RUSSIAN CHEMICAL REVIEWS
Uspekhi Khimii

December 1967

U. D. C. 547.556.4

THE REARRANGEMENT OF HYDRAZO-COMPOUNDS

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1. INTRODUCTION

In spite of the many investigations since the times of Zinin [1] and Hofmann [2], no satisfactory solution has yet been found to the problem of rearrangement as a whole.

The early papers report valuable experimental work. The labours of several chemists (Hofmann [2], Schultz and his coworkers [3-6], Jacobson and his coworkers [7,8], Täuber [9], Witt [10]) during the nineteenth century revealed four types of rearrangement—(1) benzidine, (2) biphenyline, (3) *o*-semidine, (4) *p*-semidine—a fifth rearrangement—*oo'*-biphenyl (in the benzene series)—being discovered by us [11] much later.

Special mention must be made of the work of Jacobson and his collaborators [12] and of Wieland [13], on the basis of which the intramolecular character of the rearrangement was demonstrated. Wieland [14] pointed out the possibility of obtaining hydrazobenzene hydrochloride by the action of dry hydrogen chloride on hydrazobenzene in ether. However, he found that, when certain *para*-substituted hydrazobenzenes were heated in an inert medium, the corresponding semidines were formed [15]. For a long time these observations were not developed further.

During the past two decades attention has been directed mainly at solving by kinetic methods the problem involved in the initial stage of rearrangement in the presence of ionised acids: does the hydrazo-compound react as a univalent or as a bivalent cation? No satisfactory answer has been obtained to this question.

References to what is often termed the "benzidine rearrangement" are usually concerned with the process occurring in an ionised acid medium, as a result of which benzidines and biphenylines [biphenyl-2,4'-diamines] are obtained. Small amounts of other substances are often disregarded.

An important aspect is the very little studied rearrangement in unionised acids. The reaction takes place in a heterogeneous medium, the composition of the products varying greatly with the conditions. The usual methods of investigation employed by organic chemists are applicable to these cases. It is sometimes possible to obtain good yields of monoprotonated hydrazo-compounds and to study some of their properties and reactions. At the same time the stepwise character of the process as a whole is determined: the salt of the hydrazo-compound formed in the first stage rearranges under the further action of the acid.

Not long ago we were able [16] to demonstrate, with hydrazonaphthalenes as examples, a special type of rearrangement produced by the action of heat. This so-called thermal rearrangement is especially complicated in the naphthalene series, where the results are often strongly solvent-dependent.

The present review first describes work on salts of hydrazo-compounds, together with some of their properties and reactions, then discusses rearrangement in acid media, and in conclusion considers rearrangement under the influence of heat.

2. SALTS OF HYDRAZO-COMPOUNDS—SOME OF THEIR PROPERTIES AND REACTIONS

Until recently information on the salts of hydrazo-compounds was confined in effect to Wieland's exploratory experiment [14]. A paper by Orelkin et al., [17] which contained an interesting underlying idea, did not contribute to progress in this field because the experiment was not properly thought out.

Solutions of hydrogen chloride in ether have proved most suitable for the preparation of salts of hydrazo-compounds, and they can be regarded as equilibrium systems:

$$[(C_2H_5)_2\overset{+}{O}H]\,\overline{X} \rightleftarrows (C_2H_5)_2O \ldots HX.$$

Since the acidity of the hydrogen chloride is approximately weakened as a result of intermolecular interaction in the ether, it is easy to prepare hydrochlorides of several hydrazo-compounds. To a solution of the hydrazo-compound, e.g. hydrazobenzene in ether at −8° to −10°C, an equimolecular amount of hydrogen chloride in ether is added rapidly in drops. The hydrochloride is filtered quickly (preferably in an atmosphere of nitrogen), the solution is made alkaline with methanolic sodium hydroxide, and it is oxidised with mercuric oxide, an equivalent quantity of azobenzene being obtained. Salt formation does not go to completion owing to dissociation of the hydrochloride, which is especially marked with the less basic compounds: with 2-chloro- and 3,3′-dichloro-hydrazobenzene, for example, 30–40% of the hydrazo-compound remains [unchanged] in solution, even if double the quantity of hydrogen chloride is taken.

Ethers other than diethyl ether—e.g. di-isopropyl and di-isopentyl ethers—can be used in the preparation of the salts. With hydrogen bromide 40–50% of the hydrobromides of 3-chloro- and 3,3′-dichloro-hydrazobenzene can be isolated.

By no means all hydrazo-compounds form stable salts: it has proved impossible to isolate salts of 4,4′-substituted derivatives. Table 1 gives the yields of salts of several hydrazo-compounds prepared by the method outlined for hydrazobenzene hydrochloride. If in expts. 10 and 20, immediately after precipitation of the hydrochlorides, the whole mixture is made alkaline and is oxidised with mercuric oxide, 70% and 90% respectively of the original hydrazo-compounds are regenerated as the azo-compounds.

Salts of hydrazonaphthalenes cannot be isolated. However, their existence can be demonstrated as follows: 0.002 mole of 1,1′-, 1,2′-, or 2,2′-hydrazonaphthalene is dissolved in the minimum quantity of dioxan, the solution is diluted with ether at −8° to −10°C, and 1 mole of hydrogen chloride in ether is instantly added. A copious, very finely divided precipitate comes down; the whole mixture is made alkaline and oxidised with mercuric oxide as quickly as possible. The initial hydrazo-compounds are regenerated to the extent of 70–75%. Visual inspection shows that precipitates of the hydrochlorides of the corresponding diamines (calculated quantities) are present here in only small amount.

TABLE 1. Salts of hydrazo-compounds, their basic strengths, and rates of rearrangement in 95% acetic acid at 20°C.

