(iii).—A mixture of the hydrazone (0.6 g.) and butyric acid (18 cc.), treated as in the preceding experiment, yielded 1-propyl-4-phenyl-*s*-triazolo[4,3-a]quinoxaline (Tppr), m.p. 146°, which was identified by a mixed melting point determination with an authentic sample prepared from Ip and butyryl chloride.

(4) **The Reaction between I and β-Ketonic Esters.**—The following procedures exemplify general methods; experimental details are included in Table VI.

Preparation of 1-(3-R-Quinoxalin-2-yl)-3-R′-4-R″-2-pyrazolin-5-ones. (a).—A mixture of ethyl ethylacetoacetate (0.0031 mole) and Im (0.0025 mole) was heated in an oil-bath for 2 hours at 140–150°. The mixture was chilled and triturated with cold ethyl acetate. The crude product was recrystallized from ethyl acetate (Table VI, 1, 2 and 7).

(b).—A mixture of ethyl benzoylacetate (0.0039 mole) and Ip (0.0026 mole) was heated in an oil-bath for 3 hours at 160–180°. The mixture was chilled and triturated with methanol. The crude product was recrystallized from pyridine.

Preparation of Lactone-type Pyrazolone.—A mixture of Im (0.43 g.) and ethyl acetoacetate (1.5 cc.) was heated in an oil-bath under reflux for 5 hours. The yellow needles which separated were washed with cold methanol and recrystallized from methanol–pyridine.

Preparation of 1-R′-4-R-*s*-Triazolo[4,3-a]quinoxaline.—A mixture of ethyl acetoacetate (0.003 mole) and 2-hydrazino-3-*sec*-butylquinoxaline (0.002 mole) was heated for 1 hour at 90–100° and then for 4 hours at 150–180°. The pyrolysis residue in the reaction flask was chilled and triturated with petroleum ether to remove decomposition tars. The residue was dissolved in methanol, treated with Norit, and recrystallized to give 1-methyl-4-*sec*-butyl-*s*-triazolo-[4,3-a]quinoxaline as colorless needles, m.p. 145.5°.

(5) **The Reaction between I and Diketones. Reaction of I with β-Diketones.**—The following examples illustrate a general method; experimental details are given in Table VII.

(a).—A mixture of 2-hydrazinoquinoxaline (0.0025 mole) and $CH_3COCH_2COCH_3$ (0.003 mole) was heated in an oil-bath at 120–160° until foaming ceased. The reaction mixture was chilled and triturated with cold methanol. The crude product was recrystallized from methanol to give 1-(quinoxalin-2-yl)-3,5-dimethylpyrazole as colorless needles (no. 3, 4, 5, 6, 7, 11, 12, 16, 20 and 21; Table VII).

(b).—To a solution of 2-hydrazinoquinoxaline (0.0025 mole) in ethanol (5 cc.) was added 0.003 mole of C_2H_5-$COCH_2COC_2H_5$, and the mixture was refluxed for 30 minutes. The reaction mixture was distilled under a diminished pressure and the residue was triturated with aqueous methanol. The crude product was recrystallized from aqueous methanol to give 1-(quinoxalin-2-yl)-3,5-diethylpyrazole as colorless needles (no. 8, 9, 13, 14 and 15).

(c).—A mixture of Ip (0.0025 mole) and CH_3COCH_2-COC_6H_5 (0.003) mole was heated for 5 minutes at 140–150°. The crude product was recrystallized from methanol–pyridine as colorless needles, m.p. 220°, which were identified by a mixed melting point determination with Tpm (no. 10, 18, 19, 22 and 23).

(d).—A mixture of 2-hydrazino-3-*sec*-butylquinoxaline (0.0025 mole)and $CH_3COCH_2COCH_3$ (0.005 mole) in methanol was heated for 3 hours at 200–220° in a sealed tube, the reaction mixture was triturated with petroleum ether, and the residue was recrystallized from methanol. The product separated as colorless needles; the melting point (145°) was not depressed on admixture with 1-methyl-4-*sec*-butyl-*s*-triazolo[4,3-a]quinoxaline.

Reaction of I with the γ-Diketone.—$CH_3COCH_2CH_2$-$COCH_3$. (a).—A mixture of Im (0.38 g.) and CH_3COCH_2-CH_2COCH_3 (0.38 g.) was heated for 1 hour at 150–250°. The reaction mixture was chilled and triturated with petroleum ether. The crude product (0.48 g.) was recrystallized from aqueous ethanol to give yellow needles of 1-(3-methylquinoxalin-2-yl)-3,6-dimethyl-4-hydropyridazine, m.p. 203°.

