Solvent system	2,3-Dihydroxybenzoylglycine (I)	Hydrolyzed I	
		Glycine	2,3-Dihydroxybenzoic acid
(1)	0.80	0.18	0.90
(2)	.29	.32	.39
(3)	.67	.42	.70
(4)	.39	.18	.67

The hydrolyzed sample of I gave two discrete spots in each of the four solvent systems. The two spots were identified as glycine and 2,3-dihydroxybenzoic acid by co-chromatography with authentic specimens. Glycine was identified with ninhydrin spray and the 2,3-dihydroxybenzoic acid gave under ultraviolet light a brilliant blue fluorescence which could be seen even in the lighted room. The latter compound also gave the ferric chloride and nitrous acid reactions.

Synthesis of 2,3-Dihydroxybenzoic Acid.—A good synthetic method[19] is available for this compound. However, because of their technical simplicity, the methods of Horri, *et al.*,[20] and Kawai,[21] were adopted.

The ultraviolet absorption characteristics of 2,3-dihydroxybenzoic acid were reported above. Electrometric titration in water at 25° provided apparent pK_a values of 2.8 and 10.1 and a molecular weight of 152, ±2%.

Synthesis of I.—The procedure of Sheehan and Hess[16] was followed: 1.0 gram of 2,3-dihydroxybenzoic acid and 0.7 to 0.8 g. of glycine ethyl ester were dissolved in 5 to 6 ml. of tetrahydrofuran. One and a half gram of dicyclohexylcarbodiimide in the minimum amount (3 to 5 ml.) of tetrahydrofuran was added. The reaction mixture was let stand overnight at room temperature in an atmosphere of N_2. A small amount of acetic acid was added to decompose the excess condensing reagent. The insoluble urea was removed and the solvent evaporated. The residue was dissolved in ethyl acetate and washed with a small amount of dilute HCl. Ethyl acetate was then evaporated to dryness.

The residue, mainly 2,3-dihydroxybenzoylglycine ethyl ester, was dissolved in 20 to 30 ml. of 1 *N* NaOH. The solution was stirred at room temperature for 4 hr. in an atmosphere of N_2 to prevent the decomposition of the product in the basic solution. The insoluble material was filtered out and the filtrate was acidified with 4 to 6 ml. of dilute H_2SO_4 to obtain a strongly acidic *p*H. The solution was extracted with ethyl acetate 2 or 3 times and the solvent evaporated to dryness. The residue was dissolved with the aid of dilute NH_4OH, and then (in the ice-bath) dilute HCl was added slowly to precipitate the product. The precipitate, weighing 500 mg., was recrystallized several times from the minimum amount of hot water and dried at 100° under vacuum (m.p. 210–211° with reddish coloration). A mixed melting point with the isolated product gave no depression.

Anal. Calcd. for $C_9H_9O_5N$: C, 51.16; H, 4.30; N, 6.64. Found: C, 51.09; H, 4.38; N, 6.81.

Synthetic I proved indistinguishable from natural I when examined in the following ways: paper chromatography in the various solvent systems described above, color reactions with aqueous ferric chloride, the reaction with nitrous acid, solubility characteristics, ultraviolet spectrum, infrared spectrum, apparent pK_a values and molecular weight (by titration).

Acknowledgments.—The authors are indebted to Albert N. Booth, F. H. Carpenter and James Cason for gifts of chemicals and to Keith Freeman for interpretation of infrared data.

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[19] J. Cason and G. O. Dyke, THIS JOURNAL, **72**, 621 (1950).

[20] Z. Horri, Y. Komiyama, K. Otsuki and Y. Yamamura, *J. Pharm. Soc.* (*Japan*), **72**, 1520 (1952).