Expt. No.	Hydrazo-compound	Yield of hydrazo-salt, %	Chloroaniline with which basic strength is compared	Duration of reaction between hydrazo-cpd. and acetic acid	Loss of hydrazo-cpd., %
1	Hydrazobenzene	92	between 2,4- and 2,5-di-	3 h	50.5
2	2-Chlorohydrazobenzene	66	between 2,4,5-tri- and 2,6-di-	26 h	43.3
3	3-Chlorohydrazobenzene	88	between 2,4,5-tri- and 2,6-di-	146 h	53.1
4	4-Chlorohydrazobenzene	13	between 2,4,5-tri- and 2,6-di-	26 h	64.0
5	2,2′-Dichlorohydrazobenzene	–	≪ 2,3,4,5,6-pentachloro-	720 h	trace
6	3,3′-Dichlorohydrazobenzene	54	between 2,4,6-tri- and 2,3,4,6-tetra-	720 h	3.0
7	4,4′-Dichlorohydrazobenzene	–	< 2,6-dichloro-	120 h	63.0
8	2-Methylhydrazobenzene	13	between 2,5-di- and 2,4,5-tri-	60 min	51.0
9	3-Methylhydrazobenzene	90	< 2,5-dichloro-	60 min	54.0
10	4-Methylhydrazobenzene	22(70)	> 2,5-dichloro-	8 min	57.4
11	2,2′-Dimethylhydrazobenzene	10	2,4,5-trichloro-	8 min	42.5
12	3,3′-Dimethylhydrazobenzene	90	< 2,5-dichloro-	8 min	47.4
13	4,4′-Dimethylhydrazobenzene	–	< 2,4-dichloro-	10 min	33.0*
14	2-Methoxyhydrazobenzene	–	< 2,5-dichloro-	30 s	50.0
15	3-Methoxyhydrazobenzene	26	< 2,5-dichloro-	60 min	50.0
16	4-Methoxyhydrazobenzene	–	–	30 s	40.1*
17	2,2′-Dimethoxyhydrazobenzene	10	between 2,4,5-tri- and 2,6-di-	30 s	53.6*
18	3,3′-Dimethoxyhydrazobenzene	51	> 2,4,5-trichloro-	8 min	32.0
19	4,4′-Dimethoxyhydrazobenzene	–	–	2 s	100.0*
20	2,2′-Diethoxyhydrazobenzene	65(90)	between 2,4,5-tri- and 2,6-di-	10 s	40.0*
21	3,3′-Diethoxyhydrazobenzene	29	> 2,4,5-trichloro-	10 min	40.0
22	4,4′-Diethoxyhydrazobenzene	–	–	2 s	100.0*
23	1,1′-Hydrazonaphthalene	–	–	10 s	40.8*
24	1,2′-Hydrazonaphthalene	–	–	30 s	35.1*
25	2,2′-Hydrazonaphthalene	–	–	60 s	41.8*

* Hydrazo-compound previously dissolved in dioxan.

Basic Strength of Certain Hydrazo-Compounds

Several hydrazo-compounds can be compared in basic strength with chloroanilines. Relatively definite results are obtained with hydrazo-compounds which form the more stable salts.

The procedure is to prepare the hydrobromide of a suitable chloroaniline (0.002 mole) in ether (20 ml), into which is immediately run a solution of the hydrazo-compound (0.002 mole) in ether (20 ml), the temperature lying between −8° to −10°C. After 2 min the precipitate is quickly filtered off (preferably under nitrogen), and both precipitate and solution are made alkaline and are oxidised. The quantity of azo-compound obtained indicates the distribution of the acid between the hydrazo-compound and the chloroaniline†.

With unstable salts of hydrazo-compounds the situation is greatly complicated: a pair of chloroanilines is selected of most closely similar basic strengths, and such that the rearrangement would be strongly retarded in the presence of the first member of the pair, whereas it would occur readily in the presence of the second member. As before, the hydrobromide (sometimes also the hydrochloride) of the chloroaniline having been obtained in ether and the hydrazo-compound added, after 2–3 min the whole mixture is neutralised and oxidised, the quantities of amines formed and of hydrazo-compound remaining then being determined.

Reactions of Hydrochlorides of Hydrazo-Compounds

Hydrazobenzene and 3,3′-dimethylhydrazobenzene hydrochlorides have been tested. Experiments 1 and 6 (Table 2) give for comparison results of the ordinary rearrangement of these hydrazo-compounds in ethereal hydrogen chloride. It is seen that considerable quantities of *oo′*-diamines are

† For reasons which have not been elucidated, 3,4,5-trichloroaniline and also 2,3,5,6-tetrachloroaniline are unsuitable for comparison with hydrazo-compounds.

TABLE 2. Transformation of hydrochlorides of hydrazo-compounds.

Expt. No.	Hydrazo-compound	Solvent	Temp., °C	Atm	Products, %						
					benzidines	biphenylines	oo'-diamines	o-semidines	anilines	azo-cpds.	hydrazo-cpd. reformed
1*	Hydrazobenzene	ether*	—10	N_2	53.4	24.1	7.2	7.0	0.4	0.4	—
2	»	ether	20	N_2	16.2	12.1	—	5.1	16.5	16.8	26.3
3	»	--	20	N_2	13.0	8.1	—	4.1	24.0	24.5	15.6
4	»	—	80	N_2	15.0	11.5	—	5.9	26.2	26.9	7.7
5	»	—	cooling mixture	HCl	38.2	26.6	7.4	18.4	1.0	0.9	—
6*	3,3'-Dimethyl-hydrazobenzene	ether*	—10	N_2	32.6	18.1	16.5	23.0	1.5	1.6	—
7	»	ether	20	N_2	14.2	9.2	—	5.1	24.5	25.2	14.2
8	»	—	20	N_2	15.0	8.5	—	6.5	25.1	25.6	12.2
9	»	—	80	N_2	9.7	6.4	—	8.3	26.8	27.0	13.0
10	»	—	cooling mixture	HCl	27.9	19.0	18.1	20.7	1.6	1.7	—

* Results of the usual rearrangement of hydrazo-compounds in ethereal solution.