Anal. Calcd. for $C_{15}H_{16}N_4$: C, 71.40; H, 6.39; N, 22.21. Found: C, 71.40; H, 6.47; N, 22.08.

(b).—A mixture of Ip (0.4 g.) and the γ-diketone (0.23 g.) was heated for 20 minutes at 140–150°. The crude product (0.4 g.) was recrystallized from ethanol to give colorless needles of 1-(3-phenylquinoxalin-2-yl)-3,6-dimethyl-4-hydropyridazine, m.p, 184°.

Anal. Calcd. for $C_{20}H_{18}N_4$: C, 76.41; H, 5.77; N, 17.82. Found: C, 76.85; H, 5.77; N, 17.57.

(c).—Colorless needles of 1-(3-*sec*-butylquinoxalin-2-yl)-3,6-dimethyl-4-hydropyridazine were prepared by procedure b; m.p. 142°.

Anal. Calcd. for $C_{18}H_{22}N_4$: C, 73.44; H, 7.53; N, 19.03. Found: C, 73.23; H, 7.61; N, 19.31.

OKUDA, TOYAMA, JAPAN

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

The "Thermal" Rearrangement of Hydrazo Compounds. III.[1] The Kinetics and Mechanism of the Rearrangement of 2,2′-Hydrazonaphthalene in Polar Solvents

BY H. J. SHINE AND J. C. TRISLER[2]

RECEIVED JANUARY 11, 1960

The products of rearrangement of 2,2′-hydrazonaphthalene (I) in ethanol, aqueous ethanol, acetone and tetrahydrofuran have been quantitatively isolated. The two products, 2,2′-diamino-1,1′-binaphthyl (II) and 3,4:5,6-dibenzocarbazole (III) are formed in approximately the same proportions in these solvents: that is 80–85% of II and 15–20% of III. The rates of rearrangement of I have been measured in these solvents and in others at several temperatures. At 80° the rates in anhydrous ethanol are faster than those in acetone, dioxane, tetrahydrofuran and pyridine, the rates in the last four solvents being close to each other. The rate of rearrangement in aqueous ethanol increases with water concentration and a plot of log rate constant against Grunwald–Winstein "Y" values is linear. From rates of rearrangement at 80°, 90°, 98° and 105° in ethanol, dioxane and pyridine, the activation energies and entropies of activation were found to be 23.2, 29.5 and 30.9 kcal./mole and −13.4, −4.6 and −1.6 cal./deg./mole. Attempts to obtain similar data for acetone and tetrahydrofuran solutions were not successful. It is believed that these experiments show that the rearrangement of I in hydroxylic solvents involves a transition state that is polar. It is believed that the rate is enhanced in solutions of alcohols by hydrogen-bonding from hydroxyl hydrogen to the hydrazo nitrogens. The transformation of I to II and III *via* the polar transition state thus formed is enhanced as the solvent becomes more ionizing; that is, more aqueous. The rates of rearrangement in the non-ethanolic solutions are believed to suffer some retardation by hydrogen-bonding from hydrazo hydrogen to solvent, but for the most part to be independent of the solvent.

In recent years, the mechanism of an unusual type of benzidine rearrangement, a so-called "thermal" rearrangement, has been the subject of research in several laboratories. Several interpretations have been given. The base-catalysis idea of the original discoverers, Meisenheimer and Witte,[3] was shown to be incorrect by Krolik and Lukashev-

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[1] From the Ph.D. thesis of J. C. Trisler, Texas Technological College, 1959. For Part II see ref. 5. Part of this work was presented at the Meeting of the American Chemical Society, Fall, 1958.

[2] Robert A. Welch Foundation Fellow, 1956–1959.

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

ich.[4] On the other hand, while the Russian workers described the rearrangement simply as thermal, two other views were given. Shine and, later, Shine and Snell,[5] attributed rearrangement in hydroxylic solvents to acid catalysis, the hydroxyl hydrogen behaving as the acid; whereas Vecera[6] interpreted the rearrangement as one of free-radicals.

