aryldiazonium salts has been the subject of a variety of investigations in recent years, e.g. [1–7]. In contrast to earlier investigations, the major emphasis has been on reactions in homogeneous systems.

The purpose of our investigation originally was to improve the yields of arylation products resulting when diazonium ions were the arylating reagents. Usually the yields in *Gomberg-Bachmann* arylations are relatively low, even if one uses *Hey*'s modification (addition of sodium acetate) [8], possibly due to the two-phase system used. We hoped to improve the yield by substituting the aqueous phase by a polar solvent in which diazonium salts as well as the substrate, i.e. the aromatic compound to be arylated, were very soluble. Indeed, we found [1] that in dimethyl sulfoxide (DMSO), the yield of the reactions of *p*-nitrobenzenediazonium tetrafluoroborate with benzene and with nitrobenzene increased by 10 to 20 per cent. In addition, that investigation gave an unexpected, mechanistically interesting result: The isomer ratios for the reactions with nitrobenzene indicated a homolytic decomposition for the *p*-nitrobenzenediazonium salt. Using the unsubstituted benzenediazonium salt, however, a mixture of 2-, 3-, and 4-nitrobiphenyl isomers were obtained, indicating at least a partially or krypto-heterolytic mechanism with an electrophilic phenylating reagent.

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¹) Part I see [1]. Presented in part at the Post-ISNA-Symposium on Free Radicals in Tokyo, August 30th, 1970, and at the Murphy Award Symposium, ACS Meeting, Boston, April 11th, 1972.

The latter conclusion was based only on the isomer ratios of products obtained in low yield (6 to 8%), whereas the yield with *p*-nitrobenzenediazonium salt was 55–61%. Therefore, it was necessary to supplement and improve the conclusions by additional evidence given in this paper.

2. Result and Discussion

2.1. *Reactions under Nitrogen.* The reaction conditions, yields, and the ratios of the isomeric products of our experiments are summarized in Tables 1 and 2, together with related results from other workers in this field.

Table 1. *Arylations with* p-*nitrophenyl arylating reagents*

Authors	Arylating reagent	Substrate	Solvent	Additives etc.	Temp. °C	yield	Isomer ratio		
							o	m	p
This paper	$p\text{-}NO_2C_6H_4N_2BF_4$	C_6H_6	DMSO	N_2	50	62–68	–	–	–
This paper	$p\text{-}NO_2C_6H_4N_2BF_4$	C_6H_6	DMSO	Air	50	35–38	–	–	–
This paper	$p\text{-}NO_2C_6H_4N_2BF_4$	$C_6H_5NO_2$	DMSO	N_2	50	55–61	65.3	9.5	25.2
This paper	$p\text{-}NO_2C_6H_4N_2BF_4$	$C_6H_5NO_2$	DMSO	Air	50	41–42	63.2	10.5	27.3
This paper	$p\text{-}NO_2C_6H_4N_2BF_4$	$C_6H_5NO_2$	DMSO	N_2	80	56	55.0	15.8	29.2
De Tar et al. [9]	$p\text{-}NO_2C_6H_4N_2^{\oplus}$	$C_6H_5NO_2$	H_2O	NaOAc	5–10	26.2	34 ± 5	23 ± 3	43 ± 3
Hambling et al. [10]	$(p\text{-}NO_2C_6H_4COO)_2$	$C_6H_5NO_2$	$C_6H_5NO_2$	Air	80	67	58	15	27
This paper	$(p\text{-}NO_2C_6H_4COO)_2$	$C_6H_5NO_2$	DMSO	N_2	80	0	–	–	–

At 80° the *p*-nitrophenylation of nitrobenzene (Table 1) gave a slightly lower yield but essentially the same isomer distribution as *Hambling et al.* [10] obtained using di-*p*-nitrobenzoyl peroxide as the radical source at the same temperature.

At 50° the selectivity for substitution in *o*- and *p*-positions of nitrobenzene, typical of a homolytic reaction, is increased. These isomer ratios, however, do not give evidence for or against the electrophilicity of *p*-nitrophenyl radicals as postulated by several authors [11]: If we compare our results in the arylation of nitrobenzene by the *p*-nitrobenzenediazonium ion with those which *Gadallah & Elofson* [12] obtained by the unsubstituted phenyl radical, polarographically generated from benzenediazonium salt in acetonitrile at −5°, one expects more substitution in *m*-position of nitrobenzene for our system, if the postulated electrophilicity is a dominant effect. In fact, we obtained at 50° less, and at 80° the same percentage of *m*-substitution. Similar ratios of less and more *m*-product exist when our data are compared with those of *Abramovitch & Saha* [13] for the phenylation of nitrobenzene at 75° with phenyl radicals formed in a solution of benzenediazonium salt in pyridine. On the other hand, *Kobayashi et al.* [6] found only 5.4% *m*-product in the phenylation of nitrobenzene in DMSO at 10°, generating the phenyl radicals with nitrite ions. Due to the difference in solvent and/or temperature, no accurate comparison of our data with the literature data is possible.