obtained besides benzidines, biphenylines, and *o*-semidines. The hydrochlorides of hydrazo-compounds break down after prolonged storage at 20°C in the apparatus in which they had been prepared in ether by treatment of the hydrazo-compound with hydrogen chloride at a 1 : 1 molar ratio. The hydrogen chloride formed by dissociation of the salt gradually brings about rearrangement of part of the salt. It is remarkable that no *oo'*-diamines at all are formed in the absence of a considerable excess of acid. Large quantities of amines and azo-compounds result from the redox reaction

$$2\,[RNH{-}\overset{+}{N}H_2R]\,\overline{Cl} \rightarrow RN{=}NR + 2\,R\overset{+}{N}H_3\,\overline{Cl}$$

which inevitably accompanies the rearrangement. This is revealed when, for example, hydrazobenzene hydrochloride (0.01 mole) reacts with an equimolecular quantity of another suitable compound, e.g. 2,2'-dimethoxyhydrazobenzene in ether. Neither benzidine nor aniline can be detected after such a mixture has been allowed to stand at 0°C for 24 h. The compounds obtained, besides partly regenerated hydrazobenzene and products of the rearrangement of 2,2'-dimethoxyhydrazobenzene, are 2,2'-dimethoxyazobenzene (5.3%), azobenzene (28.8%), and *o*-anisidine (32%). The proceeds by gradual conversion of the 2,2'-dimethoxyhydrazobenzene into the hydrochloride; some of this salt rearranges under the influence of traces of hydrogen chloride, while some of it, being involved in the redox reaction, acts mainly as an oxidant.

Experiments 3, 4, 8, and 9 in Table 2 give results for the breakdown of individual hydrochlorides in a gentle current of dry nitrogen, the apparatus being cooled externally to 20° and heated at 80°C. In expts. 5 and 10 the hydrochlorides were decomposed in an atmosphere of dry hydrogen chloride with external cooling by means of ice and salt. In expt. 4 about half the benzidine was obtained in the form of the monohydrochloride, which was sparingly soluble in water, and this suggested that with rise in temperature hydrazobenzene hydrochloride rearranged without the participation of a second molecule of acid; this would seem to be indicated by the material balance with respect to acid and amino-compounds during the reaction.

However, it was soon shown [18] that hydrochlorides of amino-compounds catalyse the disproportionation of free hydrazo-compounds at elevated temperatures. When, for example, an equimolecular mixture of hydrazobenzene and aniline hydrochloride is heated at 105–110°C for 15 min, disproportionation of the hydrazobenzene reaches 80%; this reaction is catalysed also by weak acids (benzoic, acetic, and butyric acids).

In the mechanism of the reaction very small amounts of hydrogen chloride, resulting from dissociation of the amine hydrochlorides, combine with the hydrazo-compound to form the corresponding hydrochloride, which undergoes a redox reaction. Among the rearrangement products it is possible to detect only traces of *o*-semidines, which are formed by the "thermal" rearrangement of hydrazo-compounds in the absence of acids (see Table 5).

So Called Diacid Salts of Hydrazo-Compounds

Pongratz et al. [19] reported the preparation of hydrazobenzene dihydriodide

$$[C_6H_5\overset{+}{N}H_2 + \overset{+}{N}H_2C_6H_5]I_2^{2-}$$

by the action of a large excess of methyl iodide on hydrazobenzene. A check revealed, however, that the "dihydriodide" could be fractionally crystallised from alcohol, when trimethylphenylammonium iodide (1 mole) and aniline hydriodide (2 moles) were isolated. This product has been synthesised also by the action of a large excess of methyl iodide on aniline [20].

The second diacid salt of hydrazobenzene was the dihydrochloride, Orelkin's "green salt" [17]. When Orelkin's experiment was repeated, a greenish product was obtained which proved to be a mixture of substances resulting from the rearrangement and the disproportionation of hydrazobenzene. Thus later references by Hammond [21] and by Carlin [23] to diacid salts of hydrazo-compounds are devoid of foundation.

Special experiments showed [24] that the formation of appreciable amounts of diacid salts of *N*-methyl-*N'*-phenylhydrazine [25] is excluded in both ethereal and benzene–toluene solutions of hydrogen chloride and hydrogen bromide. Monoprotonated aliphatic–aromatic hydrazines are evidently very weak bases, and double protonation of them is greatly hindered. This must apply even more to the double protonation of considerably more feebly basic substances such as hydrazo-compounds, many of which rearrange very rapidly in weak acids at ordinary temperatures (see Table 1).

3. REARRANGEMENT IN ACID MEDIA

Tables 3 and 4 give results for the rearrangement of hydrazo-compounds in unionised and in ionised acids respectively. The principal representatives selected were hydrazobenzene (I), 2,2'-dimethylhydrazobenzene (II), 3,3'-dimethylhydrazobenzene (III), 4,4'-dimethylhydrazobenzene (IV), 2,2'-dimethoxyhydrazobenzene (V), and 2,2'-diethoxyhydrazobenzene (VI). It is evident from Table 3 that results for the rearrangement differ markedly: in unionised acids the yields of benzidines are not very high; however, far larger quantities of biphenylines are obtained than in ionised acids. A more interesting fact, perhaps, is that with hydrazobenzene and 3,3'-dimethylhydrazobenzene were encounter new substances, *oo'*-diamines, while the quantities of *o*-semidines also increase sharply.

TABLE 3*. Rearrangement in unionised acids.

Expt. No.	Hydrazo-cpd.	Acid	Solvent	Temperature, °C	Products, %					
					benz-idines	biphenyl-ines	oo'-diamines	o-semidines	anilines	azo-cpds.
1	(I)	HCl	benz–tol	–10	36.4	29.6	12.8	12.5	0.4	0.4
2	(I)	HCl	—	from –10 to –15	21.7	20.2	17.6	29.0	1.5	1.7
3	(I)	HBr	ether	–10	33.6	30.6	7.5	16.0	1.5	1.6
4	(I)	HBr	—	from –10 to –15	17.7	18.4	10.5	25.5	11.5	1.3
5	(II)	HCl	ether	–10	44.7	25.0	—	1.5	10.5	11.5
6	(II)	HBr	ether	–10	41.1	30.4	—	9.5	6.8	6.0
7	(II)	HBr	—	from –10 to –15	14.5	16.3	—	23.0	21.0	7.0
8	(IV)	HCl	ether	–10	—	—	—	76.1	8.5	8.2
9	(V)	HBr	ether	–10	14.0	18.2	—	18.5	20.0	18.1
10	(VI)	HCl	ether	10–15	48.7	18.8	—	9.2	2.8	2.4

* See also Table 2 (Expts. 1 and 6).

