“Thermal” Rearrangement of Hydrazo Compounds in Various Solvents

1962

SovietRxiv

Abstract

Full Text

Chemistry

V. O. Lukashevich, L. G. Krolik

"Thermal" Rearrangement of Hydrazo Compounds in Various Solvents

(Presented by Academician B. A. Kazanskii, July 25, 1962)

In studying the rearrangement of hydrazo compounds, and in particular thermal rearrangement, hydrazonaphthalenes deserve special attention. Here the composition of the final reaction products is very often subject to sharp fluctuations depending on factors that have almost no effect in the rearrangement of hydrazo compounds of the benzene series. The present laborious investigation was undertaken to determine the dependence of the results of the rearrangement of $1,1'$-, $1,2'$-, and $2,2'$-hydrazonaphthalenes on the nature of the solvents. The main attention was devoted to the complex, but at the same time most interesting, rearrangement of $1,1'$-hydrazonaphthalene.

Solvents with differently expressed electrical properties were selected (see, for example, (1)); they are arranged in Table 1 in order of increasing dipole moment (partly also dielectric constant). The rate of rearrangement in alcohols, ethylene glycol, and formamide is considerably higher than in other solvents. In ethanol at 100°, after only 10 min, about 87% of the dissolved $1,1'$-hydrazonaphthalene, 53% of the $1,2'$-isomer, and 27% of the $2,2'$-isomer are destroyed; in formamide the rates are still higher. In benzene we obtained, respectively, 52, 11, and 3.5%; in acetonitrile, 45, 8, and 3.5%; and in pyridine, 23.5, 3.4, and 1.0% of transformed hydrazo compounds. Much more important, however, is that the quantitative composition of the rearrangement products is often associated with the nature of the solvents; the latter may be divided into two groups in accordance with the mechanism of their formation, as will be discussed below. The first group comprises diamines and the *o*-diamine corresponding to $2,2'$-dinaphtho-$1,1'$-imine; the second group comprises *o*- and *p*-semidines. In solvents with weakly expressed electrical properties (cyclohexane, benzene, toluene, *p*-dioxane), the amounts of semidines sometimes exceed 50% of the total rearrangement products. With increasing electrical properties of the solvents, the semidines decrease sharply: in alcohols, pyridine, acetone, and acetonitrile the amounts of semidines fall to 29–17%; in ethylene glycol about 12% is obtained; and, finally, in experiments with formamide the amounts of semidines are insignificant (see Table 1). It should be noted that in benzene and toluene, in parallel experiments, fluctuations in yields are sometimes observed, mainly of *p*-semidine and $4,4'$-diamine (see expts. 3 and 4). In absolutized dioxane, instead of *o*-semidine, products of its transformation are sometimes obtained.

The addition of water, with its high dielectric constant, to weakly polar solvents may lead to a substantial reduction in the yields of semidines; this occurs in benzene (expt. 5) and dioxane (expt. 8); a much smaller effect of water is observed in experiments with ethanol (expt. 12) and pyridine (expt. 15).

It is interesting to trace the influence of solvents on the ratios of $1,1'$- and $4,4'$-diamines. Usually the amounts of $1,1'$-diamine (together with the imine) strongly predominate: this occurs in hydrocarbons, anhydrous dioxane, ethanol, and ethylene glycol, where $1,1'$-diamine is sometimes obtained almost twice as much as $4,4'$-diamine. But in methanol (which is close to ethanol in electrical properties) the ratio of $1,1'$-diamine to $4,4'$-diamine is only 1.21.