[21] S. Kawai, *Bull. Inst. Phys. Chem. Res.* (*Tokyo*), **5**, 47 (1926).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF MICHIGAN]

The Thermal Breakdown of Diaryltetrazoles

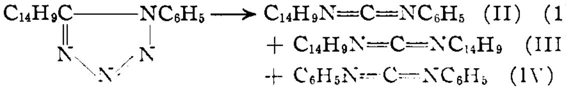
BY PETER A. S. SMITH AND EDWARD LEON[1]

RECEIVED APRIL 5, 1958

The thermal decomposition of diaryltetrazoles containing phenyl, α- and β-naphthyl and 1-phenanthryl groups has been studied. The products are diarylcarbodiimides, 2-aryl-arimidazoles or both. Unsymmetrical diarylcarbodiimides have been found to undergo a redistribution reaction when strongly heated, giving rise to the two related symmetrical carbodiimides. The von Braun–Rudolf tetrazole synthesis has been found beset with hitherto unsuspected side-reactions that lead to ureas (*via* carbodiimides) and anilinotetrazoles. These can apparently be avoided by using aqueous sodium azide in place of anhydrous hydrogen azide solutions.

The tetrazole ring system is a relatively stable one in the absence of heat-sensitive substituents. Although there have been casual references to decomposition of tetrazoles when strongly heated, surprisingly little has been reported regarding the products. 5-Diazotetrazole was reported in 1893[2] to give cyanogen and nitrogen, and in 1897, 5-phenyl- and 5-*p*-anisyltetrazole were reported to decompose on heating to give the corresponding 3,5-diaryl-1,2,4-triazoles and diaryl-*sym*-tetrazines.[3] No further work was reported until 1953, when pyridotetrazole and its 6- and 8-nitro derivatives were studied; only the last gave an identifiable product, a pyridofuroxan.[4]

A chance observation by one of us[5] that 5-(1-phenanthryl)-1-phenyltetrazole (I) decomposed when heated above its melting point to a gas and crystalline products, one of which is N-phenyl-N-1-phenanthrylcarbodiimide (II), led us to investigate this neglected field. We have since found that the unsymmetrical carbodiimide is the primary product of decomposition, resulting from a carbon-to-nitrogen rearrangement accompanying loss of nitrogen, and that the other products are the two corresponding symmetrical carbodiimides III and IV, which arise from a subsequent redistribution reaction. These previously unreported reactions


I

$$\longrightarrow C_{14}H_9N{=}C{=}NC_6H_5 \text{ (II)} \quad (1)$$
$$+ C_{14}H_9N{=}C{=}NC_{14}H_9 \text{ (III)}$$
$$+ C_6H_5N{=}C{=}NC_6H_5 \text{ (IV)}$$

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[1] From the doctoral dissertation of Edward Leon.

[2] J. Thiele and J. T. Marais, *Ann.*, **273**, 144 (1893).

[3] W. Lossen and F. Statius, *ibid.*, **298**, 96 (1897); W. Lossen and J. Colman, *ibid.*, **298**, 107 (1897).

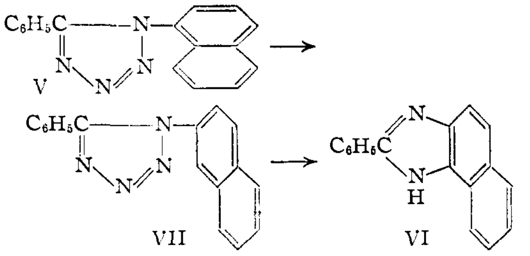
[4] J. H. Boyer, D. I. McCane, W. J. McCarville and A. T. Tweedic, THIS JOURNAL, **75**, 5298 (1953).

[5] P. A. S. Smith, *ibid.*, **76**, 436 (1954).

have now been investigated with six variations of the aryl substituents among phenyl, 1-naphthyl and 2-naphthyl (see Table I), and have been found to be general. The study of these tetrazoles has, furthermore, revealed an equally interesting competing reaction, by which 2-aryl-arimidazoles isomeric with the initial carbodiimide are formed.

The identity of the carbodiimides from I was established by hydration to the corresponding ureas, followed by hydrolysis to amines, in addition to elementary analysis and the presence of infrared absorption at 4.62 μ, characteristic of the carbodiimide system.[6] Separation of the carbodiimides in this instance was effected readily by solubility differences, since the 1-phenanthryl group prevented the usual polymerization[7] of carbodiimides. The carbodiimides from the other tetrazoles usually were not separated, since they rapidly changed to the characteristic insoluble, amorphous, carbodiimide polymers, although some separation could be achieved by fractional distillation of the monomers. They were instead converted by hydration with oxalic or hydrochloric acids to mixtures of monomeric ureas,[7] which are more readily handled. The compositions of the urea mixtures were established qualitatively by fractional crystallization, elementary analysis and infrared absorption.