TABLE 4. Rearrangement in ionised acids.

Expt. No.	Hydrazo-cpd.	Alcohol concn., %	Products, %				
			benzidines	biphenyl-ines	o-semi-dines	anilines	azo-cpds.
1	(I)	99.9	75.5	19.0	2.3	1.3	1.3
2	(I)	95.0	73.0	19.4	2.2	2.3	2.4
3	(I)	95.0	56.5	23.8	2.6	8.1	8.0
4	(I)	85.0	79.0	16.9	1.4	1.1	1.1
5	(I)	75.0	81.2	15.2	1.0	1.1	1.1
6	(I)	60.0	83.2	13.5	0.9	0.9	0.9
7	(I)	45.0	84.3	12.6	0.7	0.9	1.0
8	(II)	95.0	87.0	10.9	0.7	0.5	0.5
9	(III)	95.0	79.2	11.0	3.0	2.0	2.3
10	(IV)	95.0	—	—	58.1	23.0	16.1
11	(V)	99.9	65.7	16.9	2.6	4.7	4.5
12	(VI)	99.9	76.0	8.0	4.4	2.5	2.5

Rearrangement in Unionised Acids[24]

The hydrazo-compound (0.01 mole) is completely dissolved in absolute ether or a mixture of absolute benzene and absolute toluene (benz–tol) in the proportions 2 : 1, and a solution of hydrogen chloride or hydrogen bromide (3–4 moles) in the same solvents is added at between –8° and –10°C. In expt. 10 (Table 3) an ethereal solution of the acid (4 moles) is added at once to a solution of the hydrazo-compound in ether. When solvents are not used, a slow stream of dry hydrogen chloride or hydrogen bromide is passed over the surface of the finely divided hydrazo-compound, the apparatus being gently shaken in a mixture of ice and salt.

The almost colourless aqueous solutions of the reaction products are again shaken with ether, the feebly basic *o*-semidines and azo-compounds being extracted. *o*-Semidines can be determined quantitatively by titration with nitrite.

It is interesting that brominated *o*-semidines—2-amino-4′-bromodiphenylamine and 2-amino-4′-bromo-2′,3-dimethyldiphenylamine—are formed by the action of dry hydrogen bromide on crystalline hydrazobenzene and 2,2′-dimethylhydrazobenzene. Large quantities of aniline (expt. 4) and of *o*-toluidine (expt. 7) are also obtained. These substances result from a secondary reaction: the hydrobromides of the hydrazo-compounds which are formed are reduced by hydrogen bromide to anilines with simultaneous bromination of the substances—the *o*-semidines—which are most readily brominated in the reaction mixtures. Benzidine is reprecipitated as the sulphate; other benzidines are salted out from strongly acidified solutions and purified. The filtrates are used to determine anilines, which are volatile in steam, *oo*′-diamines, and biphenylines; these last are easily separated after conversion into the dibenzoyl derivatives, by means of their differing solubilities in alcohol and in ether.

Rearrangement in Ionised Acids[26,27]

The process is conducted in aqueous–alcoholic solutions of hydrogen chloride; in some experiments anhydrous alcohol is used. A solution of hydrazobenzene (0.01 mole) in alcohol, which has been strongly cooled under nitrogen, is at once mixed with a solution of hydrogen chloride (0.1 mole), the total volume being 100 ml and the temperature ~ 0°C. After 2 h crystals of benzidine hydrochloride are separated and are converted into the sulphate. The alcohol is evaporated off at 10–20°C. The residue is diluted with water, the major portion of the acid is carefully neutralised, and the *o*-semidine and azobenzene are completely extracted with ether. The aqueous portion contains traces of benzidine, biphenyline, and aniline. The benzidine having been separated, the total biphenyline plus aniline is determined by diazotisation, the quantity of aniline being found after repeated distillation in steam. In expt. 3 (Table 3) (I) is added to the acid at 45–50°C during 15 min. Compounds (II) and (IV)–(VI) are added steadily to a solution of hydrogen chloride (0.1 mole) in alcohol (100 ml) at 0°C steadily over 30 min. After $1\frac{1}{2}$ h the reaction mixtures are treated as in the directions just given for (I), and also for rearrangement in unionised acids.

In part of the analysis investigators are usually guided by the data of Carlin et al.[28] (who employed a spectrophotometric method), according to which hydrazobenzene is completely converted, over a wide range of conditions in 95% ethanol, into a mixture of benzidine and biphenyline in the proportions 70 : 30. Actually, we have seen (Table 4) that the ratio of benzidine to biphenyline differs from the values obtained by Carlin, and moreover is closely connected with the alcohol concentration: in 95%, 75%, and 45% ethanol the proportions are respectively 79 : 21, 84 : 16, and 87 : 13 (compared with 92.8 in aqueous hydrochloric acid). With rise in temperature the quantity of benzidine diminishes appreciably relative to biphenyline and other substances, among which is *o*-aminodiphenylamine. Finally, the amounts of disproportionation product increase greatly with rise in temperature.

With regard to other hydrazo-compounds, according to Carlin and Odioso[22] the rearrangement of 2,2′- and 3,3′-dimethylhydrazobenzenes yields solely the corresponding benzidines‡. But it is well known in industry that, even under special conditions, secondary products are inevitably obtained together with *o*-tolidine. In alcoholic medium with hydrogen chloride (Table 4, expt. 8), however, ~ 11% of 3,3′-dimethylbiphenyl-2,4′-diamine is obtained. In the case of 3,3′-dimethylhydrazobenzene (Table 4, expt. 9) 11% of 2′,4-dimethylbiphenyl-2,4′-diamine and 3% of 2-amino-3′,4-dimethyldiphenylamine are obtained.

