Behaviors of Azoxy Compounds in highly Concentrated Sulfuric Acid*

Jiro YAMAMOTO, Noriaki HAMADA and Masahiro UMEZU

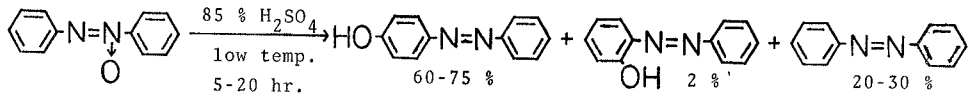
(Receivcd May 31, 1980)

Department of Industrial Chemistry, Faculty of Engineering,
Tottori University ; Koyama-cho, Tottori. 680 Japan

In the reaction of azoxy compounds with highly concentrated sulfuric acid at 80°C, much azobenzene and tarry products were formed in addition to small amounts of *o*- and *p*-hydroxyazobenzenes. The reaction of the azoxy compounds with sulfur trioxide at room temperature gave similar results with slower rates. On the basis of the results, the reaction pathways of azoxy compounds in highly concentrated sulfuric acid are discussed.

1 Introduction

The Wallach rearrangement of azoxybenzenes is usually carried out in 80-90% sulfuric acid.[1-3] Lachmann[4] and Gore and Hughes[5] investigated the Wallach rearrangement of azoxybenzene and its derivatives with sulfuric acid under various conditions, focussing their attention on the distribution of the products, namely the formation of *o*- and *p*-hydroxyazobenzenes and azobenzenes. An example is depicted below :



On the other hand, relatively few studies using highly concentrated sulfuric acid have been reported. Duffy and Hendry,[6] Buncel et al[7] [8] and Cox[9] investigated the kinetics of the Wallach rearrangement of azoxybenzene using very dilute solutions in near 100% sulfuric acid, where products other than *p*-hydroxyazobenzene and 4'-hydroxyazobenzene-4-sulfonic acid were not taken into consideration. In the present work, we have investigated the behaviors of azoxybenzenes towards near 100% sulfuric acid and sulfur trioxide (SO_3) in preparative scale, in order to see whether the use of highly concentrated sulfuric acid affects products distribution of products and whether the Wallach reaction can be used for a synthetic purpose under such

* Part XI of "Study on the Reactivity of Azoxybenzenes". Part X : Jiro YAMAMOTO, Jiro MAKI and Masahiro UMEZU, Nihonkagakukaishi, 1980, 171

conditions.

2 Experimental

2.1 Materials Symmetrically substituted azoxybenzenes such as azoxybenzene,[4] 2,2'-dimethylazoxybenzene and 3,3'-dimethylazoxybenzene[10] were prepared by the reduction of the corresponding nitrobenzenes. *β-p*-Chloroazoxybenzene[11] and *β-p*-nitroazoxybenzene[12] were prepared from the corresponding azocompounds. *β-p*-Nitroazoxybenzene was converted into its *α*-isomer by treatment with CrO_3 in acetic acid.[12] *p*-Bromoazoxybenzenes was oxidized with hydrogen peroxide in acetic acid giving a mixture of *α*- and *β-p*-bromoazoxybenzenes which were separated by fractional recrystalization using ethanol.[13] *β-p*-Methylazoxybenzene[11] was also obtained by the same method.

Concentrated sulfuric acid near 100% was prepared by diluting commercial 130% sulfuric acid calculated acid amounts of water.

2.2 Reaction of azoxybenzenes with concentrated sulfuric acid A solution of azoxybenzene (1g ; 5.4×10^{-3} mol) in 100% sulfuric acid (15ml) was heated for 10min. at 80°C. The reaction products were separated by the procedure shown in Chart 1, resulting in *o*-hydroxyazobenzene, 0.02g (2%) ; *p*-hydroxyazobenzene, 0.01 (1%) ; azobenzene, 0.27g (28%) ; tarry product, 0.69g (69wt%). Other azoxy compounds were treated by the same procedure.

2.3 Reaction of azoxybenzenes with sulfur trioxide A solution of SO_3 (0.3–0.57*M*/*l*) in chloroform-nitromethane was allowed to stand for 40hr. at room temperature with an equimolar amount of azoxybenzene. After the reaction mixture was washed with water to remove remaining SO_3 , the reaction products were separated by the procedure of Chart 1. Other azoxy compounds were also treated by the same way.