In order to clarify the issues and to provide explanations for the observations of the several groups of workers, we have investigated the influence of solvent on the rearrangement of 2,2'-hydrazonaphthalene (I). The compound I was chosen, since it is not subject to the side reactions, of unknown nature, that make investigation of the analogous 1,1'-hydrazonaphthalene difficult. It is very likely that an understanding of the intractable nature of the 1,1'-isomer will provide a fruitful insight to the rearrangement. At the present, however, we wish to report on the isomer I and its rearrangement in the solvents ethanol, aqueous ethanol, acetone, *p*-dioxane, tetrahydrofuran and pyridine.

Products.—Product analysis was carried out for the rearrangement of I in several of the solvents used. In no case was any organic product isolated other than 2,2'-diamino-1,1'-binaphthyl (II) and 3,4:5,6-dibenzocarbazole (III); nor was any evidence ever obtained that other products were formed. It has been reported by Vecera[6] that, when the 1,1'-isomer rearranges, either in solution or in the molten state, all of the benzidine rearrangement types, including the semidine and diphenylene types, are formed. Nothing of this nature was observed in the present work with the 2,2'-isomer. It is possible that this difference between the two isomers is reflected in the difficulty we have experienced in following rates of disappearance of the 1,1'-isomer by the techniques used in the present work. The amounts of II and III obtained are given in Table I. It is evident that no great differences exist among the data listed, an evidence that gives some indication that the step which leads to products may be the same in each solvent.

TABLE I

PRODUCTS OF REARRANGEMENT OF 2,2'-HYDRAZONAPHTHALENE AT 80°

Solvent[a]	Diamine, %[b]	Carbazole, %[b]	Azo, %[c]
Ethanol	77.9	21.2	7.2
Ethanol	87.3	12.9	7.0
Ethanol[d]	86.4	13.1	0.4
Aq. ethanol	80.3	19.4	9.2
Acetone[d]	76.1	19.5	77.4
Tetrahydrofuran[d]	78.2	21.7	70.0

[a] All solvents anhydrous except aqueous ethanol which contained 75.36% ethanol by weight. [b] Based on the amount of hydrazonaphthalene rearranged. [c] These figures show the amount of azonaphthalene isolated and are based on the hydrazonaphthalene originally weighed: they represent the azonaphthalene formed from not de-gassing solutions, or by base-catalyzed oxidation of unrearranged hydrazonaphthalene. [d] De-gassed solutions.

It has been established by Krolik and Lukashevich, and confirmed by work in these laboratories,[7] that III is not obtained by subjecting II to the conditions in which I rearranges. Thus, III is formed by steps which also, and preferentially do, lead to II.

Rates.—In Table II are listed the rates of disappearance of I in aqueous ethanol solutions at 80°, while in Table III are listed the rates of disappearance of I in dry solvents at several temperatures. Plots of the rates obtained from aqueous ethanol solutions against water concentration and against the Grunwald-Winstein "Y"[8] values for the solvents are given in Fig. 1. The two plots have characteristics which suggest that the rate of disappearance increases as a function of the increasing ionizing power of the solvent.

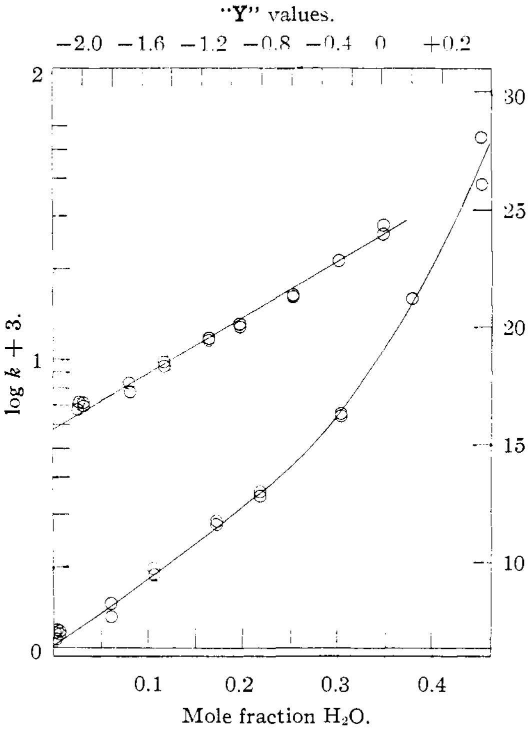

Fig. 1.—Relationships between rate of rearrangement of 2,2'-hydrazonaphthalene and water concentration in aqueous ethanol solutions: upper plot, log *k* *versus* Grunwald–Winstein "Y" values; lower plot, *k* *versus* mole fraction of water; all *k*'s in min.$^{-1}$.