Our conclusion with respect to the mechanism of the phenylations with (unsubstituted) *benzenediazonium* salt in DMSO is restricted by the low yields of phenyla-

Table 2. *Arylations with phenyl arylation reagents*

Authors	Arylating reagent	Substrate	Solvent	Additives, etc.	Temp. °C	Yield	Isomer ratio		
							o	m	p
This paper	$C_6H_5N_2BF_4$	C_6H_6	DMSO	N_2	50	17–20	–	–	–
This paper	$C_6H_5N_2BF_4$	C_6H_6	DMSO	Air	50	15–16	–	–	–
This paper	$C_6H_5N_2BF_4$	$C_6H_5NO_2$	DMSO	N_2	50	7–8	29.0	55.0	16.0
This paper	$C_6H_5N_2BF_4$	$C_6H_5NO_2$	DMSO	Air	50	6–7	28.5	55.5	16.0
This paper	$C_6H_5N_2BF_4$	$C_6H_5NO_2$	DMSO	DPHA[a]/$CaCO_3$ Air	50	8.7	43.4	37.0	19.6
This paper	$C_6H_5N_2BF_4$	$C_6H_6 + C_6H_5NO_2$	DMSO	DPHA/$CaCO_3$ Air	50	15 ($C_{12}H_{10}$) 13 ($C_{12}H_9NO_2$)	–	–	–
Kobayashi et al. [15]	$C_6H_5N_2BF_4$	$C_6H_5NO_2$	DMSO	[b]	40	7	37.3 ± 1	49.3 ± 1	13.4
Kobayashi et al. [6]	$C_6H_5N_2BF_4$	$C_6H_5NO_2$	DMSO	$NaNO_2, N_2$	10	76	67.8	5.4	26.9
Kobayashi et al. [15]	$C_6H_5N_2BF_4$	$C_6H_5NO_2$	CH_3CN	[b]	40	–	30.7 ± 2	50.1 ± 2	19.2 ± 3
Abramovitch et al. [3]	$C_6H_5N_2BF_4$	$C_6H_5NO_2$	CH_3CN	[b]	65	2.6	25.4	59.3	15.3
Abramovitch et al. [3]	$C_6H_5N_2BF_4$	$C_6H_5NO_2$	$C_6H_5NO_2$	[b]	65	5.2	24.5	57.5	17.9
Cooper et al. [4]	$C_6H_5N_2BF_4$	$C_6H_5NO_2$	$C_6H_5NO_2$	N_2	20	6	21	58	21
Abramovitch et al. [13]	$C_6H_5N_2BF_4$	$C_6H_5NO_2$	C_5H_5N	[b]	75	30–40	52.6	14.2	33.2
Gadallah et al. [12]	$C_6H_5N_2BF_4$	$C_6H_5NO_2$	CH_3CN	Polarography, N_2	0	14	59	16.9	24.3
Williams [16]	$C_6H_5N_2^{\oplus}$	$C_6H_5NO_2$	H_2O	$^{\ominus}OH, N_2$	0	39–53	58 ± 4	10 ± 2	32 ± 2
Cooper et al. [4]	$C_6H_5N_2BF_4$	$C_6H_5NO_2$	$C_6H_5NO_2$	DPHA/$CaCO_3$, N_2	20	26–42	57.5	15.2	27.3
Hey et al. [17]	$(C_6H_5COO)_2$	$C_6H_5NO_2$	$C_6H_5NO_2$	[b]	80	61	62.5	9.8	27.7

[a] DPHA = N, N-Diphenylhydroxylamine

[b] If reaction was carried out in presence or absence of oxygen, is not stated in ref.

tion products with benzene (17–20%) and with nitrobenzene (7–8%) (Table 2). The yields are, however, higher than those found by *Abramovitch* & *Gadallah* [3] in acetonitrile, whereas the isomer ratio is the same within experimental error. In our preliminary paper [1] we concluded, as did *Abramovitch* & *Gadallah* [3] that the isomer ratio indicated an electrophilic substitution by a phenyl cation.

The percentage of *o*- and *p*-isomer is, however, remarkably high for our electrophilic substitution in nitrobenzene (29 and 16%, respectively). This may be due to:

a) the extremely high reactivity of the phenyl cation formed²) which implies a correspondingly low positional and substrate selectivity, or
b) to a superposition of a homolytic phenylation together with the electrophilic substitution³), or
c) diradical type properties of the phenyl cation.

Several authors [3] [15] [18] prefer the last explanation. Following the recent EHMO calculation of *Gleiter et al.* [19] it is improbable however, that the phenyl cation has diradical character.

Alternative (b) may operate in DMSO by analogy with the homolytic decomposition induced by pyridine [13] [20]: DMSO has electron donating properties comparable with pyridine, as seen from the equilibrium constants for complex formation with iodine molecules (Table 3). At least for the solution of *p*-nitrobenzenediazonium ions in DMSO the electronic spectra clearly prove the stability of the charge transfer complexes with DMSO [24]. Therefore, the possibility has to be considered that DMSO functions as a reducing reagent for diazonium salts forming phenyl radicals. Such a mechanism may be indicated by the observation (see Table 2) that the percentage of *m*-product is slightly larger in acetonitrile (59.3%, see Table 2) than in DMSO (55.0%). The amount of *m*-product parallels the weaker electron donating properties of acetonitrile (Table 3).

Table 3. *Equilibrium constants of complexes of iodine molecules with aprotic polar solvents (25°)*

Solvent	pyridine	DMSO	CH_3CN
K (M^{-1})	101	11.3	0.42
ref.	[21]	[22]	[23]

Therefore, a more detailed investigation of these arylations in DMSO seemed to be necessary. In the following paragraphs we discuss our results under radical trapping conditions (reactions in the presence of oxygen, addition of iodine and iodobenzene) and the partial and total rate factors in competitive reactions with benzene/nitrobenzene/DMSO mixtures.

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²) The same argument applies also to a concerted substitution of the diazo group of benzenediazonium ion by the nucleophilic substrate, a mechanism analogous to that suggested for the hydrolysis of aryldiazonium ions by *E. S. Lewis et al.* [14].

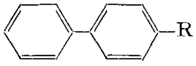
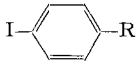
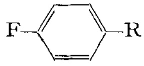
³) The alternative of a uniform mechanism with an electrophilic phenyl radical can definitely be excluded as it has been shown [3] that, if electrophilicity of aryl radicals has to be considered at all, it can be found with polarized aryl radicals containing electron attracting groups (e.g. *p*-NO_2). As discussed above, in our system the electrophilicity even of the *p*-nitrophenyl radical cannot be observed with certainty.