2.4 Behavior of the products in sulfuric acid Various compounds obtained as reaction products of the Wallach rearrangement were warmed in 90–97% sulfuric acid and the reaction mixture was worked up by the procedure of Chart 1.

2.5 Identification of the reaction products Hydroxyazobenzenes were prepared by diazo coupling of the corresponding phenols and diazonium salts.[13] *o*- and *p*-Hydroxyazobenzenes thus obtained were separated by column chromatography with benzene on silica gel G. The hydroxyazobenzenes obtained in the reaction using highly concentrated sulfuric acid were identified by direct comparison (mp and IR spectra) with these authentic samples[16-27] and by brown precipitates formation with copper

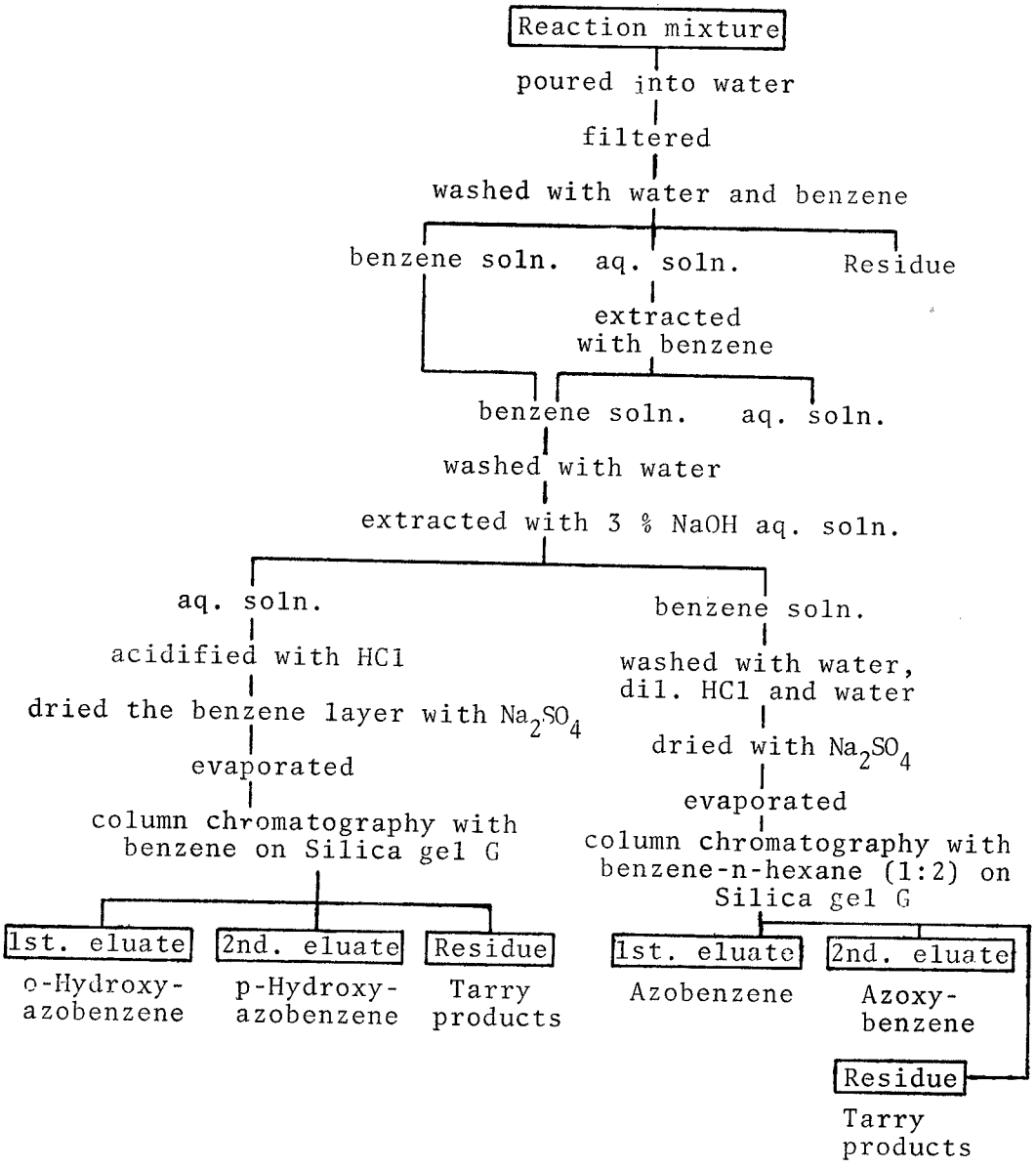


Chart 1 Separation of propucts

acetate in water-ethanol solution.[29),30)] Azobenzene, and 2,2′-and 3,3′-dimethylazobenzenes obtained by column chromatography were oxidized with hydrogen peroxide in acetic acid solution to give the correspondind azoxy compounds, which were identified by comparison (mp and IR spectra) with the starting azoxybenzenes. 4-Methyl-4-nitro-[12)] and 4-chloroazobenzene[11)] were also identified with the authentic sam-

ples (mp and IR spectra).

3 Result and Discussion