The case at hand is very similar to the thermal rearrangement of some peresters reported by Bartlett and Storey.[9] We conclude from these data, therefore, that in hydroxylic solvents the transition state in the rearrangement of I to II and III is more ionic than solvated I and that this transition state leads both to II and III.

The rate constants listed in Table III do not differ very largely in going from solvent to solvent. However, it is apparent that the rates in ethanol are always set apart from rates in the other solvents, the rates in these last solvents showing some differences but being, nevertheless, quite close in magni-

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(4) L. G. Krolik and V. O. Lukashevich, *Doklady Akad. Nauk, SSSR*, **65**, 37 (1949).

(5) H. J. Shine and R. L. Snell, *Chemistry & Industry*, 706 (1957).

(6) M Vecera, T. Gasparic and J. Petranek, *ibid.*, 299 (1957).

(7) Unpublished work, of Dr. R. L. Snell.

(8) (a) E. Grunwald and S. Winstein, THIS JOURNAL, **70**, 846 (1948); (b) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2770 (1956).

(9) P. D. Bartlett and B. T. Storey, *ibid.*, **80**, 4954 (1958).

TABLE II

RATES OF REARRANGEMENT OF 2,2′-HYDRAZONAPHTHALENE IN SOLUTIONS OF AQUEOUS ETHANOL AT 80°, HYDRAZONAPHTHALENE 0.01 *M*

Ethanol, %	$k^a \times 10^3$, min.$^{-1}$	Prob. error[b] $\times 10^3$ in k	Y[c]
99.96	7.02	0.03	−2.036
99.96	6.76	.04	
99.91	6.72	.03	−2.028
99.91	7.14	.05	
99.75	7.09	.06	−2.003
99.75	6.96	.11	
97.49	8.27	.05	−1.691
97.49	7.71	.06	
95.56	9.50	.16	−1.466
95.56	9.76	.04	
92.49	11.76	.04	−1.156
92.49	11.66	.05	
90.15	12.97	.08	−0.948
90.15	12.80	.04	
85.36	16.34	.08	−0.592
85.36	16.19	.10	
80.64	21.22	.15	−0.292
75.36	28.05	.05	+0.009
75.36	26.07	.12	

[a] Calculated by the method of least squares. [b] Calculated by the method of least squares; H. Margenau and G. M. Murphy "The Mathematics of Physics and Chemistry," D. Van Nostrand Co., Inc., 6th printing, 1946, p. 502. [c] Calculated from the equation $Y = -2.042 + 6.086N - 6.209N^2 + 6.024N^3$, where N is the mole fraction of water, given in ref. 8b.

TABLE IV

ACTIVATION ENERGIES AND ENTROPIES OF ACTIVATION OF THE REARRANGEMENT OF 2,2′-HYDRAZONAPHTHALENE

Solvent	E^{*},[a] kcal./mole	ΔS^{*}[b] at 80°, cal./deg./mole
Ethanol	23.2	−13.4
Dioxane	29.5	− 4.6
Pyridine	30.9	− 1.6

[a] From the equation $\log k = -E^{*}/RT + C$ for which the slope $E^{*}/2.303\ R$ was calculated from the data in Table III by the method of least squares. [b] From the equation $\Delta S^{*} = 2.303R\,(\log A - \log k_{\mathrm{B}}T/h) - R$, in which $\log A = \overline{\log y} - m\bar{x}$; where y are the rate constants in Table III, converted to sec.$^{-1}$, x are the reciprocal of T values given in Table III, m is the slope of the plot of $\log y$ *versus* $1/T$, k_{B} is Boltzmann's constant, h is Planck's constant, and R is the gas constant.

