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REARRANGEMENT OF HYDRAZO COMPOUNDS*

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Abstract—The rearrangement of hydrazo compounds in ionized and non-ionized acids has been investigated. The discussion of the mechanism in the presence of acids includes remarks on the rearrangement of 4,4'-disubstituted hydrazobenzenes. In the naphthalene series the thermal rearrangement of hydrazo compounds depends on the solvent used. The initial investigation included a study of the basicity of hydrazo compounds and the so-called dihydrohalides.

THE rearrangement of hydrazo compounds[1,2] is an involved process and still far from elucidated. Earlier work[3–6] providing valuable experimental data and theoretical generalizations described four types of rearrangement, namely benzidine, diphenylene, *o*-semidine and *p*-semidine, and only recently a fifth type involving *o,o'*-diphenyl (in benzene series) has been discovered.[7]

The intramolecular character of the rearrangement has been proved,[8,9] and it was found[10] that hydrazobenzene hydrochloride may be prepared by the action of dry HCl on hydrazobenzene in ether and that some *p*-substituted hydrazobenzenes when heated in an inert medium form corresponding semidines.[11]

During the last two decades the kinetics of the initial stage of the rearrangement in the presence of ionized acid has been investigated but whether the hydrazo compound reacts as a univalent or a bivalent ion has not been elucidated.

The "benzidine rearrangement" in ionized acid gives rise to benzidines and diphenylenes, small amounts of other substances not being taken into account.

In non-ionized acids the reaction proceeds in a heterogeneous medium with the

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* Translated by A. L. Pumpiansky, Moscow.

† Part of the investigation has been carried out in collaboration with L. G. Krolik.

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[2] A. W. Hofman, *Proc. Roy. Soc.* 12, 576 (1863); *Jahresber.* 424 (1863).

[3] G. Schultz, *Liebigs Ann.* 174, 201 (1874); G. Schultz and H. Schmidt, *Ber. Dtsch. Chem. Ges.* 11 1754 (1878); G. Schultz, *Liebigs Ann.* 207, 311 (1881); G. Schultz, H. Schmidt and H. Straszer, *Liebigs Ann.* 207, 348 (1881).

[4] P. Jacobson and W. Fischer, *Ber. Dtsch Chem. Ges.* 25, 992 (1892); P. Jacobson, F. Henrich and J. Klein, *Ibid.* 26, 688 (1893).

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[8] P. Jacobson, *Liebigs Ann.* 428, 84 (1922).

[9] H. Wieland and S. Gambarjan, *Ber. Dtsch. Chem. Ges.* 39, 1499 (1906).

[10] H. Wieland, *Ber. Dtsch. Chem. Ges.* 45, 484 (1912).

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TABLE 1. SALTS OF HYDRAZO COMPOUNDS, THEIR BASICITY, AND REARRANGEMENT IN 95% AcOH AT 20°

No.	Compd	Yield of salt % of theory	Chloroaniline compared in basicity with hydrazo compd	Reaction time AcOH	Amount of converted hydrazo compd % of theory
1	Hydrazobenzene	92	between 2,4- and 2,5-dichloro-	3 hr	50·5
2	2-Chlorohydrazobenzene	66	between 2,4,5-tri- and 2,6-dichloro-	26 hr	43·3
3	3-Chlorohydrazobenzene	88	between 2,4,5-tri- and 2,6-dichloro-	145 hr	53·1
4	4-Chlorohydrazobenzene	13	between 2,4,5-tri- and 2,6-dichloro-	26 hr	64·0
5	2,2′-Dichlorohydrazobenzene	—	<2,3,4,5,6-pentachloro-	720 hr	traces
6	3,3′-Dichlorohydrazobenzene	54	between 2,4,6-tri- and 2,3,4,6-tetrachloro-	720 hr	3·0
7	4,4′-Dichlorohydrazobenzene		<2,6-dichloro-	120 hr	63·0
8	2-Methylhydrazobenzene	13	between 2,5-di- and 2,4,5-trichloro-	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 sec	50·0
15	3-Methoxyhydrazobenzene	26	<2,5-dichloro-	60 min	50·0
16	4-Methoxyhydrazobenzene	—		30 sec	40·1*
17	2,2′-Dimethoxyhydrazobenzene	10	between 2,4,5-tri- and 2,6-dichloro-	30 sec	53·6*
18	3,3′-Dimethoxyhydrazobenzene	51	>2,4,5-trichloro-	8 min	32·0*
19	4,4′-Dimethoxyhydrazobenzene	—		2 sec	100·0*

TABLE 1. (contd.)

No.	Compd	Yield of salt % of theory	Chloroaniline compared in basicity with hydrazo compd	Reaction time AcOH	Amount of converted hydrazo compd % of theory
20	2,2′-Dimethoxy-hydrazobenzene	65(90)	between 2,4,5-tri- and 2,6-dichloro-	10 sec	40·0*
21	3,3′-Diethoxy-hydrazobenzene	29	>2,4,5-tri-chloro-	10 min	40·0
22	4,4′-Diethoxy-hydrazobenzene	—		2 sec	100·0*
23	1,1′-Hydrazo-naphthalene			10 sec	40·8*
24	1,2′-Hydrazo-naphthalene			30 sec	35·1*
25	2,2′-Hydrazo-naphthalene			60 sec	41·8*

* Hydrazo compound was preliminarily dissolved in dioxane.

resulting composition depending on experimental conditions. High yields of monoprotonated hydrazo compounds which may be obtained permit an investigation into their properties and conversions—the hydrazo salt first formed undergoing rearrangement upon further action of acid.

The rearrangement which takes place under the action of heat,[12] is particularly complicated in the naphthalene series the products depending on the nature of the solvent.

Salts of hydrazo compounds, some of their properties and conversions

Since the early work on hydrazo compounds[10] no additional experimental contributions have been made in support of the theoretical contributions.[13]

Salts of hydrazo compounds are best prepared in an ethereal solution of HCl which may be regarded as an equilibrium system:

$$(Et_2OH)X \rightleftarrows Et_2O \ldots HX \qquad (I)$$

Due to a weakening of HCl acidity by intermolecular reaction, hydrochlorides of some hydrazo compounds can be readily prepared in ether.

