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Abstract

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“THERMAL” REARRANGEMENT OF HYDRAZO COMPOUNDS

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On the basis of earlier work (1), it could be assumed that hydrazo compounds, when heated in an inert medium, decompose to form exclusively disproportionation products. Somewhat later, Wieland (2) showed that, in the cases of 4-methyl-, 4-methyl-4′-methoxy-, and 4-methyl-4′-chlorohydrazobenzene, the corresponding semidines must also be taken into account. According to our data (3), hydrazo compounds of the naphthalene series, especially 2,2′-hydrazonaphthalene, upon moderate heating (100°) in inert solvents form mainly rearrangement products. Finally, these products were identified qualitatively after twenty-four-hour heating (150°) of hydrazobenzene and 2,2′-dimethylhydrazobenzene (4).

Table 1

Experiment No.	Hydrazo compound	Temp., °C	Heating duration, h	Obtained, percent of theoretical: *o*-semidines	Obtained, percent of theoretical: *p*-semidines	Obtained, percent of theoretical: anilines	Obtained, percent of theoretical: azo compounds	Sum of all substances, % of theoretical
1	Hydrazobenzene	140–145	120	16.7	12.5	31.5	33.4	94.1
2	2,2′-Dimethylhydrazobenzene	140–145	120	8.3	13.1	36.0	38.0	95.4
3	4-Methylhydrazobenzene	140–145	116	18.6	8.1	33.5	35.6	95.8
4	4,4′-Dimethylhydrazobenzene	140–145	100	15.5	–	38.0	38.2	91.7
5	4-Chlorohydrazobenzene	140–145	20	–	–	45.2	47.5	92.7

Experiment No.	Hydrazo compound	Temp., °C	Heating duration, h	Obtained, percent of theoretical: *o*-semidines	Obtained, percent of theoretical: *p*-semidines	Obtained, percent of theoretical: anilines	Obtained, percent of theoretical: azo compounds	Sum of all substances, % of theoretical
6	4-Bromohydrazobenzene	110	16	–	–	46.5	50.3	96.8
7	2,2′-Dimethoxyhydrazobenzene	120–125	26	16.0	9.2	28.5	40.2	93.9

Table 2

Experiment No.	Hydrazonaphthalene	Temp., °C	Solvent	Obtained, percent of theoretical: *o*-diamines	Obtained, percent of theoretical: imines	Obtained, percent of theoretical: *p*-diamines	Obtained, percent of theoretical: *o*-semidines	Obtained, percent of theoretical: *p*-semidines	Obtained, percent of theoretical: naphthylamines	Obtained, percent of theoretical: azo compounds	Sum of all substances, % of theoretical
1	1,1′	85	abs. alcohol	4.4	26.1	26.1	6.9	7.0	12.7	8.5	91.7
2	1,1′	100	benzene	6.6	8.5	1.0	9.4	18.4	23.5	23.0	90.4
3	1,1′	145	–	4.7	10.2	1.5	13.6	23.2	19.6	19.2	91.0
4	2,2′	100	abs. alcohol	74.9	18.5	–	–	–	–	–	93.4
5	2,2′	160	benzene	70.0	23.0	–	–	–	–	–	93.0
6	2,2′	140	–	65.1	28.8	–	–	–	–	–	93.9
7	1,2′	100	abs. alcohol	30.4	56.4	–	–	–	1.0	1.5	89.3
8	1,2′	145	–	29.0	38.0	–	–	12.2	4.2	5.0	88.4

Experiment No.	Hydrazonaphthalene	Temp., °C	Solvent	Obtained, percent of theoretical: *o*-diamines	Obtained, percent of theoretical: imines	Obtained, percent of theoretical: *p*-diamines	Obtained, percent of theoretical: *o*-semidines	Obtained, percent of theoretical: *p*-semidines	Obtained, percent of theoretical: naphthylamines	Obtained, percent of theoretical: azo compounds	Sum of all substances, % of theoretical

