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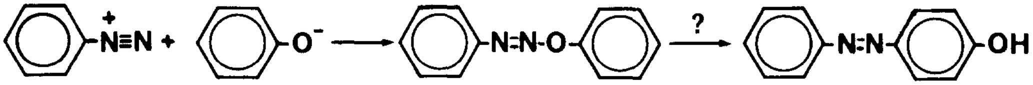
BASE AND ACID CATALYZED REACTIONS OF PHENYLAZO 1-NAPHTHYL ETHER, A NEW REACTIVE DIAZOETHER.

REPLY TO THE KEKULĒ'S MECHANISM FOR THE DIAZO COUPLING REACTION

Takahiro Tezuka,* Katsunori Sasaki, and Setsuo Ando
Department of Chemistry, University of Tsukuba,
Sakura-mura, Ibaraki 305, Japan

Abstract: The base and acid catalyzed reactions of phenylazo 1-naphthyl ether (5) yielded biphenyl (8) and 1-naphthol (9) as major products accompanied with 4-phenylazo- (6) and 2-phenylazo-1-naphthols (7). All of our observations do not support the Kekulē's diazo coupling mechanism.

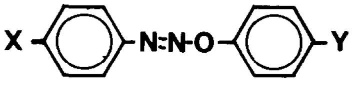
The mechanism of diazo coupling reaction has long been the target of intense investigation since Kekulē and Hidegh suggested in 1870 intermediacy of diazoether in the reaction.[1] According to this mechanism, for example, 4-phenylazophenol arises via diazoether (1):



1

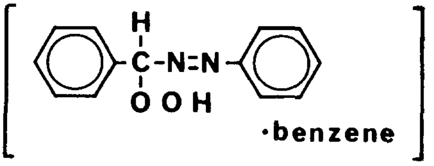
Many attempts to isolate reactive diazoether intermediate in the diazo coupling reaction have been made. However, reactive diazoether possessing no substituent at the para position such as 1 and 5 has never been isolated, while Dimroth in 1908 and Kauffmann et al. in 1960 obtained substituted diazoethers 2 and 3.[2,3] The rearrangement of reactive diazoethers to azophenols, and the chemistry of diazoether bond have not yet been elucidated.[4,5]

Recently we successfully isolated a reactive diazoether (5) by carrying out the reaction of 1-naphthol and benzenediazonium ion generated from a molecular complex of α-azohydroperoxide with benzene (4) in a solid state. In this study we tested whether or not the reactive diazoether (5) rearranges into azonaphthols (6 and 7), as suggested by Kekulē under the condition of the



2 : X=Br ; Y=NO_2

3 : X=Y=Cl



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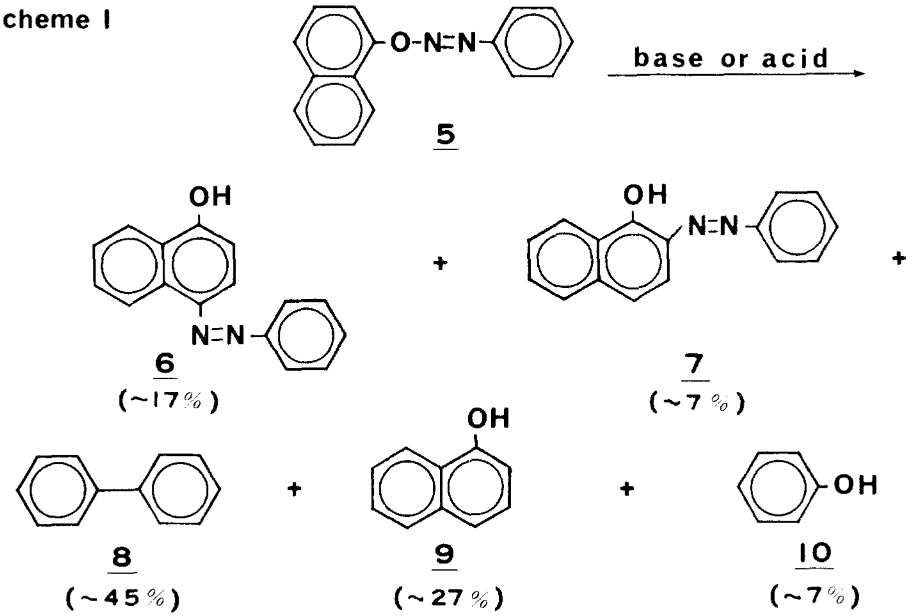
Scheme I



diazo coupling reactions, and also investigated the chemistry of the diazoether bond.

A benzene solution of diazoether 5 was prepared by the method reported in the previous paper,[6] and subsequently benzene was substituted by acetonitrile at 40 °C under reduced pressure. By repeating the substitution procedure, a pure acetonitrile solution of 5 was obtained, and this solution was instantly used for the reaction. To avoid the decomposition of 5, the solvent should not be eliminated completely during the above procedure.

An aqueous sodium hydroxide or hydrochloric acid was added to an acetonitrile solution of the diazoether 5 (10^{-2} M), and the mixture was stirred at room temperature for 40 hours in the dark. Similar experiments were conducted by changing the solvent and the kind of base or acid. The main reaction products identified by TLC separation and the HPLC analysis were 4-phenylazo-1-naphthol (6), 2-phenylazo-1-naphthol (7), biphenyl (8), 1-naphthol (9), and phenol (10) (Scheme 1). In addition to these, several minor byproducts were formed in the reaction, but the structural identification of these minor compounds could not be made. The percentage yields of these compounds 6 - 10 corrected by the control values are indicated in Table 1.