The reaction of azoxybenzene with 90–100% sulfuric acid occurred at faster rate than with 80–90% sulfuric acid. The yield of azobenzene became maximum when using 95% sulfuric acid, and the yield of *p*-hydroxyazobenzene decreased with increasing concentration of sulfuric acid as indicated in Fig. 1. The yield of *o*-hydroxyazobenzene was kept low in the whole range of sulfuric acid concentrations while the formation of tarry materials increased remarkably as the concentration of sulfuric acid became higher.

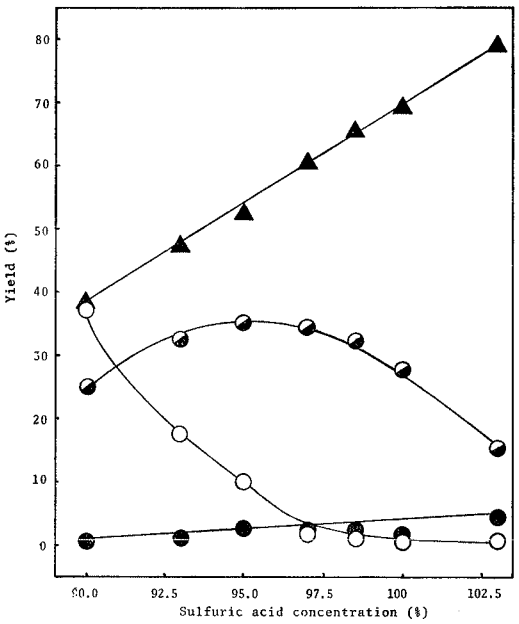


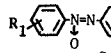
Fig. 1 Products distribution in the reaction of azoxybenzene with highly concentrated sulfuric acid

Reaction conditions—
Reaction temperature ; 80°C Reaction time ; 10min. Starting material ; 1g (5.4mmol) Sulfuric acid ; 15ml
● ; *o*-Hydroxyazobenzene ◑ ; Azobenzene
○ ; *p*-Hydroxyazobenzene ▲ ; Tarry products

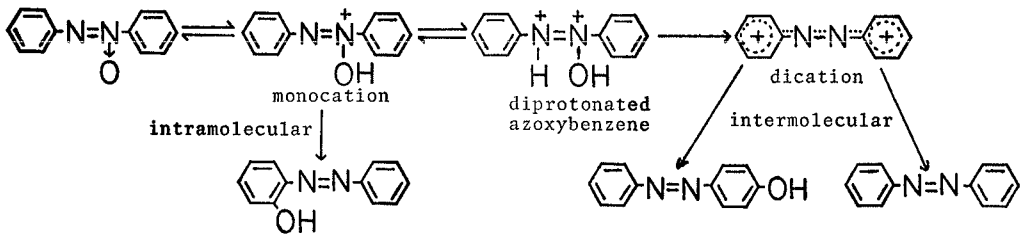
The results of the reaction of other azoxybezenens with 100% and 80 or 85% sulfuric acid are summarized in Table 1. The yield of azobenzenes and tarry products became generally high in higher concentrated sulfuric acid. The yield of *p*-hydroxyazobenzenes in the Wallach rearrangement using 80–90% sulfuric acid was remarkably higher than that in near 100% sulfuric acid.

