[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, TEXAS TECHNOLOGICAL COLLEGE]

The "Thermal" Rearrangement of Hydrazo Compounds.
I. 2,2′-Hydrazonaphthalene[1]

BY HENRY J. SHINE

RECEIVED MARCH 16, 1956

The rearrangement of 2,2′-hydrazonaphthalene to 2,2′-diamino-1,1′-dinaphthyl has been studied in a number of solvents at 80 and 90°. Contrary to earlier belief the rearrangement is not truly thermal but is catalyzed by alcohols when carried out in alcoholic solutions. In ethanol-*d* the rate of rearrangement is lower than that in ethanol, the difference in the rates being small but outside experimental error. Pyridine retards the rearrangement in ethanol solution. It has also been found that 2,2′-hydrazonaphthalene undergoes rapid base-catalysed oxidation to 2,2′-azonaphthalene.

The well-known acid-catalyzed rearrangement of hydrazobenzene to benzidine was shown recently[2,3] to be not first order in hydrogen ion, as had been commonly accepted, but second order. It was concluded by Hammond and Shine[2] that the rearranging entity was the double-protonated ion $C_6H_5N^+H_2N^+H_2C_6H_5$, a situation which enabled them to suggest that in the rearrangement the breaking of the N–N bond was caused by the mutual repulsion of the two positively charged nitrogen atoms. Subsequent work by Cohen and Hammond[4] has supported this idea, although, as yet, no clear picture can be drawn of the final steps by which this interesting intramolecular rearrangement is accomplished.

In 1903 Meisenheimer and Witte[5] reported that 2,2′-hydrazonaphthalene, which they had shown to undergo acid-catalyzed rearrangement to 2,2′-diamino-1,1′-dinaphthyl, was converted to the diaminodinaphthyl by boiling in an alcoholic solution containing aqueous sodium hydroxide, and claimed from this finding that they had discovered the first example of a base-catalyzed benzidine rearrangement. In view of the subsequent numerous investigations of the benzidine rearrangement[6] it is surprising that the claim for a base-catalyzed rearrangement went long unchallenged. However, Krolik and Lukashevich[7] in 1949 showed that instead of being base-catalyzed the rearrangement of 2,2′-hydrazonaphthalene was thermally induced since it took place in neutral ethanol and in neutral benzene solutions at 95°. They found also that the rearrangement took place much more quickly in ethanol than in benzene.

The work of Krolik and Lukashevich, although settling the question of base catalysis, raised the no less interesting question of how the diamino compound is thermally produced. This question is of particular importance since it is known that hydrazobenzene undergoes thermal dismutation to aniline and azobenzene, and the course of this dismutation is believed to involve the formation and interaction of free-radicals.[8,9] If, by analogy, hydrazonaphthalene undergoes homolytic fission prior to its rearrangement to the diamino compound, the further question is raised concerning whether the rearrangement is in this case no longer intramolecular but intermolecular.

In order to find the answers to some of these questions we have begun an investigation of the thermal rearrangement of hydrazonaphthalenes in various solvents, and are able to report here some of our findings with respect to 2,2′-hydrazonaphthalene.

Results and Discussion

The pseudo first-order rate constants for individual runs in a number of solvents are given in Table I.

TABLE I

RATES OF DISAPPEARANCE OF 2,2′-HYDRAZONAPHTHALENE IN VARIOUS SOLVENTS AT 80 AND 90°

Hydrazobenzene 0.01 *M* unless noted.