The data in the table have revealed that the azonaphthols 6 and 7 are not major products in the base and acid catalyzed reactions, but biphenyl (8) and 1-naphthol (9) are the predominant ones. This is in contrast to the fact that the azonaphthols 6 and 7 were formed in 48% and 9% yields respectively, accompanied with 8 (13%), 9 (22%), and 10 (6%), when an acetonitrile solution of 5 was kept standing in the absence of the base and acid at room temperature for one week in the dark. These indicate that the base and acid do not catalyze effectively, but rather disturb the rearrangement of 5 into 6 and 7.

Table 1. Product yields (%) in the reaction of diazoether 5.[a]

No.	Base or Acid	Solvent, Addendum	6	7	8	9	10
1.	2N NaOH	Acetonitrile	11	4	25	21	4
2.	4N NaOH	"	11	5	25	21	4
3.	8N NaOH	"	10	6	18	15	7
4.	2N NaOH	H_2O[b]	5	4	6	12	c
5.	"	Ethanol[b]	13	6	23	16	d
6.	"	Bromobenzene[e]	6	4	12	15	2
7.	"	CH_3CN, cyclohexene	8	3	16	23	d
8.	"	CH_3CN, Ph_3CH	9	7	16	23	d
9.	"	CH_3CN, 2-naphthol	8	c	10	13	d
10.	Pyridine	Acetonitrile	15	2	17	21	4
11.	Aniline	"	17	c	3	22	d
12.	AcONa	"	10	3	20	18	d
13.	NaH	Benzene	c	c	45	10	d
14.	2N HCl	Acetonitrile	7	6	27	27	d
15.	2N H_2SO_4	"	8	6	18	21	d

a: Yields were determined by the HPLC analysis. b: Contains a small amount of acetonitrile. c: Trace. d: Not identified. e: Heterogeneous reaction. Bromodiphenyls were formed in ca. 10% yield.

The isomer ratio of 6 to 7 in the sodium hydroxide catalyzed reaction of 5 in acetonitrile was found to be 2:1 (No. 1 - 3), which is inconsistent with the isomer ratio observed in the usual diazo coupling reaction of benzenediazonium ion with 1-naphthol in aqueous alkaline media (6:7 = 9:1). Various isomer ratios of 6 to 7 were observed in the cases of the other base and acid catalyzed reactions of 5 (No. 10, 11, 12, 14, and 15).

Our observations on the inefficient formation of 6 and 7 from 5, and the isomer ratios of 6 to 7 indicate that even if the diazoether intermediate 5 is formed in the usual diazo coupling reaction of benzenediazonium ion with 1-naphthol, this intermediate decays in quite unexpected ways to give low yields of azonaphthols 6 and 7 in basic and acidic media. Therefore, we conclude that the diazoether 5 is not an intermediate in the diazo coupling reaction of benzenediazonium ion with 1-naphthol. With regard to this, it should be noted that in the sodium hydroxide catalyzed reaction, 5 did not react with 2-naphthol in the dark to give a cross coupling product or 1-phenylazo-2-naphthol. This indicates that the base catalyzed reaction does not dissociate the diazoether 5 into a free benzenediazonium ion (or its equivalent species), but it leads 5 to somewhat different reaction products (vide infra).

The formation of a considerable amount of biphenyl (8) from 5 in the base and acid catalyzed reactions is important in discussing the mechanism of the reaction of the diazoether 5. The formation of biphenyl (8) was not suppressed by the addition of radical quenchers such as cyclohexene and triphenylmethane (No. 7 and 8). Biphenyl was also formed in ethanol and bromobenzene (No. 5 and 6). These our observations indicate that biphenyl (8) is not a simple radical coupling product of phenyl radicals. The fact that benzenediazonium ion was not trapped by 2-naphthol (vide supra) indicates that this ion is not a source of biphenyl. Therefore, the formation of biphenyl (8) from 5 in the base and acid catalyzed reactions poses an interesting problem. The facts that phenol (10) was formed in the base catalyzed reaction (No. 1 - 3, 6, and 10), and that a higher yield of biphenyl (8) was obtained in the sodium hydride catalyzed reaction (No. 13), will tell something about the mechanism for the decomposition of the diazoether 5 in the base and acid catalyzed reactions.[7]

Although the mechanism for the reaction must be elucidated by further studies in progress, the present study revealed for the first time that the chemical reactivity of the diazoether bond (-O-N=N-) is quite unique, and the base and acid catalyzed reactions do not convert the diazoether 5 into azonaphthols 6 and 7 effectively. All of our observations, therefore, do not support the Kekulē's mechanism involving reactive diazoether intermediate for the diazo coupling reaction.

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7. The base and acid catalyzed reactions are rather complicated, and approximately 50% of 5 came out to be several minor products. We are investigating the structural identification of these minor compounds. However, it is important to note that the reaction pattern observed in the base and acid catalyzed reactions differs from that of the thermally induced homolytic decomposition of 5, which yielded 1-naphthol in ca. 40% yield.

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