When 1,5-diphenyltetrazole was decomposed at 210–230° and the residue then distilled, a 70% yield of diphenylcarbodiimide was obtained, followed by a small amount of a higher-boiling, isomeric crystalline substance, subsequently identified as 2-phenylbenzimidazole. In another experiment, in which this basic product was isolated instead by extraction with acid, a yield of 14% was obtained. The maximum yield of arimidazole in this type of reaction was obtained from 1-(1-naphthyl)-5-phenyltetrazole (V), which gave 25% of 2-phenyl-(1,2-naphth)-imidazole (VI). The isomeric 1-(2-naphthyl)-5-phenyltetrazole (VII) also gave V in nearly the same yield, but 1,5-bis-(2-naphthyl)-tetrazole gave only 9% of 2-(2-naphthyl)-1,2-naphthimidazole. The 1-phenyl positional isomers of V and VII gave no arimidazole, but only mixed carbodiimides.

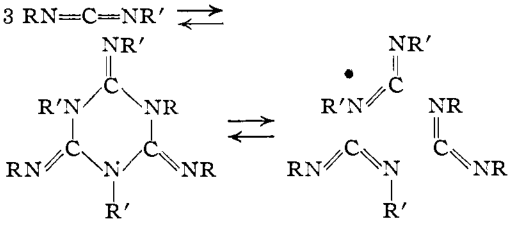


(2)

The rearrangement reaction of tetrazoles is a heat-induced analog of the acid-catalyzed rearrangement reported previously.[5,8] The free-energy difference between the tetrazole ring and its imidyl azide isomer is apparently greater than that between their conjugate acids, since a temperature higher by about 50° is required for the purely thermal rearrangement. At the temperatures required (above 200°), azides in general decompose rapidly,[9] so it is reasonable to suppose that the temperature requirement is imposed by the tetrazole–imidyl azide conversion. So considered, the rearrangement becomes the azide analog of the Tiemann rearrangement of amidoximes, which has been shown to produce cyanamides, the tautomers of carbodiimides, as the primary products.[10]

The heat-induced disproportionation of carbodiimides, suggested by the nature of the products from the pyrolysis of the tetrazoles, was confirmed by direct investigation. N-Phenyl-N-(2-naphthyl)-carbodiimide was prepared by treating the corresponding thiourea with lead oxide. A portion set aside as a control gave N-phenyl-N-(2-naphthyl)-urea in 89% yield when hydrated with hydrochloric acid, demonstrating that disproportionation is not effected by these processes. A second portion of carbodiimide was heated at 200° for one hour before hydration. From the resulting obviously mixed crystalline ureas, a small amount of N,N-bis-(2-naphthyl)-urea was isolated by fractional crystallization. The remaining fractions gave elementary analyses consistent with mixtures of N-phenyl-N-(2-naphthyl)-urea and N,N-diphenylurea in various proportions, and one of the fractions, which was a eutectic as shown by its sharp (and minimal) melting point of 203°, was duplicated by a synthetic mixture made from the two pure components. Furthermore, small amounts of the disproportionation product N,N-bis-(1-naphthyl)-urea, in addition to the expected N-phenyl-N-(1-naphthyl)-urea, were isolated from the hydration products of the carbodiimide prepared by heating N-phenyl-N′-(1-naphthyl)-thiourea with lead oxide; in this case, even the mild heating attending its preparation was sufficient to cause disproportionation.

The disproportionation of carbodiimides is presumably related to the structure of their polymers, which are of low order and have been shown to consist of trimers to a considerable extent.[11] If the polymers from unsymmetrical carbodiimides have occasional head-to-head configurations, disproportionation would be an expected result of polymer–monomer equilibrium. In the case of the triazine structure proposed for the trimers,[11] the disproportionation could occur as in equation 3.



(3)

The diaryltetrazoles used in this work were prepared from imidyl chlorides by the von Braun–

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[6] H. G. Khorana, *Chem. Revs.*, **53**, 145 (1953).