Most hydrazo compounds do not form stable salts. With 4,4′-substituted derivatives no salts could be isolated. Table 1 lists the yields of the salts prepared by the procedure described for hydrazobenzene hydrochloride. In experiments 10 and 20 the figures in brackets (70 and 90% respectively) are the yields obtained if after precipitation of the hydrochlorides the mixture was immediately made alkaline and oxidized by mercury oxide.

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[12] L. G. Krolik and V. O. Lukashevich, *Dokl. Akad. Nauk SSSR* 65(1), 37 (1949).

[13] B. P. Orelkin, A. T. Ryskal'chuk and M. A. Aizikovich, *Zh. Obshch. Khim.* 1, 696 (1931).

Although the isolation of the hydrazonaphthalene salts was unsuccessful, the experiment proves their existence.

Basicity of some hydrazo compounds. The basicity of some hydrazo compounds may be compared with that of chloroanilines. After preparing a suitable chloroaniline hydrobromide (0·002 mole) in ether (20 ml) a solution of hydrazo compound (0·002 mole) in ether (20 ml) was added at −8 to −10°. After 2 min the precipitate was rapidly filtered off and both the precipitate and the filtrate made alkaline and oxidized. The amount of the resulting azo compound indicated the distribution of the acid between hydrazo compound and chloroaniline.* The problem is more complicated with unstable salts of hydrazo compounds. Two chloroanilines as similar in basicity as possible must be chosen keeping in mind that the presence of one would hinder rearrangement whereas the other would not affect it. The chloroaniline hydrobromide (and sometimes hydrochloride) was prepared in ether, the hydrazo compound added and after 2–3 min the mixture neutralized and oxidized. The resulting amines and the remaining hydrazo compound were then determined.

Conversions of hydrochlorides of hydrazo compounds. Experiments were carried out with hydrazobenzene and 3,3′-dimethylhydrazobenzene hydrochlorides. In experiments 1 and 6 (Table 2) the products of rearrangement in ethereal solutions of HCl are presented for comparison. Experiments 2 and 7 show the degradation of hydrochlorides of the same hydrazo compounds after prolonged storage at 20° in the same apparatus in which they were prepared in ether with one molecule of HCl. The HCl resulting from salt dissociation gradually leads to the partial rearrangement of the salt. Both in experiments 2, 7 and 3, 4, 8, 9, not involving considerable excess of acid, no *o,o′*-diamines were found. The large amounts of amines and azo compounds were due to the oxidation–reduction (II) accompanying the rearrangement:

$$2(\mathrm{RNH{-}\overset{+}{N}H_2R})\overset{-}{\mathrm{Cl}} \rightarrow \mathrm{RN{=}NR} + 2\mathrm{R\overset{+}{N}H_3}\overset{-}{\mathrm{Cl}} \qquad \mathrm{(II)}$$

For example, the reaction of hydrazobenzene hydrochloride (0·01 mole) with an equimolecular quantity of another suitable compound, e.g. 2,2′-dimethoxyhydrazobenzene in ether, after standing for a day at 0° revealed neither benzidine nor aniline. Besides the partially regenerated hydrobenzene and rearrangement products of 2,2′-dimethoxyhydrazobenzene the mixture consisted of 2,2′-dimethoxyazobenzene (5·3% of theory), azobenzene (28·8% of theory) and *o*-anisidine (32% of theory). The 2,2′-dimethoxyhydrazobenzene is gradually converted into hydrochloride and a part of this salt undergoes rearrangement under the action of traces of HCl while the remainder is involved in the redox reaction and acts mostly as an oxidizing agent.

Experiments 3, 4, 8 and 9 show the degradation of isolated hydrochlorides in a slow current of dry nitrogen with external cooling to 20° or heating to 80°. In experiments 5 and 10 hydrochlorides were degraded in dry HCl and external cooling by ice–salt mixture. As in experiment 4 only about half of the benzidine is produced as monohydrochloride, at elevated temperatures the hydrazobenzene hydrochloride must undergo rearrangement without involving a second molecule of acid. This is substantiated by the material balance of reaction products in terms of acid and

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* For unknown reasons, 3,4,5-trichloroaniline and 2,3,5,6-tetrachloroaniline are not suitable for comparison with hydrazo compounds.

TABLE 2. CONVERSION OF HYDROCHLORIDES OF HYDRAZO COMPOUNDS

No.	Compd	Solvent	Temp °C	Atm	Yield % of theory							
					Benzidine	Diphenylines	*o,o*-Diamines	*o*-Semidines	Anilines	Azo compds	Unconverted hydrazo-compds	Sum of all compds %
1	I	ether	−10	N	53·4	24·1	7·2	7·0	0·4	0·4	—	92·6
2		ether	20		16·2	12·1	—	5·1	16·5	16·8	26·3	93·0
3		—	20		13·0	8·1	—	4·1	24·0	24·5	15·6	89·3
4		—	80		15·0	11·5	—	5·9	26·2	26·9	7·7	93·2
5		—	cooling mixture	HCl	38·2	26·6	7·4	18·4	1·0	0·9	—	92·5
6	III	ether	−10	N	32·6	18·1	16·5	23·0	1·5	1·6	—	93·3
7		ether	20		14·2	9·2	—	5·1	24·5	25·2	14·2	92·2
8		—	20		15·0	8·5	—	6·3	25·1	25·6	12·2	92·7
9		—	80		9·7	6·4	—	8·3	26·8	27·0	13·0	90·4
10		—	cooling mixture	HCl	27·9	19·0	18·1	20·7	1·6	1·7	—	89·0