TABLE III

RATES OF REARRANGEMENT OF 2,2′-HYDRAZONAPHTHALENE IN DRY SOLVENTS, HYDRAZONAPHTHALENE 0.01 *M*

Solvent	Temp., °C.	$k^b \times 10^5$, min.$^{-1}$	Prob. error[c] $\times 10^5$ in k	Solvent	Temp., °C.	$k^b \times 10^5$, min.$^{-1}$	Prob. error[c] $\times 10^5$ in k
Ethanol[a]	80	672	3.5	Ethanol	90	1768	3.5
Ethanol[a]	80	714	4.7	Pyridine	90	15.46	0.09
Ethanol[a]	80	702	3.3	Pyridine	90	14.03	.09
Ethanol[a]	80	676	3.6	THF	90	17.0	.75
Acetone[a]	80	8.8	0.39	THF	90	12.05	.18
Acetone[a]	80	13.9	.42	THF	90	14.1	.18
Acetone[a]	80	11.8	.20	Ethanol	98	3206	19.5
Acetone[a]	80	10.4	.45	Ethanol	98	3292	8.3
Dioxane	80	6.48	.05	Dioxane	98	54.93	0.68
Dioxane	80	7.25	.07	Dioxane	98	53.23	1.3
Pyridine	80	4.69	.03	Pyridine	98	35.78	0.53
Pyridine	80	4.38	.02	Pyridine	98	38.43	0.36
THF	80	4.20	.18	Ethanol	105	6280	41.1
THF	80	4.91	.03	Ethanol	105	6365	35.4
THF	80	5.05	.06	Dioxane	105	111.7	0.70
Ethanol	90	1702	4.2	Dioxane	105	112.0	1.3
Ethanol	90	1884	23.5	Pyridine	105	83.3	0.75
Ethanol	90	1774	15.4	Pyridine	105	88.6	0.42

[a] The rate constant given here differs slightly from that given in ref. 15; we believe this is due to the better tube sealing technique used in the present work. [b] Calculated by the method of least squares. [c] See Table II for ref.

tudes. Translation of some of these rates into activation energies and entropies of activation is given in Table IV. Activation energies, E^{*}, were calculated from data in Table III. Plots of log k *versus* $1/T$ are shown in Fig. 2. Entropies of activation, ΔS^{*}, at 80° were calculated. It appears that at a cost of some freedom of movement in the transition state, resulting in the lower value of ΔS^{*}, the process in ethanol occurs at a lower energy than in the solvents dioxane and pyridine. Similar data were not obtainable for tetrahydrofuran solutions owing to the irreproducibility of rates at 90 and 98°. The data from ethanol, dioxane and pyridine prompt us to interpret the greater rigidity of the transition state in ethanol as arising from hydrogen bonding from the solvent to the hydrazo nitrogen atoms. In turn, the bonding enhances the scission of the N-N bond by placing on each nitrogen atom some positive charge. Thus, this process is very similar to general acid catalysis in the acid-catalyzed rearrangement in hydrazo compounds.[10]

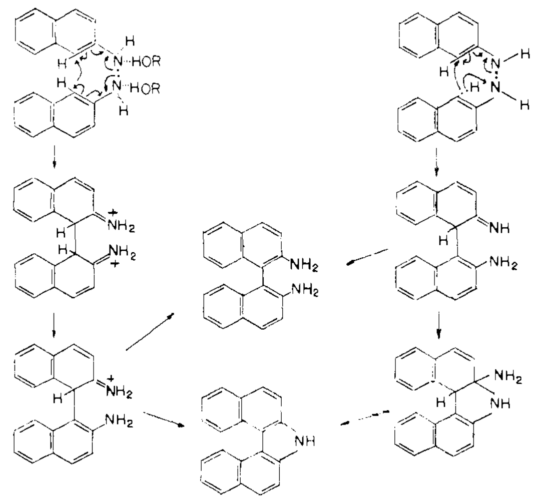
We like to interpret the behavior of I in the solvents dioxane, tetrahydrofuran and pyridine as being somewhat retarded by hydrogen-bonding from hydrazo hydrogen to solvent, but for the most part as being independent of the solvent. Here, one faces an apparent difficulty in answering not only at which step in the rearrangement in these solvents the N atoms receive their second hydrogens, but also where these hydrogen atoms originate. Rearrangement in these "non-donor" solvents appears to be truly and wholly intramolecular. That is, in these cases it appears necessary to conclude that the hydrogen atoms leaving the "*ortho*" position in

(10) M. D. Cohen and G. S. Hammond, THIS JOURNAL, **75**, 880 (1953).

I are the hydrogen atoms arriving at the nitrogen atoms in II. Further, since both II and III must be formed during this process, it would seem that the process during which I is converted to II and/or III cannot be a symmetrical one. By this we mean that the two amino groups cannot be formed simultaneously, since it has been found that II is not convertible to III under the conditions of rearrangement of I.