Solvent	$k \times 10^3$, min.$^{-1}$ at 80°	Probable error in $k \times 10^3$	$k \times 10^3$, min.$^{-1}$ at 90°	Probable error in $k \times 10^3$
Methanol	13.3	0.2		
n-Propanol	9.26	.1		
	9.16	.05		
Ethanol	7.95	.12	20.51	0.15
	7.39[b]	.06	17.96	.16
	7.56[a]	.06		
	7.53	.05		
	7.71	.04		
	4.74[c]	.04		
Ethanol-*d*	6.92	.06		
	6.83	.05		
Isopropyl alc.	5.47	.07		
	5.09	.08		
t-Butyl alc.	4.38	.05		
	4.35	.05		
Acetonitrile	0.80	.02	0.87	.02
Acetone	0.39	.02		
Aq. ethanol	15.41[d]	.1	43.07[d]	.17
	15.00[d]	.1	46.47[a,d]	.2
	26.85[e]	.15		

[a] Hydrazobenzene 0.0075 *M*. [b] Hydrazobenzene 0.015 *M*. [c] 1.25 *M* in pyridine. [d] 5.55 *M* in water. [e] 11.1 *M* in water.

From the constancy of rate constants from runs in anhydrous ethanol solutions it can be seen that the rearrangement is first order in hydrazo com-

---

[1] Presented in part at the Southwestern ACS regional meeting, Houston, Texas, December 1955, and before the Division of Organic Chemistry of the American Chemical Society, Dallas, Texas, April 1956.

[2] G. S. Hammond and H. J. Shine, THIS JOURNAL, **72**, 220 (1950).

[3] R. B. Carlin, R. G. Nelb and R. C. Odioso, *ibid.*, **73**, 1002 (1951).

[4] M. D. Cohen and G. S. Hammond, *ibid.*, **75**, 880 (1953).

[5] J. Meisenheimer and K. Witte, *Ber.*, **36**, 4153 (1903).

[6] Summarized by P. Jacobson, *Ann.*, **428**, 76 (1922).

[7] L. G. Krolik and V. O. Lukashevich, *Dok. Acad. Nauk, SSSR*, **66**, 37 (1949).

[8] Unpublished data of M. J. S. Dewar cited by M. Szwarc, *Chem. Revs.*, **47**, 151 (1950).

[9] P. F. Holt and B. P. Hughes, *J. Chem. Soc.*, 1666 (1953).

pound. Further, it can be seen that the rearrangement proceeds easily in solutions of other alcohols. Krolik and Lukashevich found that the rearrangement proceeded much more slowly in benzene than in ethanol solution. We have confirmed that the rate of disappearance of hydrazo compound in benzene is much slower than in ethanol, but we have been unable to obtain good kinetic data in the benzene solutions. In acetone and acetonitrile the rate of disappearance of hydrazonaphthalene is slow. We use the term disappearance rather than rearrangement in the last two cases since we do not really know whether the hydrazo compound disappears by rearrangement or by some other transformation. This also is the sense in which we regard the rearrangement reported by Krolik and Lukashevich as taking place in benzene. Rate measurements in benzene solution have not enabled us to say anything other than that disappearance of hydrazonaphthalene is slow and does not appear to follow simple first- or second-order kinetics. Work is under way on this phase of the problem. Further, we have not, as yet, been able to isolate 2,2′-diaminodinaphthyl from benzene solution experiments.

From the observation that the rearrangement proceeds in alcohol solutions but very slowly, if at all, in the non-alcoholic solutions we conclude that the hydroxyl hydrogen atom is involved in the rearrangement; that is, that the rearrangement is acid catalyzed, the alcohol acting as the acid. This conclusion receives support from using ethanol-*d* instead of ethanol as solvent, for although the decrease in rate which results is small it is greater than the probable error of 0.14×10^{-3} min.$^{-1}$ among the rates for the five ethanol runs given in Table I. Further, by placing in solution a competitive base, pyridine, the rate of rearrangement is lowered, as would be expected.

The rates of rearrangement in the alcohols listed decrease in the order: methanol, *n*-propanol, ethanol, isopropyl alcohol and *t*-butyl alcohol. This order is somewhat similar to the order of acidities of the alcohols determined spectroscopically by Hine and Hine[10] for solutions of the alcohols in isopropyl alcohol. What the present order means is that, for example, methanol is a stronger acid in methanol solvent than *n*-propanol is in *n*-propanol solvent.