[7] F. Zetzsche and A. Friedrich, *Ber.*, **72B**, 363 (1939).

[8] E. Lieber, R. A. Henry and W. G. Finnegan, THIS JOURNAL, **75**, 2023 (1953).

[9] *Cf.* P. A. S. Smith, J. M. Clegg and J. H. Hall, *J. Org. Chem.*, **23**, 524 (1958), and J. H. Boyer and F. C. Canter, *Chem. Revs.*, **54**, 1 (1954).

[10] M. W. Partridge and H. A. Turner, *J. Pharmacy and Pharmacol.*, **5**, 103 (1953).

[11] M. Busch, G. Blume and E. Pungs, *J. prakt. Chem.*, **79**, 513 (1909); C. Schall, *ibid.*, **81**, 191 (1910).

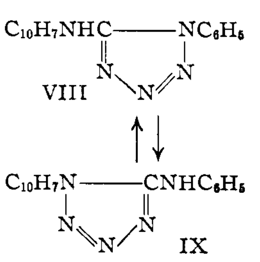
Rudolf synthesis[12] with anhydrous solutions of hydrogen azide, or by a modified process using sodium azide in buffered aqueous solution together with a water-miscible organic solvent such as acetone.[5] Difficulties with the von Braun–Rudolf synthesis in the form of unexpected side reactions have already been reported in the case of 1-phenanthryl derivatives.[5] We encountered similar behavior with several of the tetrazole preparations that we attempted, and were so led to utilize the aqueous sodium azide method, which has thus far been free of such interference.

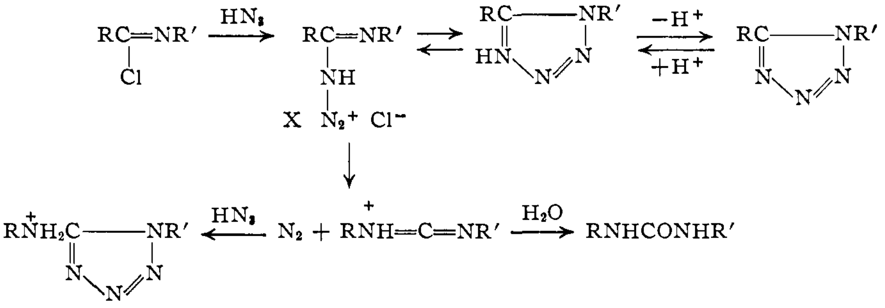
The tetrazoles whose preparation was accomplished or attempted are listed in Table I, together with their yields and the yields of other products. It can be seen that in the cases of the two dinaphthyltetrazoles, the side reactions so dominated some experiments as to preclude isolation of any tetrazole at all. The precise significance of the ratios of tetrazole to side product is obscured, however, by an unexpectedly large variation among similar experiments. The cause of this is at present still enigmatic, although there are indications that trace amounts of phosphoric acids may be responsible. We hope to treat this subject more fully later.

When α-naphthanilide was converted to its imidyl chloride with phosphorus pentachloride, freed of phosphoryl chloride, and then treated with anhydrous hydrogen azide, there was isolated in addition to the expected 1-phenyl-5-(1-naphthyl)-tetrazole, 8% of a crystalline substance containing one more nitrogen atom. From its mode of occurrence and the empirical formula, the alternate aminotetrazole structures VIII or IX can be deduced. Such isomers are known to be readily interconverted, sometimes so easily that their separate identity cannot be determined readily.[13] In another experiment, this side product (now 16%) was accompanied by N-phenyl-N′-α-naphthylurea (after hydration) in 21% yield.