Table 1

No. of experiment	Solvent	Amount of solvent, ml	Duration of heating, h	1,1′-diamine, % of theory	Imine, % of theory	4,4′-diamine, % of theory	o-semidine, % of theory	n-semidine, % of theory	Naphthylamine, % of theory	Aminoethanol, % of theory	Sum of all substances, % of theory	Ratio of semidines to rearrangement substances, %
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	4,2	10,0	2,3	12,3	25,4	20,3	19,4	93,9	69,5
4	Benzene (abs.)	20	6	3,4	14,1	8,3	10,2	20,0	19,8	17,1	92,9	53,9
5	Benzene (moist)	20	6	5,1	18,6	11,1	8,8	12,6	18,0	17,3	91,5	38,1
6	Toluene	20	6	4,7	16,9	12,2	10,2	11,8	18,8	16,0	90,6	39,4
7	Dioxane (abs.)	15	3	5,2	12,7	7,3	10,8	20,3	18,4	15,1	89,4	55,2
8	Dioxane, water	13,5; 1,5	3	12,7	12,1	18,0	8,7	14,1	14,0	9,5	89,1	34,8
9	Methanol	15	2	5,8	25,0	25,4	7,1	5,8	14,8	9,1	93,0	18,7
10	Methanol + Na	15	1,5	25,2	—	24,8	7,1	8,9	15,1	10,0	91,1	24,2
11	Ethanol	15	1,5	8,7	25,0	15,5	7,6	12,1	15,4	9,5	93,8	28,6
12	Ethanol (85%)	15	1,5	8,8	25,4	18,0	7,1	8,8	13,2	8,3	89,6	23,3

No. of experiment	Solvent	Amount of solvent, ml	Duration of heating, h	1,1′-diamine, % of theory	Imine, % of theory	4,4′-diamine, % of theory	o-semidine, % of theory	n-semidine, % of theory	Naphthylamine, % of theory	Azonaphthalene, % of theory	Sum of all substances, %	Ratio of semidines to rearrangement substances, %
13	Ethanol + Na	15	1,0	33,7	—	24,4	7,0	4,7	13,0	9,2	92,0	16,8
14	Pyridine	10	4	23,2	4,0	17,2	7,5	8,3	18,5	13,5	92,2	26,2
15	Pyridine; water	7,5; 2,5	4	26,1	5,8	25,0	6,6	7,4	14,2	7,2	92,3	19,7
16	Ethylene glycol	15	2	10,7	39,4	24,1	1,1	9,0	7,2	1,8	93,3	12,0
17	Acetone	10	3	4,3	13,5	14,1	1,8	11,4	22,2	18,3	85,6	29,3
18	Methyl ethyl ketone	10	3	9,0	10,7	14,2	2,9	9,5	21,4	20,1	87,8	27,8
19	Acetonitrile	15	2,5	5,2	18,0	18,6	5,4	4,1	21,0	17,9	90,2	18,5
20	Formamide	15	3	21,4	16,0	52,6	—	—	—	1,1	91,1	0
21	Formamide; ammonia	14; 1	2,5	40,4	11,2	33,5	traces	—	4,2	2,1	91,4	0
22	Formamide; pyridine; ammonia	6; 4; 1	2	36,7	8,6	30,0	1,0	1,8	8,5	5,1	91,8	3,6

(exp. 9), and in acetonitrile 1.25 (exp. 19). In formamide, 4,4′-diamine predominates considerably (the ratio of 1,1′- to 4,4′- is 0.67; see exp. 20); the 4,4′-diamine is obtained as the formyl derivative, whereas the less basic 1,1′-diamine is obtained in the free state. These results are reminiscent of the rearrangement of 1,1′-hydrazonaphthalene in the presence of acids. In order to impart a

definitely alkaline character to the medium, 1 ml of a 25% aqueous ammonia solution was added to formamide (14 ml) (see exp. 21); in the second case (exp. 22), a mixture of formamide (6 ml), pyridine (4 ml), and ammonia (1 ml) was taken as the solvent. As can be seen, judging by the amounts of semidines, these experiments are close to the experiment with formamide (exp. 20), but the ratios of 1,1′- to 4,4′-diamine are, respectively, 1.54 and 1.51, i.e., sharply different from the data of experiment 20.

The amounts of 2,2′-dinaphtho-1,1′-imine are also sometimes related to the nature of the solvent: in hydrocarbons, ethanol, methanol, and ethylene glycol, considerably more imine is obtained, its amounts exceeding the amounts of 1,1′-diamine by a factor of 3–4. On the contrary, in pyridine the yields of imine are very small, only 20–25% of the yields of o-diamine (exps. 14 and 15). Very interesting, with respect to all three isomeric imines, are the results associated with rearrangement in an alcohol–alkaline medium. In absolute ethanol and methanol, about 25% of the theoretical amount of 2,2′-dinaphtho-1,1′-imine is obtained; but if metallic sodium is first dissolved in such alcohol to obtain a 0.1 N solution of the alcoholate, then the rearrangement proceeds just as rapidly, yet, remarkably, no imine can be detected (see exps. 10 and 13). In this respect the behavior of 1,2′- and 2,2′-hydrazonaphthalenes is completely analogous: whereas upon rearrangement in absolute methanol (and also in ethanol) more than 50% of the theoretical amount of 1,2′-dinaphtho-1′,2-