Whether or not two alcohol molecules are involved in the rate step, one for each nitrogen atom, as with acids in the acid-catalyzed benzidine rearrangement,[4] we are unable to say. Those attempts which we have made to determine the order of alcohol participation by using varied ethanol concentrations in acetone and in acetonitrile have been so far unsuccessful, the change in rate at 80° being too insensitive to small changes in ethanol concentration to give good kinetic data. Rearrangement in aqueous ethanol is much faster than in anhydrous ethanol and the rate increases with water concentration at the concentrations used. The use of larger concentrations of water was not possible because of the insolubility of the hydrazonaphthalene. The large increase in rate brought about by the addition of water cannot be attributed only to the acidity of water, since water is only slightly a stronger acid than ethanol.[16] It is rather the change in the nature of the solvent to which this large increase is due.

It is interesting to note that if the alcohol-catalyzed rate of rearrangement of hydrazonaphthalenes is a function of the acidity of the alcohol, rates of rearrangement caused by various alcohols in an appropriate solvent should enable us to use the rearrangement to determine the relative acidities of the alcohols.[11] Work is in progress on this and on finding the order of alcohol participation in the rearrangement.

We have repeated Meisenheimer's work[5] and have confirmed his observations qualitatively. His conclusion that the rearrangement is base catalyzed is again shown to be incorrect since we obtained no 2,2′-diaminodinaphthyl on refluxing 2,2′-hydrazonaphthalene in acetone containing aqueous sodium hydroxide; instead an almost quantitative yield of azonaphthalene was obtained. In the course of investigating the action of bases on 2,2′-hydrazonaphthalene we have found that bases very rapidly catalyze oxidation to the azo compound. In the case of sodium ethoxide in anhydrous ethanol oxidation occurs rapidly even at 0°.

Our conclusions regarding the behavior of 2,2′-hydrazonaphthalene in solution are that rearrangement to 2,2′-diaminodinaphthyl is catalyzed by alcohol molecule and retarded by bases. In Meisenheimer's work and our similar experiment the rapid rearrangement in refluxing aqueous ethanol competes with the base-catalyzed oxidation to the azo compounds.

Acknowledgment.—This work was supported in part by a generous grant from the Robert A. Welch Foundation, Houston, Texas.

Experimental

Bindschedler's Green was prepared by the method of Wieland.[12] After washing well with cold absolute ethanol and ether, the dye was kept under vacuum and remained stable indefinitely. Aqueous solutions of the dye were stable over runs of eight hours length. The *p*-nitrosodimethylaniline required for the preparation of the dye was prepared according to the directions given by Hickinbottom.[13] Titanium trichloride solutions of 0.01 *N* were prepared from the 20% commercial solution and stored in an automatic buret under either nitrogen or carbon dioxide. These solutions underwent constant slow decomposition so that fresh solutions were made after periods of three or four days. Anhydrous ethanol was prepared by the diethyl phthalate method[14] and was stored in a protected automatic buret. The anhydrous methanol, *n*-propanol, *t*-butyl alcohol and acetone were prepared according to the directions given by Vogel.[15] Anhydrous isopropyl alcohol was prepared by azeotropic distillation with benzene.[16] This

---

[10] J. Hine and M. Hine, THIS JOURNAL, **74**, 5266 (1952).

[11] We are indebted to a referee for pointing out that in alcohol solution part of the effect of the alcohol will be due to its solvent nature and thus the rearrangement cannot be used to determine relative acidity of an alcohol in the alcohol as solvent.

[12] H. Wieland, *Ber.*, **48**, 1087 (1915).

[13] W. J. Hickinbottom, "Reactions of Organic Compounds," 2nd Ed., Longmans, Green and Co., London, 1948, p. 318.

[14] A. I. Vogel, "A Text-book of Practical Organic Chemistry," Longmans, Green and Co., London, new impression, 1954, p. 166.

[15] A. I. Vogel, ref. 14, pp. 168–170.

