

THE RADICAL COUPLING MECHANISM IN THE DIAZO COUPLING REACTION.
MIGRATION VS. DECOMPOSITION OF PHENYLAZO RADICAL GENERATED FROM
PHENYLAZO 1-NAPHTHYL ETHER IN THE SOLVENT CAGE

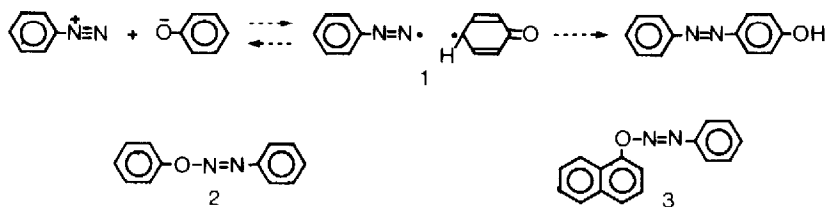
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Abstract: The thermal reaction of phenylazo 1-naphthyl ether generates a pair of phenylazo and naphthoxy radicals in the solvent cage, in which these radicals couple together at the aromatic carbon to give 4-phenylazo-1-naphthol and 2-phenylazo-1-naphthol.

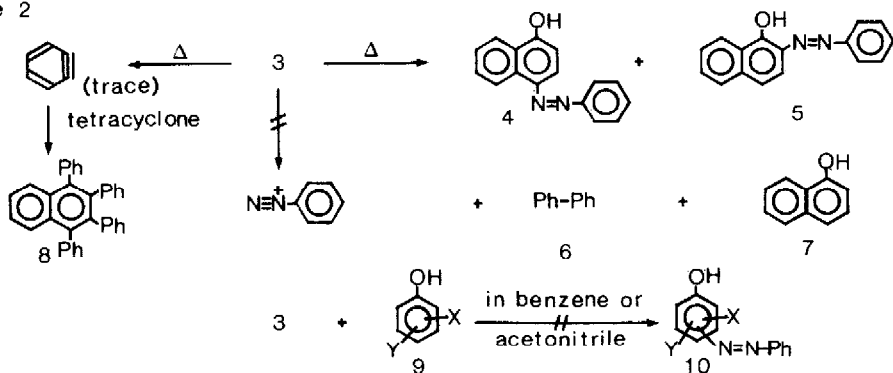
In the early 1970s, Bubnov et al. reported CIDNP evidence which indicated the existence of a radical pair (1) in the diazo coupling reaction, suggesting the involvement of the radical coupling pathway (Scheme 1).¹ Rieker et al. also observed phenoxy radicals in the diazo coupling reaction.² However, Lippmaa et al.³ have drawn a conclusion differing from that by the previous authors¹ from the CIDNP study. These posed interesting problems related not only to the diazo coupling reaction mechanism, but also to the mechanism of the substitution reactions.⁴ The crucial questions with the radical coupling mechanism are how the radical pair (1) is generated, and what is the true nature of the coupling.⁴⁻⁶

It is suggested that an electron transfer reaction between benzenediazonium and phenolate ions generates the radical pair (1).¹ However, it is also suggested that the azoether (2) possibly formed from those ions generates 1,⁵⁻⁷ although the reactive azoether possessing no substituent group at the para position of the phenoxy ring, such as 2, has never been identified and/or isolated in the reaction. Despite the obvious importance of this problem, there has not yet been any precise study of it until now. Recently, however, we have synthesized this type of reactive azoether (3),⁷⁻⁹ and thus we have attacked this long standing problem by using 3. It is thought that the thermal reaction of 3 generates a radical pair such as 11, and therefore provides

Scheme 1



Scheme 2

Table 1. Products yields in the thermal reaction of azoether (3).^a

No.	Temperature	Solvent	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>
1	5°C	Benzene	16	6	21	28
2	5°C	CH ₃ CN	12	4	- ^b	27
3	20°C	Benzene	22	8	27	32
4	20°C	CH ₃ CN	20	8	- ^b	35
5	80°C	Benzene	15	3	59	42
6	80°C	CH ₃ CN	8	1	- ^b	27

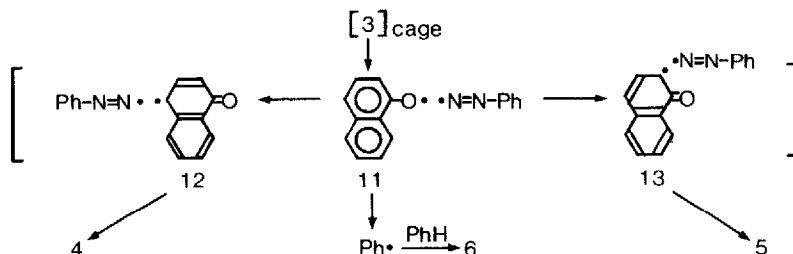
a: The yield (%) is based on 3. b: Not assigned.

a great deal of information on the mechanism.