When α-naphthoyl-α-naphthylamide was exposed to the foregoing treatment, no tetrazole could be found, but 8% of N,N′-di-α-naphthylurea and 18% of N,N′-di-α-naphthyl-α-naphthamidine were isolated. From the first experiment with the isomeric β-naphthoyl-β-naphthylamide, only di-β-naphthylurea was isolated (47% yield). In two more experiments in this series, the imidyl chloride was carefully freed of phosphoryl chloride, and then treated with hydrogen azide in one instance in benzene alone, and in the other with three molar equivalents of phosphoryl chloride added. Unlike the original experiment or our expectations, both of these experiments gave only 1,5-di-β-naphthyltetrazole. This tetrazole was found to be unaffected by refluxing with phosphoryl chloride. In a final experiment in this series, the imidyl chloride was treated with hydrogen azide in benzene in the presence of polyphosphoric acid. Both tetrazole and urea were obtained, in yields of 47 and 13%, respectively. Using aqueous sodium azide instead of hydrogen azide in benzene produced the tetrazole uncontaminated with side products, although mixed with the starting amide, from which it was separated by fractional crystallization.

The foregoing side reactions can be accounted for in terms of the mechanism previously proposed[5] for the acid-catalyzed rearrangement of tetrazoles. The reactions may be presumed to begin with the addition of hydrogen azide to the imidyl chloride to give a probably ionic chloride of a protonated imidyl azide (X). This may cyclize (reversibly) to the conjugate acid of a tetrazole, or may instead undergo rearrangement with loss of nitrogen to give the conjugate acid of a carbodiimide. This would be converted to a urea by water used in work-up, but in the presence of more hydrogen azide would be converted to an aminotetrazole, as represented in the accompanying scheme.





The opening of the tetrazole ring to give, presumably, a protonated imidyl azide, which then rearranges, already has been demonstrated.[5] However, the high temperatures (*ca.* 160°) required for the ring opening contrast with the near room temperature at which the presently observed side reactions in the von Braun–Rudolf synthesis occur. The side reactions must therefore occur before the tetrazole ring is formed, and are thus competing, not subsequent, events. By analogy with acyl azides, whose rearrangement has been shown to be acid-catalyzed,[14] the protonated imidyl azide would be expected to rearrange more readily than its conjugate base, which is presumably readily capable of cyclization to tetrazole. Under these circumstances, a strongly proton-donating environment should promote the rearrangement side-reaction, while a proton-absorbing environment (sodium azide in aqueous phosphate buffer) should retard the rearrangement and thus promote tetrazole formation. These conclusions are in accord with the observations reported.

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(12) J. von Braun and W. Rudolf, *Ber.*, **74**, 264 (1941).

(13) R. A. Henry, W. G. Finnegan and E. Lieber, THIS JOURNAL, **76**, 88 (1954); W. L. Garbrecht and R. M. Herbst, *J. Org. Chem.*, **18**, 1269 (1953).

(14) M. S. Newman and H. L. Gildenhorn, THIS JOURNAL, **70**, 317 (1948).

TABLE I

1,5-DIARYLTETRAZOLES

1-R	5-R	Yield, % Tetrazole	Yield, % Side prod.	M.p., °C.		alyses, % Calculated C	Calculated H	Found C	Found H
2-Naphthyl	Phenyl	96	0	177–178.5	$C_{17}H_{12}N_4$[15]	74.98	4.44	75.18	4.64
1-Naphthyl	Phenyl	95.5	0	130–131	$C_{17}H_{12}N_4$[15]	74.98	4.44	75.13	4.58
Phenyl	2-Naphthyl	89	2.5[a]	136.5–137.5	$C_{17}H_{12}N_4$[16]	74.98	4.44	74.96	4.37
Phenyl	1-Naphthyl	36–51	8–37[a]	133.5–134.5	$C_{17}H_{12}N_4$[15]	74.98	4.44	74.84	4.57
2-Naphthyl	2-Naphthyl	0–48[b]	0–47[a]	159–159.5	$C_{21}H_{14}N_4$[16]	78.24	4.38	77.96	4.29[c]
1-Naphthyl	1-Naphthyl	0	26[a]						

[a] See text. [b] 47% using aqueous sodium azide; for other products, see text. [c] Calcd.: N, 17.48. Found: N, 17.24.

The naphthamidine obtained in one experiment stoichiometrically does not require nitrogen from azide, although it may involve it, and it may have been formed in the treatment of the amide with phosphorus pentachloride.