2.2. *Reactions Conducted under Air.* The results of arylation conducted under an air atmosphere are included in Tables 1 and 2: In the *p-nitrophenylation*, the yield decreased but the isomer ratio did not change. This result is consistent with a homolytic mechanism in which oxygen acts as a radical scavenger [25].

For the *phenylation* reaction the yield decreased also, but only to a smaller degree. If this should indicate a partial formation of biphenyl products by a homolytic process, there should be a changed isomer ratio (lower *o/p*- and higher *m*-percentages). This, however, is not the case. A two pathway mechanism as well as a biradical-type phenyl cation is, therefore, highly unlikely.

2.3. *The Influence of Iodine and Iodobenzene.* Elementary iodine is a known radical scavenger [2b]; it does not react with phenyl cations [27]. In the presence of iodine, *p*-nitroiodobenzene was formed in the system *p*-nitrobenzenediazonium tetrafluoroborate/benzene/DMSO and the yield of 4-nitrobiphenyl decreased (Table 4). In the corresponding reaction with benzenediazonium salt, the yield of biphenyl decreased, too, but little iodobenzene was formed. The iodobenzene must be produced from the benzenediazonium salt because a blank experiment, under our reaction conditions, has shown that iodine does not react with benzene in an electrophilic substitution.

Table 4. *Influence of iodine on the* p-*nitrophenylation and the phenylation of benzene in DMSO at 50°*

Diazonium salt	Total yield[a]			
$C_6H_5N_2^{\oplus}BF_4^{\ominus}$	10.1% (18.5%)	84.4%[b]	15.6%[b]	–[d]
p-$NO_2C_6H_4N_2^{\oplus}BF_4^{\ominus}$	41.8% (65%)	14.6%[c]	80%[c]	5.4%[c]

[a] In brackets: Yield without iodine; [b] R = H; [c] R = NO_2; [d] Not determined

Since iodine forms a charge transfer complex with DMSO [22] (Table 3), it may cause an induced electron transfer to the diazonium ion similar to that suggested for the influence of iodide ions on *Pschorr* reactions [28] and on the interaction between iodide ions with peroxides [29]. The iodine molecule in the charge transfer is probably polarized:

$$\mathrm{DMSO} \rightarrow \overset{\delta\oplus}{\mathrm{I}} \rightarrow \overset{\delta\ominus}{\mathrm{I}}$$

Such an effect may cause the formation of phenyl radicals which finally yield iodobenzene. This hypothesis is also supported by kinetic measurements of the disappearance of *p*-nitrobenzenediazonium tetrafluoroborate in benzene/DMSO mixtures. As we intend to report in a later paper, the addition of $10^{-3}M$ I_2 increases the rate by a factor of about 16.

Bunnett et al. [30] and *Cadogan et al.* [31] found that iodobenzene is able to form aryliodides with aryl radicals generated from aroyl peroxides and N-nitrosoacetanilides. Therefore, we used this probe to investigate for aryl radicals generated from our *p*-nitrobenzenediazonium salt systems[4]). Table 5 gives the results for two different iodobenzene/benzene ratios.

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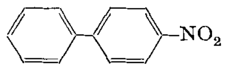
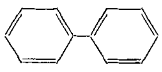
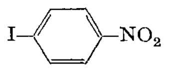
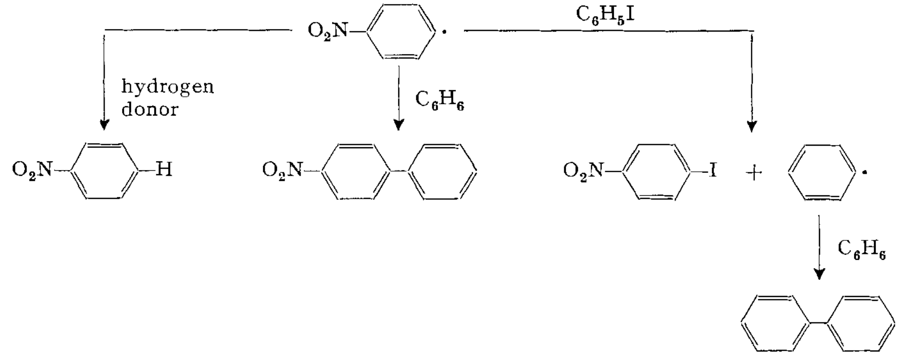
[4]) For obvious reasons it can not be applied to the reaction with benzenediazonium salt (except if iodobenzene or the benzenediazonium salt were labelled by deuterium, ^{14}C, etc.).

Table 5. *Reaction products in the system* p-*nitrobenzenediazonium salt/iodobenzene/benzene/DMSO at 50°*

Molar ratio iodobenzene: benzene	Total yield[a]			
1:26.2	87.5%	60.0%	9.6%	30.4%
1: 8.4	24.4%	40.1%	6.7%	53.2%

[a] Relative to diazonium salt.

If iodobenzene is a perfect scavenger for *p*-nitrophenyl radicals and the phenyl radicals formed from iodobenzene react either with benzene in a homolytic substitution or in a recombination reaction with another *p*-nitrophenyl radical, one expects the products to be *p*-iodonitrobenzene, 4-nitrobiphenyl, and biphenyl. Assuming *Bunnett*'s [30] mechanism (1a) for the reaction of *p*-nitrophenyl radicals, one expects equal amounts of *p*-nitroiodobenzene and biphenyl. This however is not the case. The reason may be that no suitable hydrogen abstracting species for the phenylcyclohexadiene radical is present in this system (in contrast to *Bunnett*'s and *Cadogan*'s systems) or that a recombination with *p*-nitrophenyl radicals forming 4-nitrobiphenyl occurs. Although recombination reactions in solutions of diazonium salts are known [32], it seems rather unlikely that such reactions take place in our systems. We could not find 4,4'-dinitrobiphenyl in these reactions nor a significantly higher percentage of this compound in the *p*-nitrophenylation of nitrobenzene than that expected by the usual *o*/*m*/*p*-ratios (Table 1).