TABLE 3.* REARRANGEMENT IN NON-IONIZED ACIDS

No.	Compd	Acid	Solvent	Temp °C	Yield, % of theory						
					Benzidines	Diphenylines	*o,o*-Diamines	*o*-Semidines	Anilines	Azo-compds	Sum of all compds %
1	I	HCl	b-t-m	−10	36·4	29·6	12·8	12·5	0·4	0·4	92·2
2		HCl	—	−10–15	21·7	20·2	17·6	29·0	1·5	1·7	91·7
3		HBr	ether	−10	33·6	30·6	7·5	16·0	1·5	1·6	91·0
4		HBr	—	−10–15	17·7	18·4	10·5	25·5	11·5	1·3	84·9
5	II	HCl	ether	−10	44·7	25·0	—	1·5	10·5	11·5	93·2
6		HBr	ether	−10	41·1	30·4	—	9·5	6·8	6·0	93·8
7		HBr	—	−10–15	14·5	16·3	—	23·0	21·0	7·0	81·8
8	IV	HCl	ether	−10	—	—	—	76·1	8·5	8·2	92·8
9	V	HBr	ether	−10	14·0	18·2	—	18·5	20·0	18·1	88·8
10	VI	HCl	ether	−10–15	48·7	18·8	—	9·2	2·8	2·4	81·9

* See also Exps. 1 and 6, Table 2.

amino compounds. We have, however, shown,[14] that at elevated temperatures the hydrochlorides of amino compounds catalyse the disproportionation of free hydrazo compounds. Thus, heating a mixture of equimolecular quantities of hydrazobenzene and aniline hydrochloride at 110–115° for 15 min results in up to 80% disproportionation of hydrazobenzene, this reaction being also catalysed by weak acids (benzoic, acetic, butyric). The reaction proceeds according to the following mechanism. Very small quantities of HCl resulting from weak dissociation of amine hydrochlorides are captured by the hydrazo compound to form a corresponding hydrochloride which undergoes redox conversion (II). Among the rearrangement products only traces of *o*-semidines formed on "thermal" rearrangement of hydrazo compounds in the absence of acid agents (see Table 5) could be detected.

The so-called dihydrohalides of hydrazo compounds. In 1944 Pongratz *et al.*[15] claimed that the dihydroiodide of hydrazobenzene:

$$(C_6H_5\overset{+}{N}H_2—\overset{+}{N}H_2C_6H_5)I_2^{2-}$$

is produced by the action of a large excess of methyl iodide on hydrazobenzene. Experimental check has shown that this "dihydroiodide" is a mixture of trimethylphenylammonium iodide (1 mole) and aniline hydroiodide (2 moles) and also results from the reaction of aniline with a large excess of methyl iodide.[16] Another dihydrohalide of hydrazobenzene investigated was "the green salt" discovered by Orelkin[18] which proves to be a mixture of compounds resulting from rearrangement and disproportionation of hydrazobenzene. Thus the more recent references[17,18] to dihydrohalides of hydrazo compounds are not valid.

It has been shown that it is impossible to produce dihydrohalides of N-methyl-N′-phenylhydrazine in ethereal or in benzene–toluene solution of HCl or HBr in appreciable quantities.[19] If in monoprotonated aliphatic-aromatic hydrazines which are very weak bases, double protonation is strongly hindered, then double protonation of considerably weaker bases such as hydrazo compounds, many of which rearrange readily in weak acids at room temperature (see Table 1), is still less likely.

In order to effect rearrangement of hydrazo compounds, therefore, there is no need for double protonation.

Rearrangement in acid media

Tables 3 and 4 list data on the rearrangement of hydrazo compounds in non-ionized and in ionized media for such representative compounds as hydrazobenzene (I), 2,2′-dimethyl- (II), 3,3′-dimethyl- (III), 4,4′-dimethyl- (IV), 2,2′-dimethoxy- (V) and 2,2′-diethoxyhydrazobenzene (VI).

In the presence of non-ionized acids the yield of benzidines is low and the percentage of diphenylenes is higher than with ionized acids. In the case of hydrazobenzene and 3,3′-dimethylhydrazobenzene new compounds, *o,o′*-diamines, are formed and the yield of *o*-semidines is also sharply increased.

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[14] V. O. Lukashevich, *Dokl. Akad. Nauk. SSSR*, 120(2), 316 (1958).

[15] A. Pongratz, S. Böhmert-Süss and K. Scholtis, *Ber. Dtsch. Chem. Ges.* 77, 651 (1944).

[16] L. G. Krolik, V. O. Lukashevich, *Dokl. Akad. Nauk SSSR* 87(2), 229 (1952).

[17] G. S. Hammond and W. Grundmeier, *J. Amer. Chem. Soc.* 77, 2444 (1955).

[18] R. B. Carlin and R. C. Odioso, *J. Amer. Chem. Soc.* 76, 100 (1954); R. B. Carlin and G. S. Wich, *J. Amer. Chem. Soc.* 80, 4023 (1958).

[19] V. O. Lukashevish and L. G. Krolik, *Dokl. Akad. Nauk SSSR* 129(1), 117 (1959).

TABLE 4. REARRANGEMENT IN IONIZED ACIDS

No	Compd	Alcohol	Yield, % of theory					
			Benzidines	Diphenylines	o-Semidines	Anilines	Azo-compds	Sum of all compds %
1	I	99·9	75·5	19·0	2·3	1·3	1·3	99·4
2		95·0	73·0	19·4	2·2	2·3	2·4	99·3
3		95·0	56·5	23·8	2·6	8·1	8·0	99·0
4		85·0	79·0	16·9	1·4	1·1	1·1	99·5
5		75·0	81·2	15·2	1·0	1·1	1·1	99·6
6		60·0	83·2	13·5	0·9	0·9	0·9	99·4
7		45·0	84·3	12·6	0·7	0·9	1·0	99·5
8	II	95·0	87·0	10·9	0·7	0·5	0·5	99·6
9	III	95·0	79·2	11·0	3·0	2·0	2·3	97·5
10	IV	95·0	—	—	58·1	23·0	16·1	97·2
11	V	99·9	65·7	16·9	2·6	4·7	4·5	94·4
12	VI	99·9	76·0	8·0	4·4	2·5	2·5	93·4

Rearrangement in non-ionized acids.[19] Experiments were carried out in ether or in benzene–toluene mixture (2:1). When no solvent was used a stream of HCl or HBr was passed over the finely ground hydrazo compound.