Experimental

Preparation of Tetrazoles.—The tetrazoles used in this work were prepared from known amides by treatment first with phosphorus pentachloride, then with benzene solutions of hydrogen azide.[12] The new tetrazoles are listed in Table I. Only those tetrazole preparations that gave rise to side products are described hereinafter.

1-Phenyl-5-(1-naphthyl)-tetrazole.—A mixture of 10.0 g. (0.0405 mole) of α-naphthanilide and 8.44 g. (0.0405 mole) of phosphorus pentachloride was heated gently until vigorous reaction occurred, and the resulting phosphoryl chloride was largely removed by aspirator vacuum. The residual imidyl chloride was taken up in about 20 ml. of anhydrous benzene and mixed with a benzene solution of hydrogen azide prepared from 5.27 g. (0.081 mole) of sodium azide. After four days at room temperature the solution was washed with 5% sodium hydroxide, then water, and concentrated. The precipitated solids, m.p. 124–131°, weighed 8.02 g. After two recrystallizations from absolute alcohol, the material appeared as a mixture of large prisms and fine needles. The needles were removed by decantation, and the prisms were recrystallized twice more from absolute alcohol yielding 3.61 g. (33%) of 1-phenyl-5-(1-naphthyl)-tetrazole (*cf.* Table I).

The needles were combined with the filtrates from the recrystallizations, the solvent was removed by distillation, and the mixed solids were separated by fractional crystallization from absolute alcohol and from benzene (in which the diaryl-tetrazole is the more soluble), and by mechanical separation. There was thus obtained an additional 2.17 g. (18%) of 1-phenyl-5-(1-naphthyl)-tetrazole and 1.00 g. (8%) of fine needles, m.p. 203.5–204° dec. These are apparently 1-phenyl-5-(1-naphthylamino)-tetrazole (VIII) or the tautomerically related structure 1-naphthyl-5-anilinotetrazole (IX).

Anal.[15] Calcd. for $C_{17}H_{13}N_5$: C, 71.06; H, 4.56; N, 24.38. Found: C, 70.50; H, 4.84; N, 24.06.

In a repetition of the above experiment, after five days the imidyl chloride–hydrogen azide reaction mixture was shaken with excess 5% sodium hydroxide solution. A precipitate quickly began to appear in the benzene phase, so the unseparated mixture was allowed to stand for four hours. The solid was filtered off, washed well with water, and recrystallized from absolute alcohol in four crops. There was thus obtained 2.22 g. (21%) of N-phenyl-N′-(1-naphthyl)-urea, m.p. 223°, followed by resolidification and melting anew at 242° with gas evolution. These melting temperatures and behavior were unchanged when the substance was mixed with an authentic sample.

The benzene filtrates were washed with water, concentrated, and further handled as in the first experiment. There was thus obtained 4.02 g. (36%) of 1-phenyl-5-(1-naphthyl)-tetrazole and 1.80 g. (16%) of 1-phenyl-5-(1-naphthylamino)-tetrazole (VIII) or its isomer IX.

Attempted Preparation of 1,5-Di-(1-naphthyl)-tetrazole.—A mixture of 12.0 g. (0.0405 mole) of 1-naphthoyl-1-naphthylamide and 8.44 g. (0.0405 mole) of phosphorus pentachloride would not react when heated on a steam-bath, but reacted vigorously after 1 ml. of phosphoryl chloride was added and heating continued. After removal of the phosphoryl chloride and treatment with hydrogen azide (from 5.27 g. of sodium azide) in benzene, two layers formed. A slow, steady evolution of gas from the red lower layer began immediately, and after hours the mixture had become homogeneous. After three more days, the mixture was heated on a steam-bath for three hours and then cooled and mixed with aqueous sodium carbonate. A solid, wt. 1.88 g., m.p. 245–247° dec., formed and was removed by filtration. Two recrystallizations from nitrobenzene gave 1.01 g. (8%) of N,N-di-(1-naphthyl)-urea, m.p. 285° dec. A sample was prepared for confirmatory analysis by sublimation at 0.3 mm. and washing with alcohol and chloroform, and then had m.p. 287° dec. (reported[17] 286–287° dec.).

Anal.[18] Calcd. for $C_{21}H_{16}ON_2$: C, 80.75; H, 5.16; N, 8.97. Found: C, 80.78; H, 5.24; N, 8.88.