When a benzene or acetonitrile solution of the freshly prepared azoether (3) (ca. 10^{-3}M) was kept standing at 20° and 5°C for a few weeks or heated under reflux for two hours in the dark, 3 disappeared completely to give rise to several products, among which 4-phenylazo-1-naphthol (4), 2-phenylazo-1-naphthol (5), biphenyl (6), and 1-naphthol (7) were identified as the major compounds (Table 1, Scheme 2). Besides these, many kinds of minor products were formed. For example, a trace of benzyne was identified in the thermal reaction mixture. The formation of both 4 and 5 from 3 by the thermal reaction is noteworthy, and the mechanism involving a radical pair (11) is deduced as follows.

Azonaphthols (4 and 5) are not the products of the intermolecular ionic coupling of benzenediazonium ion with 1-naphthol, because 3 does not dissociate heterolytically to give benzenediazonium ion.^{8,10,11} This was confirmed by the fact that no cross coupling products (10) were obtained when a benzene or acetonitrile solution of 3 was stirred at room temperature or refluxed in the dark in the presence of reactive phenols (9) such as 2-naphthol, 3-aminophenol, and 2,6-dimethylphenol. In these reactions, only 4 and 5 were formed

Scheme 3



together with biphenyl and 1-naphthol, although the total yields were low. Furthermore, the addition of excess 1-naphthol to the benzene or acetonitrile solution of 3 did not increase the yields of 4 and 5.

The unfavorable ionic (heterolytic) dissociation of the O-N bond of 3 was further supported by our observation that benzyne which is known to be formed by the thermal decomposition of benzenediazonium ion, was very inefficiently formed from 3. Only a trace of the adduct (8) with tetracyclone was obtained in the reaction at the reflux temperature in benzene even in the presence of a promoter for benzyne formation such as 1,1-diphenylethylene and stilbene.¹²

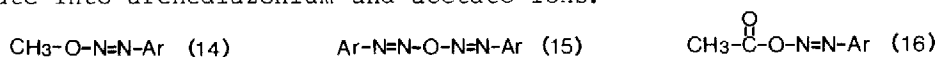
On the other hand, the fact that the 4-isomer (4) was formed in favor of the 2-isomer (5) (Table 1), rules out the possibility of the mechanism involving the concerted sigmatropic shift of the phenylazo group because the 1,5-shift of the phenylazo group giving 4 is spatially very unfavorable. The alternate possibility that free phenylazo radical attacks the naphthoxy ring intermolecularly to give 4 and 5 is also not supported, because a high concentration of 3 did not yield 4 and 5 favorably and rather disturbed the stability of 3. Also free phenylazo radical is known to be very short-lived at ordinary temperature.^{13,14} Phenylazo radical generated from 3 afforded phenyl radical,¹³⁻¹⁵ which was trapped by bromobenzene. When 3 was heated in bromobenzene, bromobiphenyls with the isomer ratio of the ortho : meta : para = 50 : 28 : 22, were formed. In addition, the thermal reaction of 3 with benzene-d₆ gave biphenyl-d₅.

Comparison of the product distribution of 4 - 7 has revealed that the ratio of (4 + 5) : (6 + 7) is ca. 1 : 5 at 80°C, while it is ca. 1 : 2 at 20°C (and 5°C) (Table 1, No. 1, 3, and 5). In the acetonitrile solvent, the ratio of 6 vs. (4 + 5) revealed the same trend (No. 2, 4, and 6). These facts indicate that lower temperatures (~20°C) give the migration products or azonaphthols (4 and 5) more favorably, while higher temperatures (~80°C) give the decomposition products (6 and 7). This suggests the existence of a common intermediate species such as 11 for the formation of 4 - 7.

All of our observations support the mechanism involving the dissociated radical pair (11) confined in the solvent cage. At lower temperatures, phenylazo radical of 11 migrates more favorably onto the naphthoxy carbon at the 4- and 2-positions to give azonaphthols 4 and 5 via 12 and 13, respectively,

in the cage. In contrast, at higher temperatures phenylazo radical escapes readily from the solvent cage giving rise to phenyl radical which yields bi-phenyl by the reaction with benzene (Scheme 3). Therefore, the temperature-dependent dual reactivity of 3 originates from the radical pair 11.

Our present results, in turn, support the possibility of the radical coupling pathway for 1 to give 4-phenylazophenol provided that 1 is generated in the solvent cage, and that for the generation of the radical pair (1) from 2. However, it is still not clear whether or not 2 can be formed in the usual diazo coupling reaction in aqueous media. It is worthy to note that the thermal reactivity of the O-N bond of 3 is rather similar to that of 14 and 15 which generate radical pairs, but differs from that of 16 which favors to dissociate into arenediazonium and acetate ions.^{12,16-18}



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- 9 We use the name "azoether" instead of "diazoether" (cf. refs. 7 and 8).
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- 11 However, we found that by the action of active Silica gel, 3 dissociated heterolytically. So, when we used a crude benzene extract of 3 obtained from a broad Silica gel TLC band, the cross coupling products (10) were formed as reported in our previous paper dealing with the structural elucidation (ref. 7). We report the active Silica gel effect in our forthcoming paper.
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