When azoxybenzenes was treated with moderately diluted sulfuric acid (80–90%), it was known that *p*-hydroxyazobenzenes is formed as the main product of the Wallach rearrangement with concomitant formation of *o*-isomers and azobenzenes.[1-3] The mechanism of the Wallach rearrangement has been generally accepted by a tracer experiment using heavy oxygen[31] and by a nmr study[32] as indicated in the following scheme.

Table 1 The Behavior of azoxybenzenes in highly concentrated sulfuric acid

	g (mmol)	H_2SO_4 (%)	(ml)	Reaction conditions Time(min)	Temp.(°C)	Product yield (%) *o-Hydroxyazo-compounds*	*p-Hydroxyazo-comounds*	*Azo compounds*	Recovered starting materials (%)	Tarry products (%)
R_1;H	1.0(5.4)	100	15	10	80	trace	2.0[22]	39.4[7]	trace	58.3
R_2;	10 (54)	80	30	120	80	43.5[16]	6.2	trace	25.7	trace
R_1; 2-CH_3	1.0(4.42)	100	15	40	80	0.5[17]	4.7[17]	47.3[18]	trace	47.0
R_2; 2'-CH_3	2.0(8.84)	80	42	30	70	50.9	Not detected	30.3	trace	11.7
R_1; 3-CH_3	1.0 (4.82)	100	15	10	80	0.3[18]	0.6[a]	6.0[18]	trace	91.2
R_2; 3'-CH_3		80	42	40 × 60	85	53.4	4.4	trace	28.0	trace
R_1; 4-CH_3	1.0 (4.85)	100	15	200 × 60	Room Temp.	1.4[19]	8.2[b]	6.0[28]	trace	80.0
R_2: H		80	30	4 × 60	32	50.5	1.0	8.0	20.3	trace
R_1; 4-Cl	1.0 (4.13)	100	15	80	80	1.1[20]	4.1[c]	10.0[11]	trace	84.8
R_2; H		80	30	60	80	33.9	7.1	39.2	3.0	trace
R_1; H	2.0 (8.22)	103	15	10	80	11.2[21]	6.4[d]	6.0[12]	trace	76.4
R_2; 4'-NO_2		85	15	60	80	54.7	4.6	trace	35.9	1.5

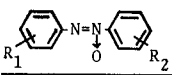
a) 2-Hydroxy-5,3'-dimethylazobenzene[24] b) 2-Hydroxy-4-methylazobenzene[25]
b) 2-Hydroxy-4'-chloroazobenzene[26] d) 2-Hydoxy-4'-nitroazobenzene[27]



80–90% Sulfuric acid which has been so far used for the Wallach rearrangement contains water molecules and H_3O^+ as main components. We now consider the behaviors in near 100% sulfuric acid which containes $H_2S_2O_7$ and $H_3SO_4^+$ no H_2O. Duffy and Hendry[6] reported that the UV absorption of azoxybenzenes in fuming sulfuric acid (corresponding 15% sulfuric acid) is shifted to longer wavelength than that in 90% sulfuric acid. For example azoxybenzene exhibits absorption at $\lambda_{max.}$: 323nm (Acidified ethanol), $\lambda_{max.}$: 390nm (90% H_2SO_4), $\lambda_{max.}$ 464nm (fuming sulfuric acid), showing the formation of different chemical species in highly concentrated sulfuric acid.

Since the formation of SO_3 by self-dissociation of 100% sulfuric acid has been suggested,[33] we examined the reaction of azoxybenzenes with SO_3 as indicated in Table 2. The distribution of products differs from that in highly concentrated sulfuric acid. As the sulfuric acid concentration becomes near 100%, the amount of $H_3SO_4^+$ in sulfuric acid increases rapidly as predicted by the following equations.[34] We examined the behavior of several Wallach rearrangement products in highly concen-