At present it is possible to report in greater detail on the results of the transformations of a series of hydrazo compounds upon heating. The optimum reaction conditions for individual representatives are far from identical: thus, for example, hydrazobenzene and 2,2′-dimethylhydrazobenzene decompose completely after 120 h at 140–145°, with the material balance of the reaction reaching up to 95% of theory; when the temperature is raised to 150°, some resinification of the reaction mixture is observed. For 4,4′-dichloro- or 4-bromohydrazobenzene, milder conditions are required, since at 140° the mass rapidly blackens and sinters. For complete decomposition of hydrazo compounds of the naphthalene series in the interval 140–150°, only a few minutes are required.

The results of transformations of a series of hydrazo compounds upon heating are given in Tables 1 and 2.

The compounds tested can be divided into three groups. First, hydrazo compounds that form almost exclusively disproportionation products; the amounts of semidines in these cases do not reach 1% of theory; these include 4-chloro-, 4,4′-dichloro-, and 4-bromohydrazobenzene.

The second group includes the majority of hydrazo compounds of the benzene series; the amount of rearrangement products sometimes exceeds 25% of theory. These are *o*- and *p*-semidines*, with one or the other isomer predominating in individual cases. It is interesting that, in the rearrangement of 4-methylhydrazobenzene, not only 2-amino-5-methyldiphenylamine is obtained, but also the second possible *o*-semidine—(2-amino-4′-methyldiphenylamine)—which was not observed by Jacobson (^{5}) in the acid rearrangement. Benzidine and diphenylines can be present only in negligibly small amounts.

The third group consists of hydrazo compounds of the naphthalene series. The rearrangement of 1,1′-hydrazonaphthalene proceeds in the most complex manner. A very considerable portion of the hydrazo compound undergoes disproportionation, but, in addition to 1,1′-azonaphthalene and α-naphthylamine, the following substances have been established quantitatively: 1) 1,1′-diamino-2,2′-dinaphthyl, 2) the corresponding carbazole derivative, 2,2′-dinaphtho-1,1′-imine,

3) 4,4′-diamino-1,1′-dinaphthyl, 4) 1-amino-2,1′-dinaphthylamine, 5) 4-amino-1,1′-dinaphthylamine. The situation is further complicated if one takes into account that rearrangement in alcohol (experiment No. 1), while resembling in its results the usual process under the action of acids, differs sharply from rearrangement in benzene (experiment No. 2) or without solvent (experiment No. 3): whereas in alcohol the chief products are diamines and the 2,2′-dinaphtho-1,1′-imine corresponding to 1,1′-diamine, in benzene and without solvent semidines predominate.

The rearrangement products of 1,2′-hydrazonaphthalene correspond only to the mixed hydrazo compound. In an alcoholic medium, an *o*-diamine is obtained and, in the predominant amount (56.4%), the corresponding carbazole derivative; without solvent, 4-amino-1,2′-dinaphthylamine is also formed. Disproportionation is insignificant. The behavior of 2,2′-hydrazonaphthalene on heating is the most uniform: irrespective of the conditions, only the *o*-diamine (75–65%) and 1,1′-dinaphtho-2,2′-imine (18.5–28.8%) are obtained. It can be shown that 2,2′-hydrazonaphthalene is capable of rearranging even at room temperature: after standing for about a year under freshly distilled ethyl alcohol filling the entire apparatus, the very small crystals of the hydrazo compound were completely destroyed. After separation of the crystalline azo compound and treatment of the alcoholic solution with large quantities of mercuric oxide (to oxidize possible hydrazo compound), about 16% of theory of pure 2,2′-diamino-1,1′-dinaphthyl was isolated; the amount of 2,2′-azonaphthalene was 76% of theory.