The question of the origin of the hydrogen atoms in the amino groups of II arises not only in rearrangements in these non-donor solvents but also in rearrangements in solvents such as benzene and cyclohexane, which we regard as non-donor solvents, and in rearrangement of I in the solid state. That is, rearrangement of I to II and III occurs in benzene, as shown by Krolik and Lukashevich.[4] This has been confirmed[7]; it has been found[7] that rearrangement occurs also in cyclohexane and, furthermore, also when I is heated at 90° (well below its melting point) and 150° in the absence of solvents.

In this sense, therefore, we regard all rearrangements in the non-donor solvents as being for the most part independent of the solvent, while, on the other hand, rearrangement in hydroxylic solvents appear to us to be undergoing general acid catalysis. The processes in the two types of solvent are not necessarily dissimilar, however. The process in non-donor solvents appears to us to be best interpreted as involving one-electron changes in a way such that a step is involved in which either II or III may be obtained. The same interpretation is applicable to donor solvents, although in this case the one-electron changes occur within a charged transition state. Indeed, we regard the case of donor solvents to include the well-known general acid catalysis of all hydrazoaromatic rearrangements. In each case, donor or non-donor solvent, we believe that a "concerted" mechanism of rearrangement obtains; that is, that carbon–carbon bond making occurs while the nitrogen–nitrogen bond is breaking. These ideas are presented pictorially.



Experimental

Materials.—2,2′-Azonaphthalene was made by the method of Cohen and Oesper.[11] The crude, dry, tan solid was extracted with chloroform in a Soxhlet apparatus until the extract solution was almost colorless. The chloroform solution was "charcoaled" with Nuchar C (West Virginia Pulp and Paper Co.) and concentrated. Orange crystals were obtained, collected and dissolved in hot benzene. This solution was "charcoaled." Light-orange plates formed on standing, m.p. 208–209°.

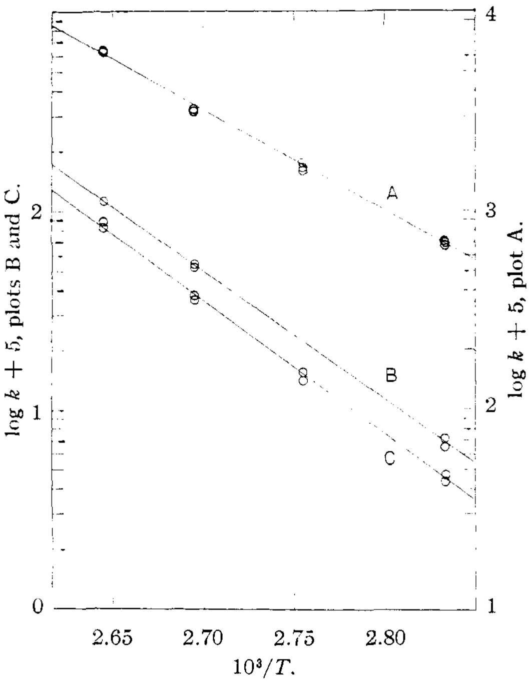


Fig. 2.—Plot of log *k versus* 1/*T* for rearrangement of 2,2′-hydrazonaphthalene in solution: A, ethanol; B, *p*-dioxane; C, pyridine; all *k*'s in min.$^{-1}$.

2,2′-Hydrazonaphthalene (I).—Approximately 2 g. of the azonaphthalene was dissolved in 250 ml. of boiling acetone. The solution was cooled in ice to give a suspension of very small crystals, and the cold suspension was shaken with zinc dust and concentrated ammonium chloride solution in sufficient quantities to produce a colorless solution. After standing in ice for 15 min. the solution was filtered under nitrogen through a sintered glass funnel. The filtrate was received in a filter flask containing approximately 1000 ml. of cold, dilute ammonium hydroxide solution, prepared from degassed water. The ammonium hydroxide served to remove zinc salts. The colorless I was coagulated by partially evacuating the filter flask while stirring with a magnetic stirrer. The colorless solid was filtered under nitrogen and dried over calcium chloride *in vacuo*, while being protected from light. The product, obtained in 90% yield, was only very slightly yellow and had m.p. 136°. The melting point of this compound, however, as is to be expected of thermally labile solids, varied with the rate of heating. The value of 136° was obtained consistently with a heating rate of 2°/min.