Table 2 The reaction of azoxybenzenes with sulfur trioxide[a)]

		g (mmol)	Reaction time(hr)	Product yield (%) *o-Hydroxyazo compounds*	*p-Hydroxyazo compouns*	*Azo compounds*	Recovered starting (%) materials	Polymer (%)
H	H	1.56 (6.75)	40	2.20	6.70	trace	62.7	10.3
		0.81 (4.10)	96[b)]	4.02	12.40	trace	78.9	5.6
2-CH_3	2'-CH_3	1.86 (6.75)	40	0.38	2.15	56.5	24.4	13.4
H	4'-CH_3	0.96 (4.76)	40	3.14[c)]	5.51	33.7	55.8	2.4
H	4'-Br	0.80 (2.92)	40	Not detected	2.40	1.2	88.0	trace

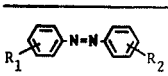
Reaction conditions: at room temperature; in nitromethane 10 ml + chloroform 15 ml
a) An equimolar amount of sulfur trioxide to azoxybenzenes was used. b) Nitromethane 30 ml was used. c) 2-Hydroxy-4'-methylazobenzene.

$$2H_2SO_4 \rightleftharpoons H_3SO_4^+ + HSO_4^-$$

$$2H_2SO_4 + SO_3 \rightleftharpoons H_3SO_4^+ + HS_2O_7^-$$

trated sulfuric acid forcussing our attention on their interconversions. The results are shown in Table 3. Since a large amount of tarry products was formed by treatment with 100% sulfuric acid in each case, 90–97% sulfuric acid was alternatively used. It was

Table 3 The behavior of the Wallach rearrangement products in sulfuric acid

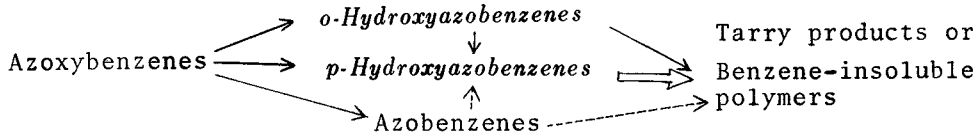
		g (mmol)	Reaction conditions H_2SO_4 (%)	H_2SO_4 (ml)	Time (min)	Temp. (°C)	Reaction products or recovered materials (%) *o-Hydroxyazo-compounds*	*p-Hydroxyazo-compounds*	*Azo compounds*	Tarry products (%)
2-OH	H	1.0 (5.04)	90	15	60	65-67	67.4	12.4	Not detected	0.3
4-OH	H	1.0 (5.04)	92	15	60	70-72	Not detected	20.0	Not detected	80.0
2-OH 6-CH_3	2-CH_3	0.06 (0.03)	95	5	40	47-50	31.0	7.3	Not detected	7.3[a)]
4-OH	4-CH_3	0.14 (0.06)	95	5	40	47-50	Not detected	11.5	Not detected	trace[b)]
H	H	0.20 (0.08)	97	5	30	50-52	Not detected	0.32	94.6	trace
4-CH_3	H	0.82 (0.43)	95	5	30	54-55	Not detected	2.9[c)]	95.6	trace