Ingold and Kidd[30] considered the intramolecular character of the rearrangement to be proved by the melting-point

‡ The same error has been made in a recent paper by Ingold and his coworkers[29], who consider that *o*-tolidine is obtained uncontaminated with its isomers.

diagrams of the mixtures of substances formed by the simultaneous rearrangement of 2,2′-dimethoxy- and 2,2′-diethoxy-hydrazobenzenes: according to their results the only substances obtained besides disproportionation products are pure 3,3′-dimethoxy- and 3,3′-diethoxy-benzidines, moreover in identical yield (73%). Actually, however, under Ingold and Kidd's conditions the yields in anhydrous ethanol are ~66% of 3,3′-dimethoxybenzidine (expt. 11) and 76% of 3,3′-diethoxybenzidine (expt. 12). Besides dianisidine ~ 20% of isomers are obtained, and in the case of diphenetidine up to 12% of isomers, which can be separated without loss of the main substances only by special acid purification.

Determinations by the Reviewer[24] indicate that hydrazobenzene rearranges more rapidly in ethereal than in 95%-ethanolic solutions of hydrogen chloride by factors of 30–40, and the rate of rearrangement in 99.9% ethanol exceeds that in 95% ethanol by a factor of ~ 150. The rates are incomparably higher in benzene–toluene solutions of hydrogen chloride than in ethereal solutions.

2,2′-Dimethylhydrazobenzene rearranges more rapidly than hydrazobenzene itself in ethereal solutions of hydrogen chloride by factors of ~ 1000, but more rapidly than in solutions of hydrogen chloride in 95% ethanol by a factor of only 4. Rates of rearrangement in ethereal and benzene–toluene solutions of hydrogen bromide exceed the rates in hydrogen chloride by factors of 10^5, results being comparable only in ethereal or in the benzene–toluene solutions.

In 95% ethanol hydrazobenzene rearranges at almost the same rate with hydrogen chloride and with hydrogen bromide. 2,2′-Dimethylhydrazobenzene rearranges twice as fast with hydrogen bromide as with hydrogen chloride.

Mechanism of the Rearrangement of Hydrazo-Compounds in the Presence of Acids

Not long ago almost all research workers considered that the rate of rearrangement in ionised acids was directly proportional to the first power of the concentration of the hydrazo-compound and the square of the concentration of protons[31]. The Reviewer published a paper opposing this hypothesis[26], and the protagonists of this theory found themselves compelled to re-examine their positions[32–37].

Hydrazo-compounds are unsuitable for important kinetic investigations, since their resemblance to diacid bases of the usual type is purely formal: although the rate of monoprotonation depends on the basic strength of the initial hydrazo-compound, the rate of the ensuing stage is related only indirectly to the basic strength of the monoprotonated molecule, being determined by a different property of the latter, its *stability in the presence of the acidic agent*. If the difference between the rates of the first and second stages is considerable, the illusion is created of a double protonation, which occurs with compounds capable of forming salts which are relatively stable to the further action of the acid (Table 1). In several cases (Table 1, expts. 13, 16, 17, 19, 20, and 22–25), however, the monoprotonated hydrazo-compounds are extremely unstable to acids: in other words, the rate of the second stage is very high. This simple fact becomes obvious from a knowledge of the salts of hydrazo-compounds; it proves the occurrence of a "spontaneous" rearrangement of monoprotonated hydrazo-compounds.

In the presence of acids rearrangement is invariably stepwise: the monoprotonated molecule which is formed rearranges *only under the further influence of the acid*. The very great difference between the results obtained in unionised and in ionised acids is probably due primarily to fundamental differences in the transition states produced. The reaction of crystalline hydrazo-compounds with hydrogen chloride or hydrogen bromide is apparently most characteristic of the former case. The process occurs in the solid phase, and can be represented as

$$[RNH—\overset{+}{N}H_2R]\,\bar{X} + H \rightleftarrows [RNH—\overset{+}{N}H_2R]\,X \ldots HX \rightarrow \text{Rearranged product}.$$

The presence of solvents has a fundamental influence: they change the strength of acids, and may to some extent dissolve the salts of hydrazo-compounds, with the result that rearrangement takes place partly in solution. Finally, the nature of the acid may very likely have an effect, as follows from a comparison of the results obtained with hydrogen chloride and with hydrogen bromide.

While disagreeing with the hypothesis of a spontaneous partial rearrangement put forward by Blackadder and Hinshelwood, the Reviewer considers that they have made a useful contribution in suggesting that in ionised acids a monoprotonated hydrazo-compound rearranges on the approach of a proton[37]. The transition state in aqueous and aqueous–alcoholic solutions can be written

$$RNH—\overset{+}{N}H_2R \quad H_3\overset{+}{O}.$$

In anhydrous alcohol the reaction is catalysed by the ethyloxonium ion. It is significant that, although the rate of the reaction is greater in 99.9% than in 95% ethanol by a factor of approximately 150, the results for the rearrangement of hydrazobenzene are almost the same (Table 4, expt. 1). And yet the results are affected by the nature of the solvent and of the acid. We have already seen that, when alcohol is diluted with water, the ratio of benzidine to biphenyline is increased. This ratio in 95% alcohol (87 : 13) is appreciably increased also by replacing hydrochloric with sulphuric acid. This may be linked with a specific effect of the unionised acid on the monoprotonated hydrazo-compound, which is probable also with rearrangement in weak acids.

From Table 1 it is possible to obtain a rough idea of the relative rates of rearrangement of a series of hydrazo-compounds, and also to find further support for the ideas on the mechanism of rearrangement. Acetic acid (95%) was used.