Thus, as a result of the decomposition of hydrazo compounds on heating, first, azo compounds and anilines are obtained; these are products of an intermolecular oxidation–reduction reaction:

$$2\mathrm{RNH}-\mathrm{NHR}\rightarrow\mathrm{RN}=\mathrm{NR}+2\mathrm{RNH}_2.$$

The second group of substances is *ortho*- and *para*-semidines. The formation of these compounds may be represented as the result of interaction of radicals arising upon rupture of the N—N bond of the hydrazo compound (4), under conditions not contradicting the accepted notions of the rearrangement as an intramolecular process.

The third group consists of substances with new C—C and C—N bonds—diamines and dinaphthoimines. It is very important that all three isomeric dinaphthoimines, sometimes formed in large amounts, cannot be obtained from ready-made diaminodinaphthyls, since more severe conditions are required for this; this has been properly verified for all three isomers. Consequently, they are formed at the moment of rearrangement. As an intermediate state, one may imagine, for example, the following:

* It is clear that in experiment No. 4 (Table 1) only *o*-semidine is obtained.

when the bond between the nitrogen atoms has not finally been broken and new bonds have not finally been formed.

In conclusion it may be noted that the thermal rearrangement has much in common with the acid rearrangement of hydrazo compounds; but whereas in the first case the hydrazo-compound molecule acquires the necessary lability on heating, in the second case, for the rearrangement to take place, addition of one proton is required, after which the monoprotonated ([6]) hydrazo compound is capable of undergoing transformations in the three directions indicated.

Experimental Part

Hydrazo compounds of the benzene series. About 0.02 mole of the hydrazo compound was heated in a sealed tube under nitrogen, after which the contents of the tube were extracted with ether or with a mixture of ether and petroleum ether and shaken with dilute sulfuric acid (1.1–1.2 g of H_2SO_4 in 30–50 ml of water). Aniline sulfates, with the exception of the sulfates of *p*-chloro- and *p*-bromoaniline, remained in solution, while the *n*-semidine sulfates crystallized out. For purification they were reprecipitated or converted into the bases, giving almost pure substances. In determining the yields of *n*-semidines, their solubility under the conditions of isolation was taken into account. In 100 ml of water acidified with 4–5 drops of H_2SO_4, at 0° about 0.03–0.04 g of 4-aminodiphenylamine dissolves; about 0.16 g of 4-amino-5,2′-dimethyldiphenylamine; 0.5–0.6 g of 4-amino-5,2′-dimethoxydiphenylamine (m.p. of this base 108°); the solubility of 4-amino-4′-methyldiphenylamine sulfate is negligible. The principal quantities of *o*-semidines are found in the ethereal solutions together with azo compounds; a small part is in the aqueous-acid solutions together with anilines, from which they can be completely extracted with ether, after which the *o*-semidines are again converted into salts by shaking the ethereal solutions with hydrochloric acid; in the case of 2-aminodiphenylamine, 10% hydrochloric acid is sufficient, but for 2-amino-4′-methyl- or 2-amino-5,4′-dimethyldiphenylamine, 20–25% acid should be used. The anilines, as usual ([7]), are redistilled with steam and determined by diazotitration. It should be noted that neither benzidines nor diphenylines were found: they cannot be detected either together with the *n*-semidines (making use of the very low solubility of dibenzoylbenzidines, for example, in acetone), or in the residues after steam distillation of the anilines ([8]).

1,1′-Hydrazonaphthalene. 1) 0.0025 mole in 10 ml of absolute alcohol was heated for 3 hours. After removal of the alcohol in vacuo, the residue was dissolved in benzene, ether was added, and the mixture was shaken with 0.5 N HCl (40 ml). The precipitate of the hydrochlorides of 4,4′-diamine and *n*-semidine was separated and converted into the bases by treatment with a small excess of NaOH in aqueous (85%) methyl alcohol, whereupon almost pure 4,4′-diamino-1,1′-dinaphthyl precipitated completely. On dilution of the solution with water a precipitate separated, which was treated with benzoyl chloride in the presence of soda, filtered off, and washed with ether, giving almost pure benzoyl-*n*-semidine with traces of dibenzoyl-4,4′-diamine (insoluble in acetone). *α*-Naphthylamine in the hydrochloric-acid solution was determined by diazotization. The benzene–ether solution was shaken with 30% sulfuric acid (10–15 ml), giving, if *o*-semidine was present, an insoluble sulfate, which on treatment with alkali was converted into pure 1-amino-2,1′-dinaphthylamine. The sulfuric-acid solution was diluted with water and