The action of dry HBr on crystalline hydrazobenzene and 2,2′-dimethylhydrazobenzene yields brominated *o*-semidines such as 4-bromo-2′-aminodiphenylamine (m.p. 127–128°) and 4-bromo-2,3′-dimethyl-2′-aminodiphenylamine (m.p. 105–107°) together with large amounts of aniline and *o*-toluidine. The latter are secondary reaction products. The hydrobromides of hydrazo compounds being reduced by HBr to anilines with simultaneous bromination of the *o*-semidines.

Rearrangement in ionized acids.[21] The process takes place in aqueous-alcoholic or alcoholic solutions of HCl.

According to the spectrophotometric evidence obtained by Carlin *et al.*,[22] hydrazobenzene is fully converted in 95% ethanol to a mixture of benzidine and diphenylene in a 70:30 ratio, this being the case under a wide variety of conditions. We have observed (Table 4) that not only is the ratio different but it is dependent on the alcohol concentration, being 79:21 in 95% ethanol, 84:16 in 75% ethanol and 87:13 in 45% ethanol (in aqueous solutions of HCl it is 92:8). With rising temperature the amount of benzidine markedly decreases at the expense of diphenylene and other substances, including *o*-aminodiphenylamine. Finally, rise in temperature leads to a strong increase in disproportionation products.

In the case of other hydrazo compounds, it is claimed[23] that 2,2′-dimethyl- and 3,3′-dimethylhydrazobenzene rearrange solely to the respective benzidines.* Actually, besides benzidines the reaction mixture contains about 11% of 3,3′-dimethyl-2,4′-diaminodiphenyl (Table 4, exp. 8). With 3,3′-dimethylhydrazobenzene (exp. 9) 11%

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* The same mistake is in the recent work by Banthorpe, Ingold and Roy.[24]

[20] L. Knorr, *Ber. Dtsch. Chem. Ges.* **39**, 3265 (1906).

[21] V. O. Lukashevich, *Dokl. Akad. Nauk SSSR* No. 1, 115 (1960); **159**(5), 1095 (1964).

[22] R. B. Carlin, R. G. Nelb and R. C. Odioso, *J. Amer. Chem. Soc.* **73**, 1002 (1951).

[23] R. B. Carlin and R. C. Odioso, *J. Amer. Chem. Soc.* **76**, 100 (1954).

[24] D. V. Banthorpe, C. K. Ingold and J. Roy, *J. Chem. Soc.* **2436** (1962).

of 4,2′-dimethyl-2,4′-diaminodiphenyl and 3% of 3,4′-dimethyl-2′-aminodiphenylamine were found to be present.

Ingold and Kidd had reported[25] that on joint rearrangement of 2,2′-dimethoxy- and 2,2′-diethoxyhydrazobenzene together with disproportionation products only pure 3,3′-dimethoxy- and 3,3′-diethoxybenzidine are obtained each in a yield of 73% of theory. Actually our experiments gave 3,3′-dimethoxybenzidine in about 66% yield (exp. 11) and 3,3′-diethoxybenzidine in a yield of 76% of theory (exp. 12). Together with dianisidine about 20% and in the case of diphenetidine up to 12% of isomeres were obtained. These could be separated without loss of major substances treatment with acid.

In ethereal solutions of HCl hydrazobenzene rearranges 30 to 40 times faster than in HCl solutions in 95% ethanol. In 99·9% ethanol the rearrangement is about 150 times faster than in 95% ethanol. In benzene–toluene solutions of HCl the rate of rearrangement is much higher than in ethereal solutions.

2,2′-Dimethylhydrazobenzene rearranges about 1,000 times faster than hydrazobenzene in ethereal solutions of HCl but only 4 times as fast as in 95% ethanol. The rates of rearrangement in ethereal and benzene–toluene solutions of HBr exceed by several hundred thousand times those with HCl, the results being comparable only in ethereal or in benzene–toluene solutions.[19]

With HCl or HBr in 95% ethanol hydrazobenzene rearranges at nearly the same rate, 2,2′-dimethylhydrazobenzene rearranges with HBr twice as fast as with HCl.

The rearrangement mechanism in the presence of acids

Until recently it was thought that in ionized acids the rate of rearrangement is directly proportional to the first order of concentration of hydrazo compound and the square of concentration of hydrogen ions.[26] We do not agree with these statements[21] and the authors have been induced to reconsider them in the light of the range of hydrazo compounds under investigation. Thus, it was concluded[27] that besides the above kinetic dependence there exists a linear dependence of the rearrangement rate on acid concentration, as exemplified by 1,1′- and 1,2′-hydrazonaphthalenes. In those cases where the kinetic order with respect to the acid is represented by a fractional number the above authors with Blackadder and Hinshelwood[28] who think that monoprotonated 2,2′dimethylhydrazobenzene undergoes a partial "spontaneous" rearrangement.

The investigators of the rearrangement kinetics formulate their unwarranted thesis as follows: if the kinetic order with respect to the acid equals 2·0, then the hydrazo compound adds two protons, excluding thereby another possibility for the protonated molecule to be affected by the acid.

Hydrazo compounds are not useful for kinetic studies because they only resemble the usual di-acid bases. The rate of monoprotonation is dependent upon the basicity of the starting hydrazo compound whereas the rate of the subsequent stage is only

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[25] C. K. Ingold and H. I. Kidd, *J. Chem. Soc.* 984 (1933).

[26] M. Večeřa, *Chem. Listy* 52, 1373 (1958).

[27] D. V. Banthorpe, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.* 2386 (1962); D. V. Banthorpe and E. D. Hughes, *Ibid.* 2402 (1962); D. V. Banthorpe, *Ibid.* 2407, 2413 (1962); D. V. Banthorpe, E. D. Hughes and C. K. Ingold, *Ibid.* 2418 (1962); D. V. Banthorpe, *Ibid.* 1429 (1962).

[28] D. A. Blackadder and C. N. Hinshelwood, *J. Chem. Soc.* 2898 (1957).

indirectly related to the basicity of the monoprotonated molecule and is determined by the stability in the presence of the acid agent. With a considerable difference in the rates of the first and second phases there is created an illusion of double protonation in case of compounds which form salts resistant to the further action of acid (see Table 1). In a number of cases monoprotonated hydrazo compounds are, however, extremely sensitive to acids and then the rate of the second phase is very high. It is just this simple fact, substantiated by the kinetic equations that has convinced investigators that these examples prove the existence of a "spontaneous" rearrangement of monoprotonated hydrazo compounds.

