PREPARATION OF *n*-SEMIDINE BY THE ACTION OF ACID ON 1,2$'$-HYDRAZONAPHTHALENE

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Abstract

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PREPARATION OF *n*-SEMIDINE BY THE ACTION OF ACID ON 1,2′-HYDRAZONAPHTHALENE

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As a result of the interaction of hydrazo compounds with acids, *n*-semidines are formed in those cases in which the principal reaction—the benzidine rearrangement—is contraindicated. Thus, in the benzene series, hydrazo compounds with substituents in the *n*-position relative to the hydrazo group

$$X-\underset{\text{phenylene}}{C_6H_4}-NH-NH-\underset{\text{phenyl}}{C_6H_5}$$

often, in the presence of additional *o*- and *m*-substituents, are converted into *o*- and *n*-semidines (^{1}) (sometimes with admixtures of diphenylines). Where there are no structural obstacles to the formation of benzidines, *n*-semidines are obtained only in traces (^{2}). Our observations concerning the formation of considerable amounts of 4-amino-1,2′-dinaphthylamine in the acid rearrangement of 1,2′-hydrazonaphthalene in the temperature interval 0—20° therefore deserve attention.

$$\text{naphthyl}\ \underset{NH-NH}{}\ \text{naphthyl}$$

For such experiments to be successful, it is necessary that the main mass of the hydrazo compound treated with acid be in the solid phase. The simplest procedure would seem to be shaking crystals of the hydrazo compound with aqueous solutions of acids. However, difficulties arise here, since 1,2′-hydrazonaphthalene in the crystalline state practically does not react even with 30% hydrochloric acid at 15—20°; with acid of higher

Table 1

No. of experiment	Hydrazo compound, mol	Acid: name	Acid: conc., %	Acid: amount, ml	Solvent: name	Solvent: amount, ml	Obtained, % of theory: *n*-semidine	Obtained, % of theory: *o*-diamine	Obtained, % of theory: imine	Obtained, % of theory: azo	Sum of all substances, %
1	0.0015	HCl	38.0	15	–	–	14.0	51.2	–	5.7	70.9
2	0.0011	HCl	18.0	15	Ethanol	15	8.0	75.0	–	not determ.	83.0
3	0.0016	HCl	9.0	30	Acetone	15	13.8	74.0	–	not determ.	87.8
4	0.0034	HCl	10.0	15	Ether	30	19.7	71.3	–	7.0	98.0
5	0.0063	HCl	17.0	30	Ether	30	24.6	68.7	–	3.5	96.8
6	0.0018	HBr	20.0	15	Ether	30	17.8	69.7	–	1.5	89.0
7	0.002	H_2SO_4	25.0	15	Ether	30	33.0	56.0	6.0	3.0	98.0
8	0.0014	HCl	10.0	15	Benzene	15	15.7	71.9	6.0	2.5	95.2
9	0.0018	HCl	10.0	30	Petroleum ether	30	23.6	63.8	2.4	2.6	94.1
10	0.0017	HCl	36.0	17	Acetone	85	–	98.0	–	–	98.0

concentration (38-40%) disproportionation and resinification occur; the amount of *n*-semidine does not exceed 14% of theory (Table 1, experiment 1). The best results are obtained by shaking the crystalline hydrazo compound with dilute acid in the presence of small amounts of an organic solvent, so that at any moment only an insignificant portion of the hydrazo compound taken is present in solution. In the main, the reaction proceeds fairly rapidly (about 1 hour) at 0°, but for completeness of interaction the mixture is left to stand for 15 hours at 15-20°. The solvents tested were alcohol, acetone, ether, benzene, and petroleum ether. As is seen from Table 1, the yield of *n*-semidine sometimes reaches 25-30% of theory.* Being completely dissolved in acetone or alcohol, 1,2′-hydrazonaphthalene readily reacts even with very dilute hydrochloric acid, being converted almost entirely into 1′,2-diamino-1,2′-dinaphthyl, and *n*-semidine cannot be detected; these data agree with the literature (^{3}).

Concerning the possible causes of so considerable a difference in the results of the rearrangement of 1,2′-hydrazonaphthalene in the first and second cases, we note the following. For the rearrangement to occur, the hydrazo compound, whether in the dissolved or crystalline state, first adds a proton:

$$\mathrm{RNH{-}NHR} + \mathrm{H^+} \rightleftarrows \mathrm{RNH{-}\overset{+}{N}H_2R},$$

after which, under the action of a second proton, the rearrangement products are formed (4):

$$\mathrm{RNH{-}\overset{+}{N}H_2R + H^+ \rightarrow \text{rearrangement products} + 2H^+}.$$

It is quite possible that the crystalline hydrazo compound, having added a proton, is capable, at least in part, of rearranging without passing into solution, and that rearrangement in the solid phase and in solution differ substantially from one another in their results. Turning to analogies, let us recall the considerable difference in the results that occurs under the action of dry HCl or HBr, on the one hand, on crystalline hydrazo compounds, and on the other hand, on their solutions in absolute ether or benzene (5).

The 1,2′-azonaphthalene needed by us was obtained by the method of Nietzki and Goll (6), taking into account the remarks of recent works (7). For this purpose β-naphthylamine hydrochloride is diazotized in hydrochloric acid and coupled with hydrochloric-acid α-naphthylamine, and in the resulting 4-amino-1,2′-azonaphthalene the amino group is eliminated in the usual way.

By reduction of 1,2′-azonaphthalene with zinc dust in alcohol or acetone in the cold, 1,2′-hydrazonaphthalene is obtained—a substance melting with decomposition at 141–142°, which, as we have established, on oxidation with mercuric oxide in a benzene-alcohol solution is again converted quantitatively into 1,2′-azonaphthalene.