(a)

Obviously there is not a good hydrogen donor present in our system since we find no nitrobenzene or benzene. This is astonishing since is it known that aryl radicals abstract hydrogen from DMSO [33][5]).

2.4. *Addition of N,N-Diphenylhydroxylamine. Cooper & Perkins* [4] found that N,N-diphenylhydroxylamine induces the formation of phenyl radicals from benzenediazonium tetrafluoroborate in nitrobenzene and in acetophenone. These reactions gave the isomeric nitrobiphenyls in fairly good yield (26–42%) and in a ratio which is

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[5]) In the decomposition *p*-nitrobenzenediazonium tetrafluoroborate in DMSO (without benzene or nitrobenzene) in the presence of pure oxygen we found 1.4% nitrobenzene.

typical for a homolytic substitution (Table 2). Their results without that addition were very similar to ours (4% yield and high *m*-percentage).

It seemed, therefore, to be worth-while to check the influence of N,N-diphenylhydroxylamine on the reactions in DMSO. The highest yield of the nitrobiphenyls that we were able to obtain was 13% with an isomer ratio *o/m/p* = 41.6/36.1/22.3%. If one assumes that 7% resulted from the reaction not assisted by N,N-diphenylhydroxylamine and that this part had the same isomer ratio as in the previous experiments, one can calculate an isomer ratio *o/m/p* = 57/14/29 for the other 6%. Considering the crude way of calculating it, this ratio is reasonably close to expectations for a purely homolytic process.

This result confirms indirectly our hypothesis that the phenylations with benzenediazonium salts in DMSO follow a heterolytic mechanism as long as there are not any compounds present which can form NO-like radicals.

Kobayashi et al. [6] have recently shown that nitrite ions have the same effect as N,N-diphenylhydroxylamine in promoting a homolytic reaction of benzenediazonium salts with aromatic substrates in DMSO solutions. In these systems the yield is even higher (76%, Table 2). Hence this is definitely the best preparative method for phenylations with benzenediazonium salts.

2.5. *Total and Partial Rate Factors.* We calculated total rate ratios and partial rate factors from the product ratios of benzenediazonium and *p*-nitrobenzenediazonium tetrafluoroborates, respectively in benzene/nitrobenzene/DMSO mixtures. In spite of the fact that their absolute values cannot be accurate, due to the dominant side reactions observed with benzenediazonium salt, they still yield some useful information[6]).

The results for the *phenylation* without additives show that benzene is substituted about twice as fast as nitrobenzene ($K_{H}^{NO_2} = 0.45$). In clearly homolytic phenylations with dibenzoyl peroxide [16], with N-nitrosoacetanilide [35] and with polarographically reduced benzenediazonium salt [12], it is nitrobenzene which reacts 2.7 to 5.0 times faster than benzene.

The total as well as the partial rate factors are qualitatively consistent with an electrophilic reagent (${}^{NO_2}_{H}K < 1.0$). It has, however, to be assumed that our phenylating reagent is unusually reactive, giving rise to a very small selectivity. As pecific solvent effect of nitrobenzene may be an additional reason for its relatively high reactivity. The two diazonium salts which we used for the investigation have some solubility in nitrobenzene, but they are practically insoluble in benzene. We assume, therefore, that the solvation sphere of the diazonium salt consists of DMSO molecules with some nitrobenzene molecules but very little or no benzene. The high viscosity of the system helps to promote the reaction in a process which is probably close to diffusion control for the reaction between the phenyl cation and the aromatic substrate. Under these conditions the usual correlation between product ratios and rate ratios is not valid. This reaction belongs, therefore, to the processes for which, in heterogenous systems, *Wei* [36] introduced the expression 'disguised kinetics'. *Rys*

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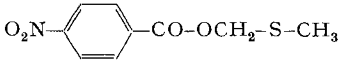
[6]) See also *Eberhardt & Eliel's* criticism of partial rate factors due to the hydrogen transfer step in arylations [34] and *Hey's* summary [11].

[37] showed that principles known from heterogenous catalysis can be applied to such cases which we call reactions in a pseudohomogeneous phase [38].

The total rate factor increases if N,N-diphenylhydroxylamine is added to the system. This is expected due to the occurrence of the additional homolytic process. The extremely high partial rate factors, which *Kobayashi et al.* [6] report for the phenylation in the presence of sodium nitrite, may be due to a solvent effect as discussed above.

This effect explains the higher reactivity of nitrobenzene relative to that of benzene in the homolytic p-*nitrophenylation* ($^{NO_2}_{H}K = 1.41$ to 1.90). From previous experience in homolytic arylations where this solvation effect is not present, one would predict a slightly lower reactivity ($^{NO_2}_{H}K = 0.69$ to 0.94)[7].

The significance of the viscosity of the solvent sphere is also indicated by the following: when we tried to arylate a benzene/nitrobenzene mixture in DMSO with di-*p*-nitrobenzoyl peroxide, we obtained no arylation products but only *p*-nitrobenzoic acid (49%) and the *p*-nitrobenzoic acid ester of methyl hydroxymethyl sulfide (**1**) in 38.5% yield.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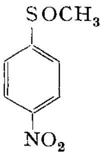
Obviously the *p*-nitrobenzoyl radical was trapped by the solvent before it was able to lose CO_2.