The rates of rearrangement of many hydrazo-compounds differ so greatly that it is not possible to express them on the same scale. In several cases, therefore, dioxan was added to slow down the rearrangement. This resulted in a marked diminution in the reaction velocity: thus in 95% acetic acid the conversion of hydrazobenzene reaches 50.5% after 3 h, whereas when 8 ml of dioxan has been added a period of 800 h is required for the transformation to attain 68%; with 2,2′-dimethylhydrazobenzene a time of 8 min produces a change of 42.5%, but on the addition of dioxan 24 h will yield 62%.

The examples of hydrazonaphthalenes selected by Banthorpe, Hughes, and Ingold were an unhappy choice for ascertaining the true nature of the rearrangement. Because of the extreme instability of the monoprotonated hydrazo-compounds, the rates of the first and second stages differ little, and it is extremely difficult to divide the rearrangement into stages, the whole process occurring very rapidly (expts. 23–25). And yet, in contrast to

these workers' results, salts of 1,1'- and 1,2'-hydrazonaphthalenes can be detected in dioxan diluted with ether, as has been stated in the Section on the salts of hydrazo-compounds.

2,2'-Diethoxy- and 2,2'-dimethoxy-hydrazobenzenes (expts. 20 and 17) can usefully be contrasted with 1,1'- and 1,2'-hydrazonaphthalenes. Their rates of rearrangement are close to those for the hydrazonaphthalenes, and there can hardly be any doubt that the "kinetic order with respect to the acid" will not differ significantly from 1.0 here. But the example of 2,2'-diethoxyhydrazobenzene clearly reveals the presence of two stages in the rearrangement: the hydrochloride of the hydrazo-compound can be isolated in 60–65% yield (Table 1, expt. 20), obviously owing to the coarse-grained character of the precipitate in ether. In spite of a lower rate of rearrangement, the quantity of 2,2'-dimethoxyhydrazobenzene hydrochloride which can be isolated does not exceed 10% (see Table 1, expt. 17).

4,4'-Dimethoxy- and 4,4'-diethoxy-hydrazobenzenes are very interesting (expts. 19 and 22). Their rates of conversion in acids are especially high, ~ 80% of disproportionation products being formed, whereas the maximum quantity of *o*-semidines which can be isolated under special conditions does not exceed 10%. Clearly, there is no possibility of recovering intermediate products, but nevertheless the stepwise character of the whole process is demonstrated perfectly by these examples: as has been stated repeatedly, disproportionation products result from a secondary reaction, the interaction of two molecules of the monoprotonated hydrazo-compound. The figures given (80% and 10%) indicate that the rate of this bimolecular reaction considerably exceeds the rate of conversion of the monoprotonated hydrazo-compound into the *o*-semidine.

Remarks on the Rearrangement of 4,4'-Substituted Hydrazobenzenes

An increasing number of attempts have been made recently to establish by kinetic methods the mechanism of the rearrangement of 4,4'-substituted hydrazobenzenes. Carlin and Wich[23] found that the rearrangement of 4,4'-dimethylhydrazobenzene is of the second order with respect to the acid: the reaction products were *o*-semidine, *p*-toluidine, and *p*-azotoluene in the proportions 40 : 40 : 20. It has already been mentioned that in reality the proportions of these products are different—58 : 23 : 16 (Table 4, expt. 10)—the slight predominance of toluidine over azotoluene being explained, in the Reviewer's opinion, by the reducing action of alcohol on the monoprotonated molecule of the hydrazo-compound.

Dewar and McNicoll[38] obtained values of 1.58 and 1.51 for the kinetic order with respect to the acid in the cases of 4-chloro-4'-methylhydrazobenzene and 4-chloro-4'-t-butylhydrazobenzene respectively, but they did not ascertain the composition of the products of the rearrangement. The results obtained by the Reviewer indicate the proportions of *o*-semidine, anilines, and azo-compound to be 24 : 33.5 : 35.5 in the former case, and 38 : 25 : 28 in the latter case.

Shine and his coworkers[39,40] studied the rearrangement of 4,4'-di-t-butylhydrazobenzene and 4,4'-divinylhydrazobenzene; in the former case 45–54% of the hydrazo-compound underwent rearrangement, and 48–50% disproportionation. In the latter case the order of the reaction with respect to acid was found to be 1.0, but the products resulting from the interaction of the divinylhydrazobenzene and hydrogen chloride in ethanol remained unknown: in any case, they were stated to be neither a semidine nor disproportionation products. From what has been stated the authors' view cannot be accepted that a "benzidine rearrangement" is taking place here.

Thus in the course of the rearrangement of 4,4'-substituted hydrazobenzenes the monoprotonation of the hydrazo-compound is followed by two parallel reactions—rearrangement of the monoprotonated hydrazo-compound to an *o*-semidine, and interaction of the latter two monoprotonated molecules to give anilines and azo-compounds.

4. "THERMAL" REARRANGEMENT OF HYDRAZO-COMPOUNDS

Meisenheimer and Witte[41] discovered that, when 2,2'-azonaphthalene dissolved in alcoholic alkali is boiled with zinc dust, 1,1'-binaphthyl-2,2'-diamine is formed. These workers, and subsequently also Jacobson[12], interpreted this phenomenon as a rearrangement under the influence of the alkali, but it has been shown[16] that it is not the alkali but the heating which leads to rearrangement both of 2,2'- and of 1,1'-hydrazonaphthalene.

A few years later the products of the rearrangement were determined, though only qualitatively, by Večeřa et al.[42] as a result of the very prolonged heating (at 150°C) of hydrazobenzene and 2,2'-dimethylhydrazobenzene (as well as of 4-methylhydrazobenzene and 1,1'-hydrazonaphthalene). Almost at the same time the "thermal" rearrangement of 2,2'-hydrazonaphthalene was studied by Shine[43], who obtained satisfactory results after only a few years[44]. With regard to 1,1'-hydrazonaphthalene, the author himself admits that this case proved to be too difficult for him.

When studying the "thermal" rearrangement is is important to establish the optimum temperature conditions. Overheating leads to copious tar formation, which probably occurred in Večeřa's experiments.