imine (see Table 2, exp. 3), and about 20% of 1,1′-dinaaphtho-2,2′-imine—in 0.1 N alcoholic alkali solution (Table 2, exp. 6), imines are not formed at all!

Table 2

No. of experiments	Hydrazonaphthalene	Solvent	Amount of solvent, ml per 1 g naphthalene	Heating duration, h	Obtained from theory, %: o-diamines	Obtained from theory, %: imines	Obtained from theory, %: p-semidines	Obtained from theory, %: naphthylamines	Obtained from theory, %: azo compounds	Sum of all substances, %
1	1,2′-	Benzene (abs.)	20	7.5	24.4	37.0	17.2	3.2	4.0	85.8
2	1,2′-	*n*-Dioxane (abs.)	15	10	46.5	15.1	24.3	1.5	2.1	89.5
3	1,2′-	Methanol	15	3	33.2	53.5	0.7	1.2	0.7	89.3
4	1,2′-	Ethanol + Na	15	3	88.7	—	—	traces	1.0	89.7

No. of experiments	Hydrazonaphthalene	Solvent	Amount of solvent, naphthalene	Heating duration, h	Obtained from theory, %: o-diamines	Obtained from theory, %: imines	Obtained from theory, %: p-semidines	Obtained from theory, %: naphthylamines	Obtained from theory, %: azo compounds	Sum of all substances, %
5	1,2′-	Acetonitrile	15	8	32.0	43.1	8.2	3.0	5.3	91.6
6	2,2′-	Ethanol + Na	20	3	90.2	–	–	–	5.0	95.2

The results of the rearrangement of 1,2′-hydrazonaphthalene are simpler: o-diamine, imine, and 4-amino-1,2′-dinaphthylamine are obtained; disproportionation is insignificant. Exactly as in the case of 1,1′-hydrazonaphthalene, in benzene and dioxane the *p*-semidine is obtained in very considerable amounts (Table 2, exps. 1 and 2), whereas in alcohols the semidine is practically not formed. If all that has been stated about the influence of the nature of the solvent on the results of the rearrangement is taken into account, the existence of intermolecular interaction between the rearranging molecules and the solvent molecules appears quite possible not only at the very beginning, but also throughout the period of rearrangement; thus, the solvent, by promoting an increase in the lability of the molecule of the hydrazo compound, facilitates the initial stage of the process and, in addition, affects the composition of the final substances.

If the rearrangement is hindered, o- and *p*-semidines are obtained; this occurs in the benzene series, and also in a number of the cases considered for 1,1′- and 1,2′-hydrazonaphthalenes. It is quite possible that the formation of semidines is due to a radical reaction under conditions that do not contradict the concepts of rearrangement as an intramolecular process; in other words, either this is an intramolecular radical reaction, or, if the radicals are kinetically independent, their lifetime is extremely short. Solvents with strongly pronounced electrical properties facilitate rearrangement, which leads to a significant reduction in the amounts of semidines in the cases with 1,1′- and 1,2′-hydrazonaphthalenes at the expense of increased yields of diamines and dinaphthylamines; as already stated ([2]), the formation of both the former and the latter is conceivable through a transition state:

Experimental Part

Rearrangement of 1,1′-hydrazonaphthalene, m.p. 147–148° (with decomposition); crystallizes in very dense plates or parallelepipeds (from aqueous ace-

Structural scheme of a transition state with two naphthalene fragments connected by hydrazo nitrogens, with dashed H ··· H and N ··· N interactions shown.