2.6. *By-products.* Apart from the arylation products there are numerous by-products in these reactions. We investigated only those compounds which were detectable by gas-liquid, column and thin layer chromatography, but not the high-molecular weight products (diazo tars). We isolated the compounds **2** to **6** from the reaction of *p*-nitrobenzenediazonium tetrafluoroborate with benzene in DMSO under nitrogen in addition to *p*-nitrobiphenyl (Table 1, 62 to 69% yield).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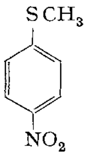
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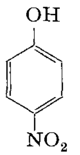
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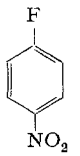
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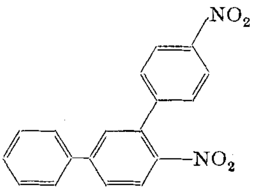
6 0.5%

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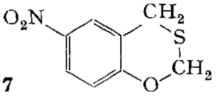
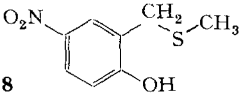
[7] One might argue that it is difficult to understand a total rate factor $^{NO_2}_{H}K \geqslant 1$, as the yield in the *p*-nitrophenylation of benzene is higher than that of nitrobenzene. A more elaborate analysis of these results has, however, little significance due to the principal limitation involved in the significance of so-called rate factors in reactions with complex kinetics [34]. See also the recent paper of *Ohta et al.* [39] on the use of nitrobenzene for homolytic aromatic substitutions.

Compounds **2**, **3**, and **4** were characterized by their mixed m.p., IR. and NMR. spectra. Compound **5** was identified by its retention time on gas-liquid chromatography, b.p. and IR. spectrum. *2,4'-Dinitro-5-phenylbiphenyl* (**6**) which does not seem to have been described in the literature, was characterized by elemental analysis, mass and NMR. spectra (see Experimental Part).

4-Nitrophenyl methyl sulfoxide (**2**) and 4-nitrothiophenol methyl ether (**3**) seem to originate from the attack of the *p*-nitrophenyl radical on the sulfur atom of DMSO. Formation of **3** would also account for the partial *p*-nitrophenol (**4**) formation if an oxygen transfer from **2** (or an intermediate involved in its formation) to the arylating species is conceived. *p*-Nitrophenol, however, might also result from the direct interaction of the arylating species with the oxygen atom of DMSO. Formation of phenols in fair to good yields from the homolytic and heterolytic decompositions of diazonium salts in DMSO in the presence or the absence of aromatic substrates has been claimed by numerous investigators [40] [41]. In heterolytic reactions, however, it is formed in significantly higher percentages, *e.g.* 25% phenol from benzenediazonium tetrafluoroborate [40]. 4-Nitro-fluorobenzene (**5**) is, in our opinion, not formed by the radical mechanism suggested by *Roe* [42] involving the formation of fluorine atoms (radicals). This mechanism would require the tetrafluoroborate to act as a reducing reagent for the diazonium ion, and it appears highly improbable when one considers the oxidation potential of fluoride ions (−2.95 V at 25° [43]). We propose that the ion pairs decompose heterolytically and form the product of the *Schiemann* reaction. Such a mechanism is supported by the observation (Table 4) that in the presence of iodine the yield of *p*-nitro-fluorobenzene even increased (5.4% instead of of 3.9%).

The *m*-terphenyl derivative **6** arises from the free radical attack on *p*-nitrobiphenyl initially formed in the reaction. Under nitrogen, we found neither 6-nitrobenzo[*e*]-1,3-oxathiene (**7**) nor (5-nitro-2-hydroxybenzyl)methylsulfide ether (**8**) in the reaction products. 3.4% **7** was formed, however, in presence of oxygen. The corresponding compounds without nitro groups were found by *Kobayashi et al.* [6] [15] to be degradation products of heterolytic decompositions of aryldiazonium tetrafluoroborate in DMSO. Since the mechanism of the formation of these compounds is not clearly established, we do not think, that they are unambiguous indications for a heterolytic decomposition of aryldiazonium salts in DMSO.


7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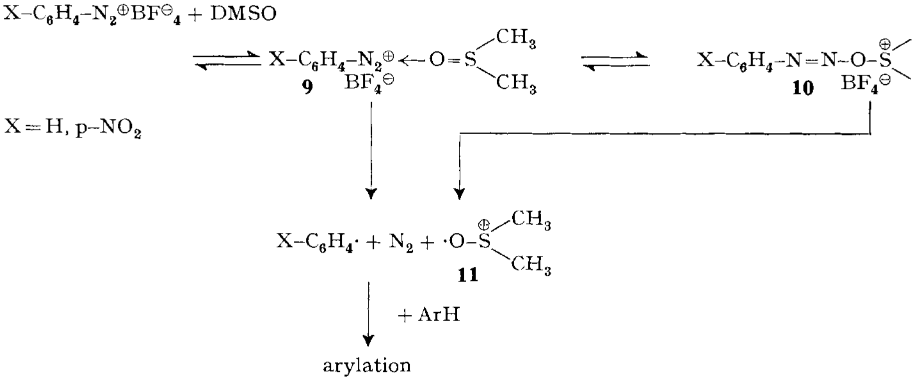
With respect to the formation of nitrobenzene, we refer to footnote [5]) of this paper. With the probable exception of the *Schiemann* reaction, all products are, therefore, compatible with a homolytic decomposition of *p*-nitrobenzenediazonium tetrafluoroborate in DMSO.

3. Conclusions. – The results discussed in part 2 of this paper clearly prove that arylations with *p*-nitrobenzenediazonium tetrafluoroborate are homolytic processes, whereas there is a strong indication that the analogous arylations with benzenediazonium tetrafluoroborate are almost exclusively heterolytic reactions.