The spontaneous rearrangement is further disproved if we recall the above disproportionation reaction of hydrazo compounds by heating in the presence of traces of HCl or weak acids.[14] Had there been a spontaneous rearrangement it would have undoubtedly resulted in a considerable quantity of rearrangement products together with disproportionation compounds. This, however, does not usually take place, particularly in the important case of 2,2′-dimethylhydrazobenzene, used by Blackadder and Hinshelwood for their hypothesis.

In the presence of acids the rearrangement always proceeds stepwise. The monoprotonated molecule formed undergoes rearrangement only when the acid exerts continued action. A very great divergence in data obtained for non-ionized and ionized acids appears to be first of all due to the fact that the transition states formed are essentially different. In the first instance the most characteristic reaction seems to be that of crystalline hydrazo compounds with HCl or HBr. The process proceeds in a solid phase and may be shown as follows:

$$(\mathrm{RNH{-}\overset{+}{N}H_2R})\overset{-}{\mathrm{X}} + \mathrm{HX} \rightleftarrows (\mathrm{RNH{-}\overset{+}{N}H_2R})\overset{-}{\mathrm{X}} \ldots \mathrm{HX} \rightarrow \begin{array}{c}\text{rearrangement}\\ \text{products}\end{array} \qquad \text{(III)}$$

Solvents, if present, play an important role in that they change the strength of the acids and to some extent may dissolve the salt of hydrazo compounds resulting in rearrangement proceeding partly in solution. Finally, the nature of the acid is important as evidenced by the results obtained with HCl and HBr.

Without agreeing with the hypothesis of Blackadder and Hinshelwood concerning the partial spontaneous rearrangement we accept their suggestion that in ionized acids the monoprotonated hydrazo compound undergoes rearrangement just when the proton is approaching.[28] In aqueous and aqueous-alcoholic solutions the transition state may be represented by:

$$\mathrm{RNH{-}\overset{+}{N}H_2R} \quad \mathrm{H_3\overset{+}{O}} \qquad \text{(IV)}$$

In anhydrous alcohol the reaction is catalysed by an ethoxonium ion. It is essential that though the reaction rate in 99·9% ethanol is about 150 times as fast as in 95% ethanol the results of hydrazobenzene rearrangement are almost similar. The nature of the solvent and acid does, however, affect the results. We have already seen that when alcohol is diluted with water this brings about a rise in the benzidine to diphenylene ratio. When H_2SO_4 is substituted for HCl in 95% alcohol the above ratio also increases and reaches 87:13. This might be caused by the specific action of non-ionized acid on the monoprotonated hydrazo compound, the same being also possible for rearrangement in weak acids.

Based on the data in Table 1, the relative rearrangement rates of a number of hydrazo compounds may be deduced and, at the same time, this data further substantiates our conception of the rearrangement mechanism. The 95% acetic acid used was obtained by diluting pure 98–99% standard commercial acids with water, the results sometimes varying depending on the particular acid used.

The difference in rearrangement rates of many hydrazo compounds is so great that they cannot be expressed on one scale. In order to accommodate these rates, dioxan was added (8 ml dioxan and 20 ml acetic acid were taken per 0·002 mole of hydrazo compound).

Let us consider some examples. Hydrazonaphthalenes are not suitable for the elucidation of the true nature of rearrangement. Owing to the extreme instability of monoprotonated hydrazo compounds (fine dispersion of salts in a heterogeneous medium) the difference in the rates of the first and second phase is negligible and it is very difficult to differentiate between the stages of the rearrangement as the process proceeds very rapidly. And yet this proved possible with salts of 1,1'- and 1,2'-hydrazonaphthalenes in dioxan diluted with ether.

It is more expedient to use 2,2'-diethoxy- and 2,2'-dimethoxyhydrazobenzene, whose rearrangement rates are close to those of the above-mentioned hydrazonaphthalenes. 2,2'-Diethoxyhydrazobenzene clearly exemplifies the two-phase course of the rearrangement and the hydrochloride of the hydrazo compound can be isolated in a 60–65% yield of theory. In contrast, the amount of 2,2'-dimethoxyhydrazobenzene hydrochloride isolated does not exceed 10% of theory, inspite of the lower rate of rearrangement.

Of great interest are 4,4'dimethoxy- and 4,4'-diethoxyhydrazobenzenes, whose conversion rates in acids are particularly high. The reaction results in about 80% of disproportionation products whereas the maximum yield of *o*-semidines does not exceed 10% of theory. These examples serve as unequivocal proof of the stepwise character of the whole process. It has already been said that the disproportionation products result from a secondary reaction, that of interaction of two molecules of the monoprotonated hydrazo compound. The figures obtained (80% and 10%) also show that the rate of this bimolecular reaction substantially exceeds that of the conversion of the monoprotonated hydrazo compound to *o*-semidine.

Some remarks on the rearrangement of 4,4'-*substituted hydrazobenzenes*

Recently many attempts have been made to establish kinetically the rearrangement mechanism of 4,4'-substituted hydrazobenzenes. In the rearrangement of 4,4'-dimethylhydrazobenzene the kinetic order with respect to the acid is 2·0, the reaction products being *o*-semidine, *p*-toluidine and *p*-azotoluene in a 40:40:20 ratio.[29] Actually this ratio was found to be 58:23:16 (Table 4, exp. 10). We think that the higher percentage of toluidine than azotoluene is accounted for by the reductive effect of alcohol on the monoprotonated molecule of hydrazo compound.

The kinetic order has been determined[30] with respect to the acid for 4-methyl-4'-chlorohydrazobenzene (1·58) and 4-t-butyl-4'-chlorohydrazobenzene (1·51). The authors did not determine the composition of the rearrangement products. It is

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[29] R. B. Carlin and G. S. Wich, *J. Amer. Chem. Soc.* **80**, 4023 (1958).