In the rearrangement of 1,2′-hydrazonaphthalene the following substances are possible:

1. 1′,2-diamino-1,2′-dinaphthyl (*o*-diamine),
2. 1,2′-dinaphtho-1′,2-imine (imine),
3. 2,4′-diamino-1,1′-dinaphthyl (dinaphthylin),
4. 1′-amino-2,2′-dinaphthylamine (*o*-semidine),
5. 2-amino-1,1′-dinaphthylamine (*o*-semidine),
6. 4-amino-1,2′-dinaphthylamine (*n*-semidine).

The predominant product formed is *o*-diamine. Its structure is beyond doubt: it was obtained by catalytic reduction of 1′,2-

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* As we have recently established, *n*-semidine is also obtained in considerable amounts in the so-called thermal rearrangement of 1,2′-hydrazonaphthalene.

dinitro-1,2′-dinaphthyl (^{3}); moreover, we proved the position of the amino groups by converting the diamine dihydrochloride into 1,2′-dinaphtho-1′,2-imine (with brief heating to 240°). This imine is formed in some cases in the rearrangement of 1,2′-hydrazonaphthalene. The third rearrangement product, 4-amino-1,2′-dinaphthylamine (*n*-semidine), is identical with the substance obtained by Levi and Faldino (^{8}) by azo coupling of *n*-diazobenzenesulfonic acid with 1,2′-dinaphthylamine in hydrochloric-acid medium, followed by reduction of the azo compound with hydrosulfite. The same authors found that, if the azo coupling is carried out in acetic-acid medium, then after reduction 1′-amino-1,2′-dinaphthylamine is obtained; it is clear that this compound cannot be formed in the rearrangement of 1,2′-hydrazonaphthalene.

Experimental Part

4-Amino-1,2′-azonaphthalene. A fine suspension of β-naphthylamine hydrochloride (0.3 mole) in 12% hydrochloric acid (500 ml) was cooled to 0°, ice (600 g) and sodium nitrite (21 g) were added. The diazo solution was filtered, and, with good cooling (0–4°) and stirring, a hot solution of α-naphthylamine (0.3 mole) in 5% hydrochloric acid (750 ml) was added. After 15 h the precipitate was filtered off, washed, suspended in water, and made alkaline with ammonia. The technical product melted at 135–138°; yield about 95% of theory. For purification it was crystallized from toluene with addition of activated charcoal. The pure substance formed four-sided prisms (from alcohol), m.p. 145.5–146.5°.

1,2′-Azonaphthalene. To a solution of 4-amino-1,2′-azonaphthalene (0.05 mole) in ethyl alcohol (950 ml) sulfuric acid (45 g) was added, and at 55–60° sodium nitrite (22.5 g in 30 ml of water). The solution was boiled for 40 min, cooled, and diluted with water (500 ml). After 15 h the precipitate was filtered off, washed, dried, and treated with carbon tetrachloride in a Soxhlet apparatus. The yield of product, melting in the range 128–130°, was about 50% of theory; the product was purified by repeated crystallization from carbon tetrachloride, adding alumina during this purification. The pure substance formed dense four-sided prisms (from alcohol), m.p. 144–144.5°.

1,2′-Hydrazonaphthalene. To a solution of the azo compound (1.00 g) in acetone (80 ml) was added 20% aqueous ammonia (16 ml), and at 15–20° zinc dust until complete decolorization of the solution; it was cooled to 0°, filtered, and diluted with ice water (40 ml). The separated crystals of the hydrazo compound were filtered off, washed with ice water and ether. M.p. 141–142° (with decomposition).

Rearrangement of 1,2′-hydrazonaphthalene. We describe in detail the experiments summarized in Table 1 (see experiment 4). A suspension of the hydrazo compound (1.00 g) in ether (30 ml) was shaken with 10% hydrochloric acid (15 ml) in an atmosphere of nitrogen at 0°, after which it was left to stand for 16 h at room temperature. The precipitate of *n*-semidine hydrochloride was filtered off, washed with 10% acid (25 ml) and ether, and converted into the base (0.194 g, m.p. 142-144°). From the hydrochloric-acid solution, on alkalization with ammonia, *o*-diamine was isolated (0.703 g, m.p. 134-136°). After evaporation of the ether, a mixture of the azo compound and imine remained (0.07 g), from which the azo compound is washed out with petroleum ether; the residue is treated with benzene, which dissolves the imine (to separate it from possible impurities).

1′,2-Diamino-1,2′-dinaphthyl crystallizes in very narrow prisms (from alcohol), m.p. 146-147°; the dibenzoyl derivative of *o*-diamine forms four-sided prisms (from acetone), m.p. 253-254°.

1,2′-Dinaphtho-1′,2-imine. Anhydrous dihydrochloride of 1′,2-diamino-1,2′-dinaphthyl, obtained by the action of anhydrous HCl on a benzene solution of 1′,2-diamino-1,2′-dinaphthyl, is heated for 5 min at 240° in a sealed—

tube. Yield of imine about 90% of theory. Narrow prisms (from alcohol), m.p. 236-237°.

Found %: C 89.77; H 5.11; N 5.16
$C_{20}H_{13}N$. Calculated %: C 89.89; H 4.87; N 5.24

4-Amino-1,2′-dinaphthylamine. Tetrahedral prisms (from alcohol), m.p. 151-152°; 4-acetylamino-1,2′-dinaphthylamine—narrow prisms (from alcohol), m.p. 182-183°.

Found %: C 80.95; H 5.63; N 8.55
$C_{22}H_{18}N_2O$. Calculated %: C 80.98; H 5.52; N 8.59

4-Benzoylamino-1,2′-dinaphthylamine—prisms (from alcohol), m.p. 246-247°.

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