The obvious mechanistic explanation is based on the higher electrophilicity of the *p*-nitrobenzenediazonium ion: The equilibrium with DMSO molecules (b) lies more on the side of the addition products with the nitro derivative. Charge-transfer complex formation (**9**) is substantiated by the electronic spectra investigated by *Koller* in our laboratory [24]: *p*-Nitrobenzenediazonium tetrafluoroborate in water displays two typical maxima in the ultraviolet region ($\lambda_1 = 310$ nm, $\log \varepsilon_1 = 3.14$; $\lambda_2 = 259$ nm, $\log \varepsilon_2 = 4.22$); in DMSO/$H_2O$ 19:1 there is an additional, very broad band between 310 and 440 nm, $\log \varepsilon$ (360 nm) ≥ 3.48[8]).



(b)

For the purpose of the following discussion, we also include the covalent sulfoxonium product **10** in the addition equilibria although we have no experimental evidence for it. The essential problem in these homolytic arylations in DMSO as well as in other arylation systems using diazo compounds as the source for aryl radicals is to know of whether a 'free' electron transfer takes place between a non-covalently bound electron donator and the diazonium ion (as in **9**), or if a covalent adduct (in our case **10**) is an intermediate in the reaction coordinate. Although this problem has been discussed by various authors [4] [5] [7] [20] [44], an unambiguous answer to it, in our opinion, has not been furnished.

All reactions proceeding via phenyl radicals or krypto-radicals by catalysis with transition metal ions (*Sandmeyer* and *Meerwein* reactions and *Pschorr* cyclizations [45]) and the polarographically formation of phenyl radicals [12] [20] indicate that a one-electron transfer to diazonium ions is, indeed, possible. This does not exclude, however,

$$ArN_2^{\oplus} + B^{\ominus} \underset{\longleftarrow}{\xrightarrow{\text{fast}}} Ar{-}N{=}N{-}B \longrightarrow Ar\cdot + N_2 + \cdot B \qquad \text{(c)}$$

$$\begin{tikzcd} ArN_2^{\oplus} + B^{\ominus} \arrow[r, "\text{one electron transfer}"] \arrow[d, shift right, "\text{fast}"'] & Ar\cdot + N_2 + \cdot B \qquad \text{(d)} \\ Ar{-}N{=}N{-}B \arrow[u, shift right] & \end{tikzcd}$$

---

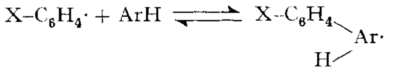
[8]) An exact extinction coefficient can not be given as the complex formation equilibrium was not determined.

covalent adducts with nucleophiles such as nitrite ions, diazotate ions, anions, etc. Yet, the fact that such adducts exist, does not prove that they are the actual intermediates: It is well known that rapidly formed adducts may be true intermediates as in the general mechanism (c) or they may be involved only as products of a side-equilibrium as shown in (d).

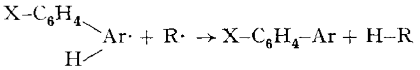
In the reaction of diazonium ions with DMSO there are even two different adducts to which the ambiguity of mechanisms (c) and (d) can be applied! Unfortunately, the classical method to differentiate between (c) and (d) – kinetics with a steady-state intermediate – cannot be applied to (b) as steady-state kinetics can give an unambiguous answer only if an additional reagent is necessary for the product forming step. The rate dependence for that reagent has to be non-linear to give a distinct proof for the two-step mechanism.

As pointed out by *Rüchardt et al.* [44], the ambiguity between a free electron transfer between diazonium and diazotate ions *versus* the covalent diazoanhydride intermediate exists also in the classical *Gomberg-Bachmann* reaction[9]: In both alternatives a diazotate radical ($Ar{-}N{=}N{-}O\cdot$) is formed. Indeed, it was directly detected by *Cadogan*'s observation of an ESR. spectrum attributable to it [47].

The formation of the diazotate radical is important for the second step of the homolytic substitution proper (d) where a hydrogen atom has to be released from the σ-complex, the phenyl-cyclohexadienyl radical **12**.



$$X{-}C_6H_4\cdot + ArH \rightleftharpoons \begin{matrix} X{-}C_6H_4 \\ H \end{matrix}\!\!>\!Ar\cdot \quad (e)$$



$$\begin{matrix} X{-}C_6H_4 \\ H \end{matrix}\!\!>\!Ar\cdot + R\cdot \rightarrow X{-}C_6H_4{-}Ar + H{-}R \quad (f)$$

12

For that step a radical $R\cdot$ or at least a radical precursor is necessary. In benzoyl peroxide arylations there is a large deuterium isotope effect ($k_H/k_D = 6.6$) [48], whereas in nitrite assisted arylations in DMSO there it is small ($k_H/k_D = 1.01$ to 2.36) [49]. In the *Gomberg-Bachmann* and the N-nitrosoacetoanilide reactions no deuterium isotope effect has been found [6] [50]. The above indicates that the 'gegen-radicals' for these three types of arylations increase in reactivity for step (f), the diazotate radical being the most reactive. For the phenylations discussed in this paper, the dimethyl sulfoxide radical cation **11** is in all probability the 'gegen-radical'.

We think, therefore, that our results can be rationalized by their relationships to aroyl peroxide arylations, to classical *Gomberg-Bachmann-Hey* arylations in two-phase systems and to nitrite or N,N-diphenylhydroxylamine or transition metal assisted arylations in DMSO:

1) The peroxide and all DMSO arylations have the advantage of being one-phase reactions.
2) The peroxide reaction easily yields aryl radicals but not efficient 'gegen-radicals'. In addition, the fact that benzoyl radicals are the primary homolytic fission products, accounts for side reactions.
3) Nitrite, N,N-diphenylhydroxylamine, and transition metals form, in a relatively easy manner, diazo radicals ($Ar{-}N_2\cdot$) and secondary aryl radicals. At the same time

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[9] Some qualitative observations, e.g. the lack of reactivity of benzoate ions as water-soluble substrates in *Gomberg-Bachmann* reactions [46] are in favour of but do not prove the mechanism with a non-ionized intermediate, i.e. the diazoanhydride.

good 'gegen-radicals' for the second step of the actual substitution (f) are formed. DMSO seems to facilitate transfer of electrons in redox systems as shown for inorganic [51] and organic systems [52].