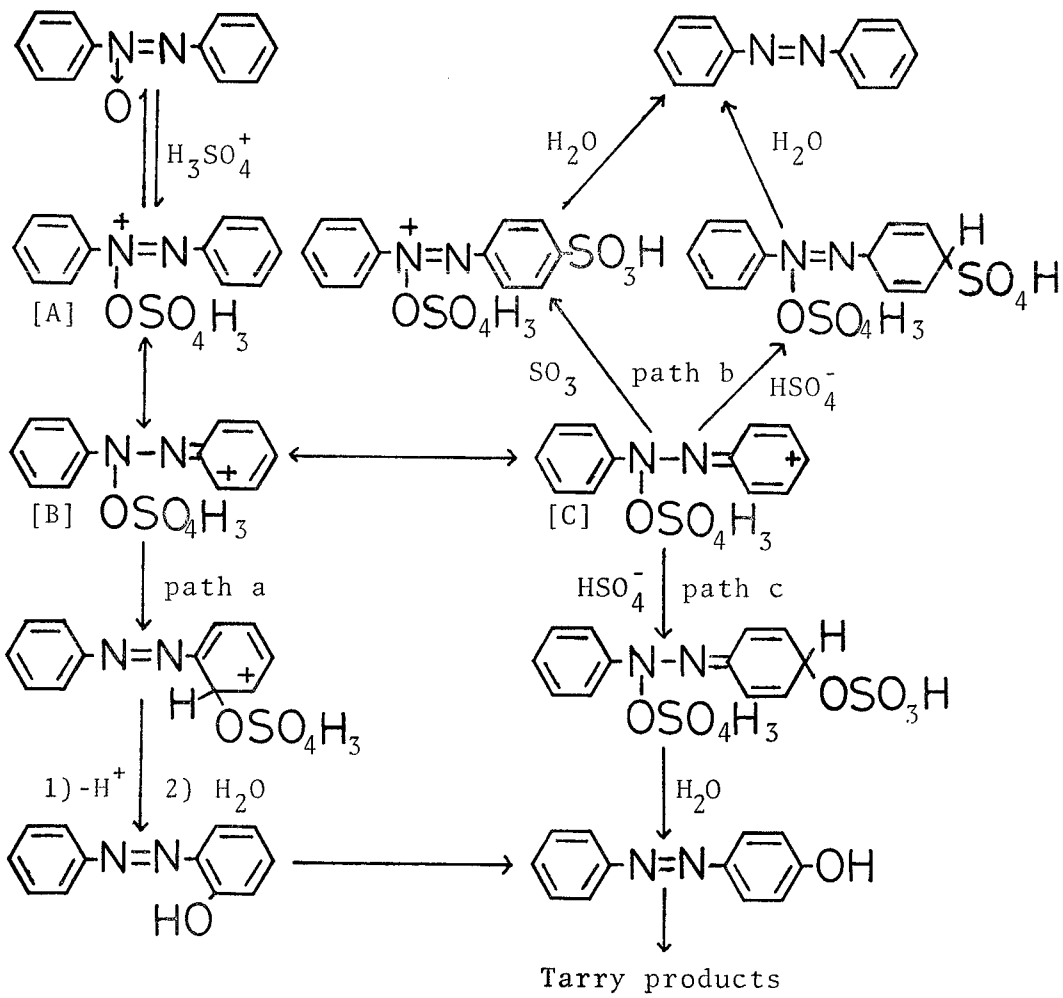
a) Benzene-insoluble material(25 mg;45.5 wt. %) was obtained. b) Benzene-insoluble material(140 mg;100 wt. %) was obtained. It was not molten below 230 °C. c) An alkali-soluble yellow material having mp 128-130 °C was obtained.

found that *o*-hydroxyazobenzenes were converted into their *p*-isomers in moderate yields and that *p*-hydroxyazobenzenes were formed from azobenzenes in low yields. Benzene-insoluble polymers were obtained from 2-hydroxy-6,2'-dimethylazobenzene and 4-hydroxy-4'-methylazobenzene accompanying with other products. Thus, the

reaction pathways of the Wallach rearrangement products in highly concentrated sulfuric acid may be summarized in Scheme 1.

On the basis of the above experimental results, possible reaction pathways of azoxybenzene in highly concentrated sulfuric acid are proposed as Scheme 2. A cationic species formed by the attack of $H_3SO_4^+$ to the oxygen atom of azoxybenzene is delocalized as shown by three resonance structures [A], [B] and [C]. The ortho





Scheme 1

rearrangement from [B] may occur via intramolecular migration of the OSO_4H_3 group (path a), while [C] seems to follow two different routes. One is a nucleophilic attack on the para position by SO_3 or by the sulfur atom of HSO_4^- leading to azobenzene (path b) and the other is a nucleophilic attack on the para position by an oxygen atom of leading to *p*-hydroxyazobenzene (path c).

Considering the results of Fig. 1 and Table 1, path b seems to be the main route and path c to be the minor one. The participation of SO_3 in the path b may be predominant only with methylazoxybenzenes as indicated in Table 2. On the other hand, since a large amount of tarry prodeucts or polymrs is formed by the action of the *p*-hydroxyazobenzenes with 90—97% sulfuric acid as shown in Table 3, most of tarry products seem to be derived from *p*-hydroxyazobenzenes in the reaction of azoxybenzenes with highly concentrated sulfuric acid. This suggests that path c is also important in the reaction of azoxybenzenes in highly concentrated sulfuric acid.