[30] M. J. S. Dewar and H. McNicoll, *Tetrahedron Letters*, No. 5, 22 (1959).

now possible to report that in the former case the ratio of *o*-semidines:anilines:azo compounds is 24:33·5:34·5 and in the latter 38:25:28.

In the rearrangement of 4,4′-di-t-butylhydrazobenzene it was found[31] that 45–54% of the compound rearranges and 48–50% disproportionates. With 4,4′-divinylhydrazobenzene the authors determined the order of the reaction with respect to the acid (1·0) but did not identify the products obtained in the reaction of the compound with HCl in ethanol. The authors do not consider them to be either semidine or disproportionation products but in the light of facts presented, the assertion of the authors about a "benzidine rearrangement" is not warranted.

TABLE 5. "THERMAL" REARRANGEMENT IN THE BENZENE SERIES

No	Compd	Temp °C	Heating (hr)	Yield, % of theory *o*-Semidines	*p*-Semidines	Anilines	Azo-compds	Sum of all compds %
1	Hydrazobenzene	140–145	120	16·7	12·5	31·5	33·4	94·1
2	4-Chlorohydrazobenzene	140–145	20	—	—	45·2	47·5	92·7
3	4-Bromohydrazobenzene	110	16	—	—	46·5	50·3	96·8
4	4-Methylhydrazobenzene	140–145	116	18·6	8·1	33·5	35·6	95·8
5	2,2′-Dimethylhydrazobenzene	140–145	120	8·3	13·1	36·0	38·0	95·4
6	3,3′-Dimethylhydrazobenzene	140	100	32·0	8·2	26·2	29·1	95·5
7	4,4′-Dimethylhydrazobenzene	140–145	100	15·5	—	38·0	38·2	91·7
8	2,2′-Dimethoxyhydrazobenzene	120–125	26	16·0	9·2	28·5	40·2	93·9

To sum up, in the rearrangement of 4,4′-substituted hydrazobenzenes, the monoprotonation of hydrazo compound is followed by two parallel reactions, namely, the rearrangement of the monoprotonated hydrazo compound to yield *o*-semidine and the interaction of two monoprotonated molecules to give anilines and azo compounds (see II). An attempt to determine the kinetic order of two parallel reactions is without justification.

"Thermal" rearrangement of hydrazo compounds

Meisenheimer and Witte[32] discovered that boiling 2,2′-azonaphthalene in alcoholic alkali with zinc dust results in 2,2′-diamino-1,1′-dinaphthyl. They concluded, as later did Jacobson,[8] that their data pointed to a rearrangement under the action of alkali. It has, however, been shown[18] that the rearrangement of 2,2′- as well as of 1,1′-hydrazonaphthalene is caused by heat rather than alkali.

[31] H. G. Schine and J. T. Chamness, *J. Org. Chem.* **28**, 1232 (1963); *Tetrahedron Letters* No. 10, 641 (1963).

[32] J. Meisenheimer and E. Witte, *Ber. Dtsch. Chem. Ges.* **36**, 4153 (1903).

More recently Večeřa *et al.*[33] determined qualitatively the rearrangement products resulting from prolonged heating (150°) of hydrazobenzene and 2,2′-dimethylhydrazobenzene (as well as 4′-methylhydrazobenzene and 1,1′-hydrazonaphthalene). "Thermal" rearrangement of 2,2′-hydrazonaphthalene attracted the attention of Shine[34] who after several years obtained satisfactory results.[35] As to 1,1′-hydrazonaphthalene the author acknowledged the case to be too involved.*

Rearrangement of hydrazo compounds of the benzene series. The compounds investigated can be classified into two groups. The first group comprises hydrazo compounds forming almost exclusively disproportionation products, such as 4-chloro-, 4-bromo- and 4,4′-dichlorohydrazobenzene. The second includes most hydrazo compounds (Table 5). The reaction yields disproportionation products together with rearrangement products, which sometimes exceed 25% of theory. These were *o*- and *p*-semidines, one of them predominating. 4-Methylhydrazobenzene gives not only 2-amino-5-methyldiphenylamine (bundles of needles from alcohol, m.p. 87°) but also 2-amino-4′-methyldiphenylamine (compact quadrangular plates from alcohol, m.p. 75–76°)—not observed on acid rearrangement by Jacobson,[38] nor found on "thermal" rearrangement by Večeřa.[33]

In a number of cases an appreciable amount of *p*-semidines were notated although these were not formed during rearrangement of these compounds in acid medium. Benzidines and diphenylenes were not found in appreciable amounts.

Rearrangement of hydrazo compounds of the naphthalene series, influence of solvents. In the "thermal" rearrangement of hydrazonaphthalenes the composition of the end products depends on factors that do not affect the rearrangement of hydrazo compounds of the benzene series. The more complicated but very interesting rearrangement of the 1,1′-isomer,[39] the rate in alcohols, ethylene glycol and formamide is much higher than it is in other solvents.

The nature of the solvent often affects the quantitative composition of the rearrangement products which may be divided into two groups. The first group consists of *o*- and *p*-diamines and 2,2′-dinaphtho-1,1′-imine, corresponding to *o*-diamine, the second one involves *o*- and *p*-semidines. In solvents with weak electric properties, the yield of semidines can exceed the overall rearrangement products by 50% but the

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* It is extremely difficult to understand the recent results of Banthorpe and Hughes,[36] and Banthorpe, Hughes and Ingold,[37] concerning the "thermal" rearrangement of 1,1′-hydrazonaphthalene. Besides alcohols the authors used as solvents acetonitrile, acetone, and benzene and also studied rearrangement in the absence of solvents. Actually they have been mainly concerned with oxidation of 1,1′-hydrazonaphthalene rather than rearrangement. The yields of 1,1′-azonaphthalene under the above conditions proved to be 30, 60, 25 and 60%, respectively, with the rearrangement products amounting to as little as 14, 10, 30 and 3%. No appreciable amount of semidines was detected. One must, however, bear in mind that according to the authors they had no semidines available even for their "control" experiments.

Our data on rearrangement of 1,1′-hydrazonaphthalene in different solvents are summarized in Table 6.