4) The last mentioned factor helps also in unassisted arylations in DMSO. It is, however, effective only with strongly electrophilic diazonium ions (which are, therefore, relatively strong oxidation reagents) because the electron transfer capability of DMSO molecules are relatively small, in spite of their fairly strong electron donating effect in complex formation. In addition it is questionable if the DMSO cation radical is a good 'gegen-radical'.

We thank Dr. *G. K. Zwolinski* (ETHZ) for interesting discussions and for his help in the preparation of the English manuscript of this paper.

Experimental Part

Reagents. Merck Analar thiophene free benzene was used without further purification. Dimethyl sulfoxide was dried and distilled over calcium hydride at reduced pressure and was kept in an air-tight flask out of light and of contact with moisture. Aniline and nitrobenzene were distilled twice prior to use. Commercial *p*-nitroaniline was recrystallized twice from ethanol before being used. Benzenediazonium and *p*-nitrobenzenediazonium tetrafluoroborates were prepared by known methods [42] using sodium nitrite and 31% fluoroboric acid. N, N-Diphenylhydroxylamine was prepared according to *Wieland*'s method [53] and was stored under nitrogen in a refrigerator; it was used shortly after it had been synthesized. Di-*p*-nitrobenzoyl peroxide was synthesized by the standard method using *p*-nitrobenzoyl chloride and was crystallized from ether (m.p. 156° [54]).

Reference Compounds. p-Nitrofluorobenzene, *p*-nitro-iodobenzene, iodobenzene, biphenyl, 2-nitrobiphenyl, and 4-nitrobiphenyl were commercially available. The solid reference compounds were purified by recrystallization from a suitable solvent. The liquids were distilled under reduced pressure. No impurities were detected by gas-liquid-phase chromatography (glpc) analysis and the melting and boiling points corresponded to those in the literature. 3-Nitrobiphenyl and 3,4'-dinitrobiphenyl were prepared according to the literature [11] and had m.p.s of 61° and 189°, respectively, as reported in the literature. 2,4'-dinitrobiphenyl, m.p. 93°, was prepared by the method of *Gull & Turner* [55] and 4,4'-dinitrobiphenyl m.p. 233° was synthesized according to the method of *Schultz* [56].

Quantitative Analysis. The yields of the reaction products were determined by glpc unless otherwise stated. A 3 m × 2 mm column of 5% silicone rubber SE-52 on chromosorb W was used to effect separation. It was operated at a column temperature of 220° with a helium flow rate of 80–90 ml/min. The yields were calculated using the method of an internal standard, for which the following were used: Biphenyl, in the case of the decomposition of *p*-nitrobenzenediazonium tetrafluoroborate and of di-*p*-nitrobenzoyl peroxide; 4,4'-dinitrobiphenyl was used in the case of the decomposition of benzenediazonium tetrafluoroborate with nitrobenzene, and 4-nitrobiphenyl for the decompositions of benzenediazonium tetrafluoroborate in benzene. The difference in the thermal conductivity responses of the different products were determined using a known mixture of the reference compounds.

Arylation Reactions with Diazonium Salts, Analytic Scale. The diazonium salt (0.01 mol) was dissolved in degassed dimethyl sulfoxide (8–10 ml) in a three-neck flask wrapped in aluminium foil and provided with an efficient stirrer, a reflux condenser equipped with a calcium chloride dry tube and a gas inlet tube. The aromatic substrate (25 ml of benzene or 38 ml of nitrobenzene) was added and the reaction mixture stirred under a nitrogen atmosphere at 50° ± 1° or 80° ± 1° for 27 or 3 h, respectively. Completion of the reaction was confirmed by absence of coupling with 2-naphthol. 20–30 ml of ice water was added to the reaction mixture, and stirring continued for another 30 min, followed by the addition of 100 ml of ether. The ether layer was first washed with water, then with aqueous carbonate (approx. 10%) followed again by distilled water until the washings were neutral. The ether was dried over sodium sulfate and a known amount of internal standard was added. Most of the ether was distilled off using an efficient fractionating column and the residue was analyzed by glpc.

Reactions under Atmospheric Oxygen. These reactions were performed in the same manner as above, except that solvents were used without degassing and nitrogen was not bubbled through the reaction mixture.

Reactions in the Presence of Iodine. The reactions were carried out similarly. Iodine (1.26 g, 5 mmol) was added to the solution of 10 mmol of aryldiazonium salt in 8–10 ml of DMSO and 25 ml of benzene.

Reactions in the Presence of Iodobenzene. The reactions were performed with 10 mmol of iodobenzene with either 8 or 21 ml of benzene as the substrate in different runs.

The Competitive Reactions. The diazonium salt (10 mmol) was dissolved in 8–10 ml of DMSO and the molar ratio of DMSO, benzene and nitrobenzene was 1:1.17:1.47.

Arylations in the Presence of Diphenylhydroxylamine. Phenyldiazonium tetrafluoroborate (5.2 mmol) was dissolved in a preheated and degassed mixture of 10 ml of DMSO and 10 ml of nitrobenzene containing 5.2 mmol of calcium carbonate (in competitive reactions, 0.14 mol of DMSO, 0.225 mol of nitrobenzene and 0.225 mol of benzene were used). After the addition of 50 mg (0.31 mmol) diphenylhydroxylamine, the decomposition became vigorous and was completed within a few minutes. The reaction was worked-up and analyzed as described above.