The authors wish to thank professor Teruo Matuura Kyoto University for helpful advice and discussion.

References

1) E. Buncel" *Mechanisms of Molecular Migrations*" Vol. 1 (Ed., B. S. Thyagarajan) Interscience Publ., New york, 1968 p 61
2) E. J. Shine, "Aromatic Rearrangement" Elsevier Publ. Co., Amsterdam, 1967 p 272
3) R. A. Cox and E. Buncel, "*The chemistry of hydrazo, azo and azoxy group*" Part 2 (Ed., S. Patai) John & Sons, New York, 1975 p 775
4) A. Lachmann, *J. Amer. Chem. Soc.*, **24**, 1178 (1902)
5) P. H. Gore and G. K. Hughes, *Aust. J. Chem. Res.*, **3A**, 136 (1950)
6) D. Duffy and G. K. Hendry, *J. Org. Chem.*, **33**, 1918 (1968)
7) E. Buncel and B. T. Lowton, *Can. J. Chem.*, **43**, 862 (1965)
8) E. Buncel and W. T. Strachan, *ibid.*, **48**, 377 (1970)
9) R. A. Cox, *J. Amer. Chem. Soc.*, **96**, 1056 (1972)
10) L. Zeichmeister and R. Rom, *Chem. Ber.*, **59**, 57 (1962)
11) E. Bamberger, *ibid.*, **29**, 728 (1896)
12) A. Angeli and K. Alesandry, *Atti. accad. Lincei*, **20**, 896 (1910) : *Chem. Absrtra.*, **5**, 3408 (1911)
13) L. G. Behr, *J. Amer. Chem. Soc.*, **76**, 3672 (1954)
14) D. Vigiavi and V. Sabatelli, *Gazz. Chem. Ltali*, **57**, 557 (1927) : *Chem. Abstra.*, **22**, 395 (1928)
15) L. Gattermann and H. Wieland, "*Praxis des Organischen Chemiker*" Walter de Gruter Co., Berlin, 1961 p 174
16) O. Wallach and L. Belli, *Chem. Ber.*, **13**, 525 (1800)
17) R. C. Former and A. Hantzsch, *ibid.*, **32**, 3099 (1899)
18) H. Klinger and R. Pitschke, *ibid.*, **18**, 2511 (1885)
19) W. Mcpheson and C. Boord, *J. Amer. Chem. Soc.*, **33**, 1530 (1911)

20) J. H. Hewit, *Chem. Ber.*, **26**, 2978 (1893)
21) A. Angeli and B. Valori, *Atti. accad Lncei*, **21**, 729 (1911) *Chem. Abstra.*, **6**, 2747 (1912)
22) E. Bamberger, *Chem. Ber.*, **33**, 3192 (1900)
23) G. E.Lewis and J. A. Reiss, *Aust. J. Chem.*, **19**, 1887 (1947)
24) G. E. Lewis and A. Hantzsch, *ibid.*, **19**, 1888 (1947)
25) W. Mcpheson and C. Boord, *J. Amer. Chem. Soc.*, **33**, 1531 (1911)
26) A. W. Smith and C. Boord, *ibid.*, **44**, 1451 (1922)
27) J. Yamamoto, K. Kagehi, H. Aimi, H. Hamada and M. Umezu, *Reports of the Faculty of Engineering Tottori University*, **9**, [1], 64 (1976)
28) W. Lischke, *Ann. Chem.*, **303**, 368 (1878)
29) M. Elkins and L. Hunter, *J. Chem. Soc.*, **1935**, 1958
30) D. K. Drew and J. K. Landquist, *ibid.*, **1928** 292
31) S. Oae, T. Fukumoto and M. Yamagami, *Bull. Chem. Soc. Jpn.*, **36** 601 (1963)
32) G. A. Olah, K. Dume, D. P. Kelly and Y. K. Mo, *J. Amer. Chem. Soc.*, **94**, 7438 (1972)
33) K. Outhi, "*Ryusan*" **7**, 141 (1954)
34) M. Liler "*Reaction mechanisms of sulfuric acid*" Academic Press., New york, 1973 p 11