[33] M. Večeřa, J. Gasparic and J. Petranek, *Chem. & Ind.* No. 10, 299 (1957).

[34] H. J. Shine, *J. Amer. Chem. Soc.* **78**, 4807 (1956).

[35] H. J. Shine and J. C. Trisler, *J. Amer. Chem. Soc.* **82**, 4054 (1960).

[36] D. V. Banthorpe and E. D. Hughes, *J. Chem. Soc.* 2849 (1964).

[37] D. V. Banthorpe, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.* 2864 (1964).

[38] P. Jacobsen and W. Lischke, *Liebigs Ann.* **303**, 367 (1898).

[39] V. O. Lukashevich and L. G. Krolik, *Dokl. Akad. Nauk SSSR*, **147**(5), 1090 (1962); *Ibid.* (1), 110 (1961).

TABLE 6. "THERMAL" REARRANGEMENT OF 1.1'.hydrazonaphthalene

No.	Solvent	Solvent (ml)	Reaction time (hr)	Yield, % of theory								
				1,1 - Diamine	Imine	4,4'- diamine	o- Semi- dine	p-Semi- dine	Naphthyl- amine	Azonaph- thalene	Sum of all compds %	Semidines % of the sum of re- arrangement products
1	—	—	12	6·6	25·0	20·5	8·4	23·4	5·0	2·3	91·2	37·9
2	Cyclohexane	25	6·5	4·7	13·5	9·8	12·9	24·9	15·2	11·0	92·0	57·4
3	Benzene (abs)	20	6·0	3·4	14·1	8·3	10·2	20·0	19·8	17·1	92·9	53·9
4	Benzene + H_2O	20	6·0	5·1	18·6	11·1	8·8	12·6	18·0	17·3	91·5	38·1
5	Toluene	20	6·0	4·7	16·9	12·2	10·2	11·8	18·8	16·0	90·7	39·4
6	Dioxane (abs.)	15	3·0	5·2	12·7	7·3	10·8	20·3	18·4	15·1	89·4	55·2
7	Dioxane + H_2O	13·5 1·5	3·0	12·7	12·1	18·0	8·7	14·1	14·0	9·5	89·1	34·8
8	Methanol	15	2·0	5·8	25·0	25·4	7·1	5·8	14·8	9·1	93·0	18·7
9	Methanol + Na	15	1·5	25·2	—	24·8	7·1	8·9	15·1	10·0	91·1	24·2
10	Ethanol 1	15	1·5	8·7	25·0	15·5	7·6	12·1	15·4	9·5	93·8	28·6
11	Ethanol 85%	15	1·5	8·8	25·4	18·0	7·1	8·8	13·2	8·3	89·6	23·3
12	Ethanol + Na	15	1·0	33·7	—	24·4	7·0	4·7	13·0	9·2	92·0	16·8
13	Pyridine	10	4·0	23·2	4·0	17·2	7·5	8·3	18·5	13·5	92·2	26·2
14	Pyridine + H_2O	7·5 2·5	4·0	26·1	5·8	25·0	6·6	7·4	14·2	7·2	92·3	19·7
15	Ethylenegoycol	15	2·0	10·7	39·4	24·1	1·1	9·0	7·2	1·8	93·3	12·0
16	Acetone	10	3·0	4·3	13·5	14·1	1·8	11·4	22·2	18·3	85·6	29·3
17	Acetontriles	15	2·5	5·2	18·0	18·6	5·4	4·1	21·0	17·9	90·2	18·5
18	Formamide	15	3·0	21·4	16·0	52·6	—	—	—	1·1	91·1	0
19	Formamide + NH_4OH	14 1	2·5	40·4	11·2	33·5	traces		4·2	2·1	91·4	0
20	Formamide + pyridine + NH_4OH	6 4 1	2·0	36·7	8·6	30·0	1·0	1·8	8·5	5·1	91·8	3·6

yield becomes lower as the electric property of solvent increases. Addition of water with its high dielectric constant to weakly polar solvents may lead to a considerably lower yield of semidines, this being the case in benzene and dioxan.

The ratio of 1,1′- to 4,4′-diamine depends on the solvent, a much higher percentage of 1,1′-diamine (as sum total with imine), as is the case in hydrocarbons, anhydrous dioxan, ethanol and ethylene glycol. However, in methanol the ratio of 1,1′- to 4,4′-diamine is as low as 1·21 and in acetonitrile it is 1·25. In formamide there is a strong predominance of 4,4′-diamine as a formyl derivative whereas the less basic 1,1′-diamine is present in a free state.

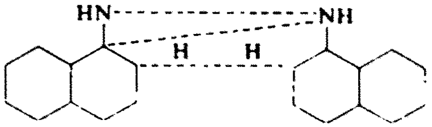
The data obtained for rearrangement of the three isomeric imines in alcoholic–alkaline medium are extremely interesting. In anhydrous methanol and ethanol the reaction gives rise to about 25% of 2,2′-dinaphtho-1,1′-imine, over 50% of 1,2′-dinaphtho-1′,2-imine, and about 20% of dinaphtho-2,2′-imine. If, however, the metallic sodium is dissolved in anhydrous alcohol to obtain 0·1N solution, the rearrangement proceeds quickly but, no imines are formed.

The data for the rearrangement of 1,2′- and 2,2′-hydrazonaphthalenes are more straightforward.[39] The reaction with 1,2′-isomer results in *o*-diamine, imine and 4-amino-1,2′-dinaphthylamine and negligible disproportionation. Just as with 1,1-′ hydrazonaphthalene, in benzene and dioxan the percentage of *p*-semidine is very high whereas in alcohols the compound is almost absent. The reaction with 2,2′-hydrazonaphthalene gives only *o*-diamine and imine.

Probably an intermolecular reaction takes place between the molecules undergoing rearrangement and the solvent molecules not only before the process begins but also during its complete course. Thus, by making the molecule of the hydrazo compound more labile the solvent facilitates the initial stage of the process and, moreover, affects the composition of the resulting products.