Bindschedler's Green was prepared as described earlier,[12] except for a modification of one step. In the reduction of the *p*-nitrosodimethylaniline, instead of adding alternate portions of zinc and warm, aqueous *p*-nitrosodimethylaniline hydrochloride slurry to the hydrochloric acid, all of the *p*-nitrosodimethylaniline hydrochloride was suspended in the acid and cooled to 5°. Zinc dust was added slowly and the temperature kept below 30°. After addition of the zinc the colorless solution was cooled to 10° and filtered. The remaining procedure was as given earlier. Preparations with the above modification consistently gave a product with the equivalent weight 236 (calcd. 231).

3,4:5,6-Dibenzocarbazole was prepared from 2,2′-azonaphthalene by the method of Corbellini and Debenedetti.[13]

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(11) S. Cohen and R. Oesper, *Ind. Eng. Chem., Anal. Ed.*, **8**, 306 (1936).

(12) H. J. Shine, R. L. Snell and J. C. Trisler, *Anal. Chem.*, **30**, 383 (1958).

(13) A. Corbellini and E. Debenedetti, *Gazz. chim. ital.*, **59**, 391 (1929).

Crystallization from acetic acid or from aqueous ethanol gave colorless needles, m.p. 157–158°.

Anhydrous ethanol was prepared by both the sodium-diethyladipate method and the aluminum foil method. Constant boiling aqueous ethanol was prepared from technical 95% ethanol by refluxing with potassium hydroxide and silver nitrate for 5 hr. and distilling through a 7-ft., helices-packed column. The product was found to be 95.56% ethyl alcohol.

1,4-Dioxane.—Four liters of dioxane (Distillation Products Industries) was refluxed for 18 hr. with 60 ml. of concentrated hydrochloric acid and 300 ml. of water. The cooled solution was shaken with solid potassium hydroxide until no more would dissolve. The dioxane layer was removed, refluxed with sodium overnight and distilled into a flask containing lithium aluminum hydride. The dioxane was distilled from the hydride just prior to use.

Tetrahydrofuran.—Commercial tetrahydrofuran (Matheson, Coleman and Bell) containing an inhibitor was refluxed with sodium overnight and then distilled and stored as in the case of dioxane.

Acetone.—Four liters of reagent grade acetone was refluxed with potassium permanganate overnight and distilled. The distillate was refluxed for 4 hr. with 1 lb. of Drierite (Hammond Drierite Co.) and distilled through a 4-ft., helices-packed column. The distillate was stored under nitrogen.

Cyclohexane.—Phillips pure grade cyclohexane was refluxed for several hr. over type 4A, 8 × 12 beads, molecular sieve (Linde Co.). The cyclohexane was then left over the sieve and distilled as needed. A column of the sieve was placed between the still-pot and receiving flask.

Pyridine was reagent grade and was used without further treatment.

Aqueous ethanol solutions of known concentration were made from anhydrous ethanol and distilled water. The density of each solution was determined at 20 ± 0.01° and translated to ethanol concentration from standard tables.[14]

Kinetic Method.—The analytical procedure has been described earlier.[15] The tubes in which aliquots were sealed were cleaned either by chromic acid or by scrubbing with detergent solution; if chromic acid was used the tubes were soaked in ammonium hydroxide after washing copiously with water, and then washed with water again. All tubes were dried at 110° prior to use. For rates in ethanol and aqueous ethanol the nitrogen flushed tubes were filled and sealed under nitrogen without prior cooling in Dry Ice and without prior de-gassing. It was found that cooling in Dry Ice in cork-stoppered tubes prior to sealing[15] gave slightly higher rates. For slow rates in acetone, tetrahydrofuran, dioxane and pyridine, the tubes used were sealed to $^{19}/_{38}$ tapers. The tubes were flushed with nitrogen before filling and when filled were placed on the high-vacuum manifold. De-gassing at better than 10^{-4} mm. was repeated four times on each tube. Liquid nitrogen was used for freezing. The tubes were brought to room temperature prior to placing them in the thermostated bath. Rates of disappearance of I in anhydrous solvents were determined at 80, 90, 98 and 105° with a range of ±0.1° at each temperature. At 98 and 105° the rates in tetrahydrofuran were not reproducible. It is not known why, although it was observed that the titrated aliquots quickly became green again after the end-point had been reached. The continual cracking of tubes containing acetone made further work with this solvent unattractive.