Figure 1: Structural scheme of a transition state with two naphthalene fragments connected by hydrazo nitrogens, with dashed H ··· H and N ··· N interactions shown.

tone). 0.005 mole of the hydrazo compound is heated under nitrogen under the conditions indicated in Table 1, after which the contents of the tube are dissolved in a mixture of benzene (70–80 ml) and ether (30–20 ml); the exceptions are experiments Nos. 20 and 21 with formamide or alcoholic alkali, where the sparingly soluble 4,4′-diformyldiamino-1,1′-dinaphthyl or, respectively, 1,1′-diamino-2,2′-dinaphthyl is more suitably washed off

from accompanying substances. The benzene–ether solutions, by repeated shaking with water, are freed from solvents miscible with water, shaken with 0.5 N hydrochloric acid (50 ml), and left to stand for 15–20 h at 0°, after which the completely precipitated hydrochlorides of 4,4′-diamine and of *p*-semidine are separated. The acidic solution contains α-naphthylamine, determined by diazotization, while the benzene–ether solution contains the remaining rearrangement products and the azo compound. The precipitate of hydrochlorides is treated in the cold with an excess of a solution of sodium hydroxide in methanol (10–20 ml), separated, washed with 85% methyl alcohol and finally with ether, giving almost pure 4,4′-diamino-1,1′-dinaphthyl; the pure substance melts at 201–202° and crystallizes in rhombic plates (from alcohol). The solution in methyl alcohol is strongly diluted with water, the precipitate is taken up in ether and treated in an aqueous soda solution with large excesses of benzoyl chloride, giving benzoyl-*p*-semidine containing dibenzoyl-4,4′-diamine, almost insoluble in acetone. On evaporation of the acetone, 4-benzoylamino-1,1′-dinaphthylamine is obtained, melting at about 225°. M.p. of the pure substance 228–229°; it crystallizes in tetragonal prisms (from acetone). The main benzene–ether solution is shaken with 30% sulfuric acid (20 ml) at 0°; after 15–20 h the sulfate of *o*-semidine is separated, dissolved in methanol and strongly diluted with water, whereby the base of *o*-semidine is completely precipitated (m.p. 185–190°). Pure 1-amino-2,1′-dinaphthylamine forms narrow tetragonal prisms (from alcohol), m.p. 194–195°.

From the sulfuric-acid solution, on alkalization, 1,1′-diamino-2,2′-dinaphthyl precipitates (m.p. 270–275°; that of the pure substance is about 280°). The benzene–ether solution is evaporated to dryness, the residue is boiled with methanol (10 ml), cooled, and the pure azo compound is separated. The imine remaining after evaporation of the methanol is freed from slight impurities of the azo compound by heating with petroleum ether, giving an almost pure substance (m.p. 218–220°). 2,2′-Dinaphtho-1,1′-imine crystallizes in tetragonal plates (from alcohol), m.p. 222–223°. To separate the diamines in the experiments with for-

mamide, the sparingly soluble precipitate (see above) is boiled for 2 h with 25% hydrochloric acid; in this process 4,4′-diformyldiamino-1,1′-dinaphthyl is quantitatively converted into 4,4′-diamine, while 1,1′-diamine is likewise smoothly converted into 2,2′-dinaphtho-1,1′-imine.

Rearrangement of 1,2′-hydrazonaphthalene, m.p. 154–155° (with decomposition); the substance is isolated by careful dilution with water of its solution in acetone, in the form of dense tetragonal plates or prisms. The rearrangement is carried out at 100°; the remaining conditions are given in Table 2. The contents of the tube are dissolved in a mixture of benzene and ether; the solvents miscible with water are extracted with water; the benzene–ether solution is shaken with 1/1-N hydrochloric acid at 0°; after 15–20 h, the hydrochloride of *p*-semidine is separated, dissolved in methanol and, after alkalization with sodium bicarbonate, an almost pure base is obtained (m.p. 143–145°). Otherwise the procedure is as already described ([2]). The pure substances were characterized in one of the earlier works ([3]).

Scientific Research Institute
of Organic Intermediates and Dyes

Received
25 VII 1962

CITED LITERATURE

[1] A. Weissberger, E. Proskauer et al., *Organic Solvents*, 1958.
[2] L. G. Krolik, V. O. Lukashevich, DAN, **139**, No. 1, 110 (1961).
[3] L. G. Krolik, V. O. Lukashevich, DAN, **135**, No. 5, 1139 (1960).

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