[16] J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier Publishing Co., New York, 1950, p. 316.

was found to be the only satisfactory way of drying isopropyl alcohol well enough to give consistent kinetic data.

2,2'-Azonaphthalene.—This was prepared by the diazo-coupling of 2-naphthylamine according to the procedure given for the preparation of 1,1'-azonaphthalene.[17] In our preparation considerable frothing occurred during the sodium sulfite addition stage of the coupling reaction. It was found expedient to keep the mixture at 60° for two days after the addition in order to facilitate filtration. The crude azo compound was dried under vacuum at room temperature and then extracted in a Soxhlet apparatus with 95% ethanol until the dark red color of the ethanol solution became pale yellow. The ethanol extract was then discarded and extraction continued with chloroform. On cooling to room temperature the chloroform solution deposited tan plates, m.p. 205°.

2,2'-Hydrazonaphthalene was prepared from the azo compound by the method of Krolik and Lukashevich.[7] Rather than filter the concentrated benzene solution to obtain the hydrazonaphthalene as directed by these authors it was found simpler to evaporate the dried benzene solution to dryness at 25° under low pressure. The light pink solid obtained was then taken up in a small amount of acetone, diluted with ethanol and then with ice-cold, freshly-boiled distilled water. The turbid suspension quickly deposited a light pink, fluffy solid which was filtered quickly, washed with cold aqueous ethanol and dried and stored under vacuum. Our product was never almost colorless, as described by Krolik and Lukashevich, but rather a yellowish-pink. In two separate preparations we obtained m.p. 133°. This is the melting point given by Krolik and Lukashevich, and is the basis on which they described the product, m.p. 140–141°, obtained by Meisenheimer as probably containing some of the rearrangement product, the diaminodinaphthyl. On a fourth occasion our product had m.p. 128–129°, and was lighter in color than the products of the previous three preparations. Nevertheless, all four preparations rearranged at the same rate in anhydrous ethanol. It appears, therefore, that the melting point of pure 2,2'-hydrazonaphthalene may still be under question.

Ethanol-*d*.—Diethyl sulfite,[18] 440 g. (3.16 moles), was hydrolyzed by boiling with deuterium oxide,[19] 58 ml. (3.18 moles), until the evolution of sulfur dioxide was almost imperceptible, a period of 13 hours. It was necessary to add a total of 6 drops of concentrated sulfuric acid to take the hydrolysis to completion. The ethanol-*d*, 298 g. (99.5% yield) was distilled off at 78.5° (680 mm.), and placed over anhydrous potassium carbonate for several days to remove entrained sulfur dioxide. The product was then dried by the magnesium method[15] and distilled from the magnesium through a 24-inch helices-packed column; b.p., 78.8° (685 mm.).

Kinetic Method.—Standard solutions of the hydrazo compound were made in the appropriate solvent. Five-ml. aliquots were sealed under nitrogen in dried, nitrogen-flushed ampules. The sealed ampules were placed in a bath kept at the appropriate temperature ±0.1°. At intervals ampules were removed, chilled quickly under running water and opened. The contents were added quickly to 20-ml. aliquots of Bindschedler's Green solution in a nitrogen-flushed flask, and the excess dye was back-titrated in an atmosphere of nitrogen with approximately 0.01 N titanium trichloride solution.[20] Where the solvent contained pyridine the ampule contents were added to the Bindschedler's Green solution and followed after 30 seconds by 2 ml. of 6 N hydrochloric acid. Blanks contained the appropriate amount of pyridine and hydrochloric acid. Plots of log titanium trichloride (blank minus titer) against time gave good straight lines. First-order rates were obtained by calculation using the method of least squares.