If the rearrangement is hindered the reaction yields *o*- and *p*-semidines. In accordance with the suggestion by Večeřa[33] it is quite possible that semidines result from the interaction of radicals formed when the —HN—NH— bond of the hydrazo compound is broken. It should, however, be added that such a radical reaction must comply with conditions not contradicting our concept of rearrangement as being an intramolecular process. That is to say either it is an intramolecular radical reaction[40] or, if the radicals are kinetically independent, their life period should be extremely short.

Solvents with pronounced electrical properties favour rearrangement, thus considerably lowering the yield of semidines in the case of 1,1′- and 1,2′-hydrazonaphthalenes at the expense of an increase in the production of diamines and dinaphthoimine. It is of great importance that the three isomeric dinaphthoimines formed sometimes in very large amounts cannot result from diaminodinaphthyls as this would have required more rigid conditions. This fact has been carefully checked for the three isomers. It follows that they are formed at the moment of rearrangement. One could conceive the transition state as:



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[40] H. E. De La Mare and F. F. Rust, *J. Amer. Chem. Soc.* **81**, 2691 (1959).

with the bond between nitrogen atoms not having been completely broken and no new bonds yet formed.

The intermolecular oxidation–reduction reaction leads to azo compounds and anilines.

In the naphthalene series disproportionation takes place primarily with 1,1′-hydrazonaphthalene where rearrangement is more favoured than with 1,2′- and 2,2′-isomers. 1,1′-Hydrazonaphthalene also involves a very fast redox reaction. It is to be noted that the percentage of naphthylamine sometimes considerably exceeds that of 1,1′-azonaphthalene. This refers particularly to experiments with alcohols, ethylene glycol, aqueous pyridine and aqueous dioxan. It is quite possible that in these solvents one should also take into consideration the reductive action of water and alcohols on 1,1′-hydrazonaphthalene.

EXPERIMENTAL

Salts of hydrazo compounds. To an ethereal soln of hydrazo compound, e.g. hydrazobenzene (0·005 mole) at −8 to −10° an equimolecular amount of HCl in ether was added dropwise, the overall quantity amounting to 40–50 ml. The snow-white hydrochloride was quickly filtered off (preferably under N), made alkaline with NaOH in MeOH and oxidized with HgO the amount of azobenzene produced being equivalent to that of the salt. Due to the dissociation of hydrochloride the salt formation is not always complete particularly in compounds with low basicity. In the case of 2-chloro- and 3,3′-dichlorohydrazobenzene as much as 30–40% of the hydrazo compound remains in soln even if 2 moles of HCl are used.

Salts of hydrazo compounds can also be prepared in isopropyl or isoamyl ethers and with HBr it is possible to isolate 40–50% of 3-chloro- and 3,3′-dichlorohydrazobenzene hydrobromides.

The following experiment proves the existence of the hydrazonaphthalene salts. When 1,1′-, 1,2′- or 2,2′-hydrazonaphthalene (0·002 mole) was dissolved in dioxan (8 ml), diluted with ether (40 ml) at −8 to −10° and 1 mole HCl in ether (25 ml) added, an abundant, very finely dispersed ppt formed immediately. If the mixture was made alkaline as quickly as possible and oxidized with HgO 70 to 75% of starting hydrazo compound (as azo compounds) was regenerated. A visual estimate indicated that the hydrochlorides of corresponding diamines (calculated amounts) were produced only in small quantities.

Rearrangement in non-ionized acids. The hydrazo compound (0·01 mole) was dissolved in absolute ether or in a mixture of absolute benzene and toluene (b–t–m) in a 2:1 ratio and a soln of HCl or HBr (3–4 moles) in the same solvents added at −8 to −10°. In experiment 10, the ethereal soln of acid (4 moles) was added at once to the soln of hydrazo compound in ether. In experiments without solvents, a stream of HCl or HBr was slowly passed over the surface of a finely ground hydrazo compound in a small apparatus agitated in an ice-salt mixture. The almost colourless aqueous solns of the reaction products on extraction with ether yielded the weakly basic *o*-semidines and azo compounds. *o*-Semidines may be determined quantitatively by titration with $NaNO_2$. The characteristics of the less known compounds are as follows: 3,4-dimethyl-2′-benzoylaminodiphenylamine bundles of needles from alcohol, m.p. 152–153°; 2,3-diethoxy-2′-benzoylaminodiphenylamine needles from alcohol, m.p. 148–149°.

After separating *o*-semidines and azo compounds benzidine was reprecipitated as sulfate and other benzidines were salted out from strongly acidified solns and purified. The filtrates on steam distillation yielded *o*-*o*′-diamines and diphenylenes. These could be separated as dibenzoyl derivs owing to their different solubility in alcohol and ether. The characteristics of less known compounds are as follows: 4,4′-Dimethyl-2,2′-dibenzoyldiaminodiphenyl prisms from alcohol, m.p. 161–162°; 2,4′-dimethyl-4,2′-dibenzoyldiaminodiphenyl quadrangular plates from alcohol, m.p. 212–213°; 3,3′-diethoxy-2,4′-dibenzoyl-diaminodiphenyl prisms from alcohol, m.p. 229–230°; 3,3′-diethoxy-4,4′-dibenzoyldiaminodiphenyl narrow prisms from acetone, m.p. 243–244°.

Rearrangement in ionized acids (Table 4). In a number of experiments an alcoholic soln of hydrazobenzene (001 mole) strongly cooled under N was mixed at once with a soln of HCl (0·1 mole); overall volume 100 ml, about 0°; In 2 hr benzidine hydrochloride crystals were separated and converted to sulfate. The alcohol was evaporated at 10–20°, the remainder diluted with water, the main bulk of the acid carefully neutralized and *o*-semidine and azobenzene completely extracted with ether; the aqueous part contained traces of benzidine, diphenylene and aniline. After separation of benzidine the yield of diphenylene and aniline was determined by diazotation and the amount of aniline estimated after repeated steam distillation. In experiments 3, 1 was added to the acid during 15 min at 45–50°. Compounds II, IV, V and VI were uniformly added to HCl soln (0·1 mole) in alcohol (100 ml) during 30 min at 0°. After 90 min the reaction mixtures were treated as mentioned above for I and for rearrangement in non-ionized acids.