Rearrangement of Hydrazo-Compounds of the Benzene Series

The compounds which the Reviewer has tested can be divided into two groups: the first comprises hydrazo-compounds which form disproportionation products almost exclusively, this group including 4-chloro-, 4-bromo-, and 4,4'-dichloro-hydrazobenzenes; the second group contains the principal hydrazo-compounds (Table 5). Heating was conducted in an atmosphere of nitrogen in sealed tubes. Products of rearrangement are formed as well as products of disproportionation, their quantity sometimes exceeding 25%. They are *o*- and *p*-semidines, with one or other isomer predominating in individual cases. 4-Methylhydrazobenzene gives not only 2-amino-5-methyldiphenylamine but also a second possible isomer—2-amino-4'-methyldiphenylamine—which had not been observed by Jacobson[45] in the acid rearrangement, and was not detected in Večeřa's "thermal" rearrangement[42].

In several cases considerable quantities of *p*-semidines appear, which are not formed at all in the rearrangement of the same hydrazo-compounds in acid media. Benzidines and biphenylines could not be detected in any appreciable quantities.

TABLE 5. "Thermal" rearrangement in the benzene series.

Substituted hydrazobenzene	Temp., °C	Duration of heating, h	Products, %			
			o-semidines	p-semidines	anilines	azo-cpds.
Hydrazobenzene	140—145	120	16.7	12.5	31.5	33.4
4-Chloro-	140—145	20	—	—	45.2	47.5
4-Bromo-	110	16	—	—	46.5	50.3
4-Methyl-	140—145	116	18.6	8.1	33.5	35.6
2,2′-Dimethyl-	140—145	120	8.3	13.1	36.0	38.0
3,3′-Dimethyl-	140	100	32.0	8.2	26.2	29.1
4,4′-Dimethyl-	140—145	100	15.5	—	38.0	38.2
2,2′-Dimethoxy-	120—125	26	16.0	9.2	28.5	40.2

Rearrangement of Hydrazo-Compounds of the Naphthalene Series—Influence of Solvents

Hydrazonaphthalenes are worthy of special attention in the study of the "thermal" rearrangement. The composition of the final products varies greatly depending on factors which have hardly any effect on the rearrangement of hydrazo-compounds of the benzene series. Attention has been paid mainly to the more complicated but also more interesting rearrangement of the 1,1′-isomer[46,47]. The rate of rearrangement is considerably greater in alcohols, ethylene glycol, and formamide than in other solvents. In ethanol at 100°C some 87% of the dissolved 1,1′-hydrazonaphthalene has decomposed after only 10 min, the corresponding proportions of the 1,2′- and 2,2′-isomers being 53% and 27% respectively; the rates are still higher in formamide. In benzene 52%, 11%, and 3.5% are obtained respectively, in acetonitrile 45%, 8%, and 3.5%, and in pyridine 23.5%, 3.4%, and 1.0% of transformed hydrazo-compounds. However, a far more important fact is that the quantitative composition of the rearrangement products is often linked with the nature of the solvent. These products can be divided into two groups according to the mechanism of their formation, which will be discussed below. The first group comprises *o*- and *p*-diamines and the 2,2′-binaphthyl-1,1′-imine [dibenzocarbazole] corresponding to the *o*-diamine; the second group comprises the *o*- and *p*-semidines. In weakly polar solvents (cyclohexane, benzene, toluene, 1,4-dioxan) the quantities of semidines sometimes exceed 50% of the total rearrangement products. The quantity of semidines diminishes with increasing polarity of the solvent. The addition to weakly polar solvents of water, having a high dielectric constant, may result in a considerable decrease in the yields of semidines; this occurs in benzene and in dioxan, but water has far less effect in experiments with ethanol and with pyridine.

It is interesting to trace the influence of solvents on the relative proportions of 1,1′- and 4,4′-diamines. The ratio of 1,1′- to 4,4′-diamine is usually 0.67, the latter being obtained as the formyl derivative, whereas the less basic 1,1′-diamine is obtained in the free state§.

The quantities of dibenzocarbazole also depend sometimes on the nature of the solvent: far more is obtained in hydrocarbons and alcohols, in amounts exceeding those of the 1,1′-diamine by factors of 3–4; in pyridine, however, the yields of the dibenzocarbazole are very low, only ~ 20% of those of the *oo*′-diamine.

§ There appears to be an omission in the Russian text, since there is no reference to the solvent in this sentence (Ed. of Translation).

Rearrangement in alcoholic alkali gives very interesting results for all three isomeric dibenzocarbazoles. In anhydrous methanol and ethanol ~ 25% of dibenzo[*ai*]-carbazole is obtained, together with more than 50% of the [*ag*] isomer and ~ 20% of the 2,2′-dinaphthylamine. If, however, metallic sodium has first been dissolved in dehydrated alcohol to obtain a 0.1 *N* solution of the alkoxide, rearrangement is just as rapid, but it is remarkable that no dibenzocarbazoles are formed at all.

Results for the rearrangement of 1,2′- and 2,2′-hydrazonaphthalenes are simpler[47]. The former isomer yields an *oo*′-diamine, a dibenzocarbazole, and 4-amino-1,2′-dinaphthylamine; disproportionation is insignificant. Just as with 1,1′-hydrazonaphthalene, very considerable quantities of the *p*-semidine are obtained in benzene and in dioxan; the semidine is almost completely absent in alcohols. Only the *oo*′-diamine and the dibenzocarbazole are formed from 2,2′-hydrazonaphthalene.

In view of the above observations on the influence of the solvent on the rearrangement, it seems possible that the molecules undergoing rearrangement may interact with the solvent molecules not only before but also during the reaction. Thus the solvent, by tending to increase the lability of the hydrazo-compound, facilitates the initial stage in the process and also influences the composition of the final products.