Synthetic Scale Reaction and Structure Elucidation of By-products. The reaction studied was the decomposition of *p*-nitrobenzenediazonium tetrafluoroborate in DMSO in the presence of benzene, on a 0.1 molar scale. The procedure and working-up were the same as described above. The neutral fraction was column-chromatographed (aluminium oxide grade I – neutral). The column was packed in petrol-ether (60–80°) and eluted with petrol-ether, benzene and chloroform in quick succession. The following fractions were isolated: 3.9%, *p*-nitro-fluorobenzene b.p. 205°/735 Torr, lit. 205.3°/735 Torr [57]; 0.7% 4-nitrothiophenol methyl ether m.p. 72° lit. 72° [53]; 0.8% 4-nitrophenyl methyl sulfoxide m.p. 150°, lit. 149° [59]; 62% 4-nitrobiphenyl m.p. 113°, lit. 114° [60]; 0.5% *2,4′-dinitro-5-phenyl-biphenyl.* The last compound showed the following characteristics: m.p. 193°. NMR.: protons 3′,5′: 8.41 (2 H, *d*, $J = 9$ Hz); protons 2′,6′: 7.63 (2 H, *d*, $J = 9$ Hz); proton 3: 8.21 (1 H, *d*, $J = 8.5$ Hz); proton 4: 7.88 (1 H, *d*, $J = 8.5$ Hz and 2.0 Hz); protons 2″–6″: 7.63 (6 H, *m*, including 1 *H*, *d* of proton 6). Mass spectrum, *m/e* (% of base peak): 321 (3), 320 (13.5), 243 (6.5), 226 (4), 198 (8), 197 (100), 180 (11), 163 (9), 153 (8), 152 (44), 151 (8), 150 (8), 135 (15), 106 (18), 79 (19), 77 (19), 65 (13), 50 (11), 46 (27).

$C_{13}H_{12}N_2O_4$ Calc. C 67.5 H 3.75 N 8.75% Found C 67.23 H 3.68 N 8.56%

The carbonate extract from the above reaction was acidified and extracted with ether. The ether extract was washed with distilled water, dried over sodium sulfate, and the ether removed under reduced pressure to leave an oily residue which, when crystalized from water, yielded 2.1% *p*-nitrophenol m.p. 113–114°, lit. 114° [60]. The mother liquor on tlc examination showed the presence of two more compounds which, however, were not isolated.

Decomposition of p-*Nitrobenzenediazonium tetrafluoroborate in DMSO under Oxygen without Aromatic Substrates.* The procedure was the same as for the arylation reactions. From the neutral fraction, a mixture of 1.4% nitrobenzene and 1.1% of *p*-nitro-fluorobenzene was isolated by preparative tlc (silicagel, multiple development with CCl_4), the composition of which was determined by mass spectral analysis: the relative intensities of the molecular peaks were compared with those of a known sample. From the same tlc 3.4% of *6-nitro-benzo*[*e*]*-1,3-oxathiene* was isolated. After crystallization from petrol-ether, then chloroform, the compound showed the following characteristics: m.p. 134–135°. IR. spectrum in potassium bromide pellet: 3050, 2910, 1600, 1582, 1510, 1490, 1335, 1220, 1090, 985, 960, 912, 858, 820, 812, 773, 747 cm^{-1}. NMR.: 4.12 (2 H, *s*), 5.50 (2 H, *s*), 7.02 (2 H, *d*, $J = 8$ Hz), 8.02 (1 H, *m*). Mass spectrum, *m/e* (% of base peak): 197 (100), 180 (12), 167 (5), 164 (9), 152 (36), 151 (8), 136 (15), 77 (17), 65 (14), 51 (30), 39 (9).

*Decomposition of Di-*p-*nitrobenzoyl peroxide in a Mixture of DMSO, Benzene and Nitrobenzene:* The di-*p*-nitrobenzoyl peroxide (6.02 mmol) was dissolved in a mixture of 15 ml (0.212 mol) of DMSO, 30 ml (0,339 mol) of benzene and 39.5 ml (0.339 mol) of nitrobenzene. After 72 h at 80°, the reaction was worked-up as described for the arylations with diazonium salts. The neutral fraction contained only one substance detectable by glpc which showed all the characteristics of the *p*-nitrobenzoic acid ester of methyl hydroxymethyl sulfide reported in the literature [41] with respect to m.p., IR., UV., NMR. and Mass spectra. The acid fraction was *p*-nitrobenzoic acid, identified by m.p., mixed m.p. and IR. spectrum.

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155. Notiz über das Vorkommen von 4′,5-Dihydroxy-3,3′,6,7-tetramethoxyflavon (Chrysosplenetin) in *Plectranthus marrubioides* HOCHST (*Labiatae*)

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(3. V. 72)

Summary. Chrysosplenetin (4′,5-dihydroxy-3,3′,6,7-tetramethoxyflavon) has been isolated from the leaves of *Plectranthus marrubioides* HOCHST (*Labiatae*).

Bei der Untersuchung von Blättern und Infloreszenzen von *Plectranthus marrubioides*[2]) auf chinoide Diterpene stiessen wir bei den benzollöslichen Anteilen auf ein

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[1]) Diplomarbeit Universität Zürich (1971).

[2]) Die Pflanze kommt wild im abessinischen Hochland vor. Die für diese Arbeit verwendeten Blätter und Blütenstände stammten von Pflanzen, die 1969 in Nairobi aufgezogen worden waren. Wir danken Herrn *P. R. O. Bally* auch hier für seine Hilfe bei der Beschaffung des Pflanzenmaterials.