Product Analysis. Acid-catalyzed Rearrangement.—To a solution of 0.2507 g. (0.885 mmole) of 2,2'-hydrazonaphthalene in 50 ml. of absolute ethanol was added 1 ml. of concentrated hydrochloric acid. The solution was placed in the dark for 2.5 hours and then diluted with 200 ml. of cold, freshly boiled distilled water. To this solution was added 10% sodium hydroxide solution until the supernatant liquid was alkaline to litmus. The precipitated solid was filtered and dried in a vacuum desiccator. A light tan solid was obtained, weighing 0.2310 g. (92.4%) and having m.p. 180–184°. Crystallization from aqueous ethanol after decolorization with charcoal gave colorless needles, m.p. 188–189°.

Rearrangement at 90° in Ethanol.—A flask containing 0.310 (10.9 mmoles) of 2,2'-hydrazonaphthalene was flushed with nitrogen and into it was measured 30 ml. of anhydrous ethanol. The flask was cooled in Dry Ice and sealed. It was then immersed in a bath thermostatically controlled at 90° and left for five hours. The bath was then allowed to cool slowly during 12 hours to 53°. The sealed flask was removed, cooled and opened. The orange solution was transferred to an erlenmeyer flask, decolorized with charcoal, and diluted with cold, freshly boiled water to give a colorless granular precipitate, m.p. 187–199°, weighing 0.2332 g. (75%). Recrystallization gave colorless needles, m.p. 188–190°; melting point of a mixture with the product from acid-catalyzed rearrangement, 188–190°.

Rearrangement in Ethanolic Sodium Hydroxide.—A solution was made of 0.2510 g. (0.885 mmole) of 2,2'-hydrazonaphthalene in 30 ml. of anhydrous ethanol. To this was added by pipet 3 ml. of 10% aqueous sodium hydroxide. The solution was boiled under reflux for five hours, allowed to cool, stoppered and placed in the dark for 12 hours. A mixture of yellow platelets and colorless needles was deposited. This was filtered off, washed with water and ethanol, and dried under vacuum. The weight was 0.131 g. (52%). The colorless material was extracted with warm 95% ethanol and after decolorizing with charcoal was diluted with water and cooled to give 0.081 g. (32%) of colorless needles, m.p. 188–189°; melting point of a mixture with the product from acid-catalyzed rearrangement, 188–190°.

Oxidation in Sodium Hydroxide–Acetone Solution.—Thirty ml. of anhydrous acetone was measured into a 50-ml. flask containing 0.250 g. (0.88 mmole) of 2,2'-hydrazonaphthalene. To this was added by pipet 3 ml. of 10% sodium hydroxide solution, not all of which was miscible with the acetone. The mixture was boiled under reflux for five hours with occasional swirling. The cooled flask was then stoppered and placed in the refrigerator overnight. A deposit of yellow plates was obtained. Filtration, washing with water and aqueous ethanol and drying gave 0.225 g. (92%) of yellow-orange plates, m.p. 203–204°.

Oxidation in Sodium Ethoxide Solution.—A solution of 0.301 g. (1.06 mmoles) of 2,2'-hydrazonaphthalene in 45 ml. of anhydrous ethanol was prepared in a nitrogen flushed flask. To this was added 5 ml. of 0.53 M sodium ethoxide solution. The flask was stoppered and placed in the dark. Within 6 minutes small crystals of 2,2'-azonaphthalene appeared. After standing overnight in the refrigerator the solution was filtered, giving 0.2954 g. (98%) of yellow platelets, m.p. 202–204°. The product was triturated with 10% hydrochloric acid, filtered, washed with water and ethanol and dried leaving 0.2694 g. (89.5%) of yellow platelets, m.p. 202–204°. The acid filtrate was made alkaline with 10% sodium hydroxide and failed to give a precipitate.

LUBBOCK, TEXAS

---

[17] S. Cohen and R. E. Oesper, *Ind. Eng. Chem., Anal. Ed.*, **8**, 306 (1936).

[18] Voss and Blanker, *Ann.*, **486**, 258 (1931).

[19] Stuart Oxygen Co., San Francisco, Calif.

[20] M. J. S. Dewar, *J. Chem. Soc.*, 777 (1946).