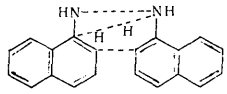
If rearrangement is difficult, *o*- and *p*-semidines are obtained; this occurs in the benzene series, and also in several cases with 1,1′- and 1,2′-hydrazonaphthalenes. In agreement with Večeřa's hypothesis[42] it is very likely that the formation of semidines results from the interaction of radicals produced by cleavage of the HN—NH bond in the hydrazo-compound. It must be added, however, that such a radical reaction should be associated with conditions consistent with our views on the rearrangement as an intramolecular process: in other words, either this is an intramolecular radical reaction[48] or, if the radicals are kinetically independent, their lifetime is extraordinarily brief.

Solvents having well defined polarity facilitate the rearrangement, resulting in a considerable diminution in the

TABLE 6. "Thermal" rearrangement of 1,1′-hydrazonaphthalene.

Solvent	ml	Duration of reaction, h	Products, %							Semidines total products %
			1,1′-diamine	dibenzocarbazole	4,4′-diamine	o-semidine	p-semidine	naphthylamine	azonaphthalene	
—	—	12	6.6	25.0	20.5	8.4	23.4	5.0	2.3	37.9
Cyclohexane	25	6.5	4.7	13.5	9.8	12.9	24.9	15.2	11.0	57.4
Benzene (abs.)	20	6.0	3.4	14.1	8.3	10.2	20.0	19.8	17.1	53.9
Benzene + H_2O	20	6.0	5.1	18.6	11.1	8.8	12.6	18.0	17.3	38.1
Toluene	20	6.0	4.7	16.9	12.2	10.2	11.8	18.8	16.0	39.4
Dioxan (abs.)	15	3.0	5.2	12.7	7.3	10.8	20.3	18.4	15.1	55.2
Dioxan + H_2O	13.5 1.5	3.0	12.7	12.1	18.0	8.7	14.1	14.0	9.5	34.8
Methanol	15	2.0	5.8	25.0	25.4	7.1	5.8	14.8	9.1	18.7
Methanol + Na	15	1.5	25.2	—	24.8	7.1	8.9	15.1	10.0	24.2
Ethanol	15	1.5	8.7	25.0	15.5	7.6	12.1	15.4	9.5	28.6
85% Ethanol	15	1.5	8.8	25.4	18.0	7.1	8.8	13.2	8.3	23.3
Ethanol + Na	15	1.0	33.7	—	24.4	7.0	4.7	13.0	9.2	16.8
Pyridine	10	4.0	23.2	4.0	17.2	7.5	8.3	18.5	13.5	26.6
Pyridine + H_2O	7.5 2.5	4.0	26.1	5.8	25.0	6.6	7.4	14.2	7.2	19.7
Ethylene glycol	15	2.0	10.7	39.4	24.1	1.1	9.0	7.2	1.8	12.0
Acetone	10	3.0	4.3	13.5	14.1	1.8	11.4	22.2	18.3	29.3
Acetonitrile	15	2.5	5.2	18.0	18.6	5.4	4.1	21.0	17.9	18.5
Formamide	15	3.0	21.4	16.0	52.6	—	—	—	1.1	0
Formamide – NH_4OH	14 1	2.5	40.4	11.2	33.5	traces		4.2	2.1	0
Formamide + pyridine + NH_4OH	6 4 1	2.0	36.7	8.6	30.0	1.0	1.8	8.5	5.1	3.6

quantities of semidines from 1,1′- and 1,2′-hydrazonaphthalenes and a corresponding increase in the yields of diamines and dibenzocarbazoles. It is very significant that none of the three isomeric dibenzocarbazoles, which are sometimes formed in very large quantities, can be obtained from the binaphthyldiamines, since this would require more severe conditions [16]. This has been verified with all three isomers. Hence they must be formed at the instant of rearrangement. A conceivable transition state is



when the bond between the nitrogen atoms is not finally broken, and nor are new bonds finally established.

Azo-compounds and anilines are formed by an intermolecular redox reaction. In the benzene series, where rearrangement is greatly hindered, predominantly disproportionation products are obtained; but in the naphthalene series disproportionation occurs mainly in the case of 1,1′-hydrazonaphthalene, where rearrangement goes far more easily than with the 1,2′- and 2,2′-isomers. It is obvious that the redox reaction also goes very rapidly with 1,1′-hydrazonaphthalene. A striking feature is that usually the quantity of naphthylamine considerably exceeds that of 1,1′-azonaphthalene, especially with alcohols, ethylene glycol, aqueous pyridine, and aqueous dioxan. It is very likely that in these solvents we must reckon with water and alcohols exerting a reducing action on 1,1′-hydrazonaphthalene.

In conclusion it must be noted that the exceptional instability of certain hydrazo-compounds permits their rearrangement to be accomplished at ordinary temperatures. Thus 1,1′-hydrazonaphthalene dissolved in a mixture of formamide and pyridine, for example, is completely decomposed after 3 weeks, 50% of the *oo′*-diamine, 2% of the dibenzocarbazole, 40% of the *pp′*-diamine, and ~ 2% of the azo-compound being obtained. The breakdown of 1,2′-hydrazonaphthalene in a mixture of formamide and pyridine is somewhat slower, ~ 80% of the *oo′*-diamine being obtained together with small quantities of the dibenzocarbazole and the azo-compound. 2,2′-Hydrazonaphthalene decomposes far more slowly: after extremely prolonged storage under freshly boiled alcohol filling the whole apparatus, ~ 16% of pure 1,1′-binaphthyl-2,2′-diamine was formed together with a large quantity of an azo-compound. 4,4′-Dimethoxy- and 4,4′-diethoxy-hydrazobenzenes decompose very rapidly in a mixture of pyridine and formamide: no hydrazo-compound remained in the reaction mixtures after only a few days. They were oxidised mainly to azo-compounds (45–50%); in addition, 25–30% of the corresponding arylhydroxylamines and small quantities of anilines were formed. In other solvents the decomposition of hydrazo-compounds takes place more slowly. For example, 4,4′-dimethoxyhydrazobenzene in a solution of dioxan and methanol disappears completely after storage for 1 month, ~ 50% of an azo-compound, 25% of the arylhydroxylamine, and 8% of the aniline being obtained.

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