neutralized, isolating 1,1′-diamino-2,2′-dinaphthyl. The benzene–ether solution was evaporated, boiled with methyl alcohol (8–10 ml), cooled, and the imine solution was separated from the azo compound. After removal of the alcohol, there remained imine contaminated with an admixture of the azo compound, which was removed by repeated treatment of the imine with boiling petroleum ether; for purification, 1,1′-azonaphthalene was recrystallized from ethyl alcohol.

2) 0.0042 mole was heated for 6 hours in 40 ml of benzene. The work-up is similar to the preceding one, but the difference in the results is very large: the amount of 4,4′-diamine is insignificant, whereas the amounts of *o*- and *n*-semidines increase greatly.

3) 0.0025 mole was heated in a sealed tube: after 2–3 min the hydrazo compound begins to melt, the mass turns red, swells, and rapidly settles to the bottom of the tube. After opening the tube it was dissolved in benzene and worked up as before.

1,2′-Hydrazonaphthalene*. 1) 0.0031 mole in 10 ml of absolute alcohol was heated for 3 hours at 100°. After removal of the alcohol, the residue was treated with 10 ml of benzene and the undissolved portion was washed with petroleum ether; the residue was pure 1,2′-dinaphtho-2,1′-imine. The solution in hydrocarbons was shaken first with 0.5 N HCl (40 ml), and then with 2.0 N HCl (15 ml). Small resinous precipitates give no reaction for either para- or ortho-semidine. The first solution was made alkaline with soda and treated with benzoyl chloride; after washing with ether, almost pure dibenzoyl-*o*-diaminodinaphthyl remained on the filter. On evaporation of the ether, a small precipitate was obtained, melting in the interval 100–110° (dibenzoyl derivatives of α- and β-naphthylamine). On alkalinizing the solution in 2.0 N HCl, *o*-diamine precipitated. For purification, the hydrocarbon solution was shaken with 4.0 N HCl, washed with water, the solvent was evaporated, and the residue was boiled with a mixture of benzene and petroleum ether in the ratio 1 : 2 (10 ml); the precipitate was pure imine.

2) 0.0031 mole of the hydrazo compound was heated in a sealed tube under nitrogen for 5 min. The mass was dissolved in benzene and treated generally as above. On shaking with 0.5 N HCl, a precipitate of 4-amino-1,2′-dinaphthylamine hydrochloride separates here.

2,2′-Hydrazonaphthalene*. 1) 0.0035 mole in 20 ml of absolute alcohol was heated for 3 hours. The precipitate was pure *o*-diamine, which was washed with petroleum ether. The solvent was removed, the residue was dissolved in ether, shaken with 3 N HCl and made alkaline, isolating an additional amount of pure *o*-diamine. The ethereal solution contained 1,1′-dinaphtho-2,2′-imine contaminated with 2,2′-azonaphthalene; the substances are readily separated with the aid of methyl alcohol, in which the azo compound is sparingly soluble.

2) 0.0035 mole in 50 ml of benzene was heated for 3 hours. Separation of the reaction products is similar to that described in experiment No. 1.

3) 0.0054 mole of the hydrazo compound was heated for 5 min in a sealed tube; the glassy mass was leached with ether and part of the *o*-diamine was separated. Subsequently the procedure was as indicated above.

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* The starting 1,2′-hydrazonaphthalene contained about 6% 1,2′-azonaphthalene, and the 2,2′-isomer about 2% 2,2′-azonaphthalene.

Note: Figure translations are in progress. See original paper for figures.

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