Products.—Products were isolated from rearrangements at 80° in the solvents: anhydrous ethanol, aqueous ethanol, acetone and tetrahydrofuran. Approximately 1.5 g. of 2,2′-hydrazonaphthalene was placed in a dry, nitrogen-flushed, 500-ml. round-bottom flask. To this was added 200 to 300 ml. of the appropriate solvent. In the case of aqueous ethanol and one experiment with anhydrous ethanol the flask was then sealed. In a second experiment with anhydrous ethanol and in experiments with acetone and tetrahydrofuran the flask was sealed under vacuum after four cycles of the customary liquid-air freezing and thawing degassing technique. De-gassing was carried out on a manifold evacuated by a triple stage, oil diffusion pump. The sealed flask was then placed in a bath at 80 ± 0.1° and left there for a period of time depending on the solvent in the flask. With ethanol and aqueous ethanol, sufficient time, calculated from the half-life of rearrangement, was allowed to ensure virtually complete disappearance of the 2,2′-hydrazonaphthalene. Since rearrangement in acetone and tetrahydrofuran was so slow, the flasks containing these solvents were removed after 20–30% rearrangement had occurred. After cooling the solutions, the mixture of products was recovered as follows. In the cases of ethanol and aqueous ethanol the absence of hydrazo compound in solution was first confirmed by testing with Bindschedler's Green solution. The solution of products was then poured into a large volume of distilled water, and the precipitate was allowed to coagulate. In initial experiments with these solvents the solution was evaporated to dryness for recovering of products. It was subsequently found that precipitation in water gave almost quantitative recovery and was, therefore, used for the complete product analysis. The precipitate was filtered, washed well with water, dried over calcium chloride *in vacuo*, weighed and dissolved in benzene.

In the cases of acetone and tetrahydrofuran an aliquot of the solution was analyzed for hydrazo compound by the Bindschedler's Green–titanous chloride method. The remaining solution was then made alkaline with a few ml. of sodium hydroxide solution, cooled in ice and oxidized with a gentle stream of oxygen for 4 to 5 hr. This method was found to be cleaner and more reliable than the use of mercuric oxide.[4] It was established that both 2,2′-diamino-1,1′-binaphthyl and 3,4:5,6-dibenzocarbazole were quantitatively recoverable when separately treated this way, while the hydrazo compound was converted quantitatively to the azo compound. The oxidation solution was evaporated to dryness at room temperature, and the residue was extracted with benzene.

The benzene solution obtained in either one of the procedures above was extracted with 10% hydrochloric acid. The acid solution was neutralized with ammonium hydroxide and the precipitated diamine collected, washed, dried and weighed. In every case the crude diamine melted in the range 189–191°.

The remaining benzene solution was evaporated to dryness at room temperature and the residue was taken up in the minimum amount of hot 95% ethanol. Where the residue contained a large proportion of azo compound, as in the acetone and tetrahydrofuran cases and in the non-degassed ethanolic solutions, the azonaphthalene crystallized out and was collected.

The residual ethanol solution contained the dibenzocarbazole and a small amount of azonaphthalene. Evaporation to dryness gave a dark brown solid with a melting range 152–157°. In initial experiments with product analysis the attempts made to recrystallize quantitatively this brown solid failed. It was found, incidentally, in these attempts, that 3,4:5,6-dibenzocarbazole crystallized in two forms: crystallization from petroleum ether sometimes gave small, snowy plates, m.p. 120–121°, and sometimes long, colorless needles, m.p. 155–156°. The needles, m.p. 156–157°, were also obtained by crystallization from aqueous ethanol. The two forms were interconvertible by going from one solvent to the other. Their ultraviolet spectra in ethanol were identical. A mixture of the two forms had m.p. 156–157°. Because of crystallization losses the amounts of dibenzocarbazole and azonaphthalene in the dark residue were determined spectroscopically in the ultraviolet, using a Beckman DK-2 instrument. Optical densities were measured at 332 and 277 mμ. Mixtures of pure dibenzocarbazole and azonaphthalene were used for calibration. Composition calculations were made by the customary simultaneous equation method.

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[14] N. A. Lange, "Handbook of Chemistry," 8th edition, Handbook Publishers, Inc., Sandusky, Ohio, 1952, pp. 1207–1209.

[15] H. J. Shine, THIS JOURNAL, **78**, 4807 (1956).