The benzene filtrate from the isolation of the urea was evaporated, leaving a gum which could not be crystallized from absolute alcohol. An alcohol–acetone mixture produced from it 3.42 g. of a yellow solid, m.p. 169–171°, in two crops. Recrystallization of this material from alcohol-acetone mixture gave a further 0.06 g. of dinaphthylurea and 2.09 g. (18%) of yellow, crystalline N,N′-di-1-naphthyl-1-naphthamidine. The melting point, 190.5–191.5°, was raised to 191–192° by further recrystallization, and was not depressed by mixture with an authentic sample prepared from N-(2-naphthyl)-2-naphthimidyl chloride and 2-naphthylamine by the method used to prepare N,N′-diphenylbenzamidine.[19]

Anal.[18] Calcd. for $C_{31}H_{22}N_2$: C, 88.12; H, 5.25; N, 6.63. Found: C, 87.62; H, 5.13; N, 6.78.

The oxalate was prepared in dioxane, and had m.p. 209° crude, and 211.5° after three recrystallizations from alcohol.

Anal.[18] Calcd. for $C_{33}H_{24}N_2O_4$: C, 77.33; H, 4.72; N, 5.47. Found: C, 77.57; H, 4.46; N, 5.82.

1-Phenyl-5-(2-naphthyl)-tetrazole.—The conversion of 10.0 g. of β-naphthanilide to tetrazole was carried out as described with α-naphthanilide. The imidyl chloride–hydrogen azide reaction mixture deposited a colorless solid during five days standing, after which the entire mixture was stirred with 5% sodium hydroxide solution. More benzene was added until almost all the solid dissolved, and the remainder was filtered off and washed with water and benzene. It weighed 0.25 g., and recrystallization from aqueous alcohol gave 0.22 g., m.p. 315° with prior sintering and darkening. The benzene filtrate was evaporated and the residue recrystallized from absolute alcohol to give 9.84 g. (89%) of 1-phenyl-5-(2-naphthyl)-tetrazole (*cf.* Table I).

1,5-Di-(2-naphthyl)-tetrazole.—A mixture of 12.0 g. (0.405 mole) of β-naphthoyl-β-naphthylamide, 8.44 g. (0.405 mole) of phosphorus pentachloride and 1 ml. of phosphoryl chloride was heated until vigorous reaction began. After the evolution of hydrogen chloride ceased, the phosphoryl chloride was removed on a steam-bath at 20 mm. A solution of hydrogen azide in 110 ml. of benzene, prepared from 5.27 g. (0.081 mole) of sodium azide, was added to the cooled imidyl chloride. A slow, steady evolution of gas began from the upper surface of the benzene-insoluble layer, and lasted nearly two days. After four days, the mixture was heated for three hours on a steam-bath; a benzene-insoluble layer remained present. Addition of aqueous

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[15] Analysis by Dr. Goji Kodama, University of Michigan.

[16] Analysis by Mrs. Anna Griffin, University of Michigan.

[17] A. E. Dixon, *J. Chem. Soc.*, **79**, 102 (1901).

[18] Analysis by Clark Microanalytical Laboratory, Champaign, Ill.

[19] C. Gerhardt, *Ann.*, **108**, 219 (1858).

sodium carbonate to the cooled mixture transformed the sticky lower layer into a yellowish solid by a rather vigorous reaction. The collected solid was triturated with boiling absolute alcohol, leaving 5.85 g. (47%) of N,N′-di-(2-naphthyl)-urea, m.p. 270° dec. Recrystallization once from nitrobenzene gave 4.50 g. (36%), m.p. 296° dec., and three more recrystallizations raised the m.p. to 300° dec. (reported[20] m.p. 300° dec.) for a confirmatory analytical sample.

Anal.[18] Calcd. for $C_{21}H_{16}ON_2$: C, 80.75; H, 5.16; N, 8.97. Found: C, 80.21; H, 5.07; N, 9.02.

The original benzene filtrate was washed with water and concentrated, and the residue recrystallized from alcohol. A total of 0.75 g. of light yellow solid was obtained in four crops, with m.p. dropping from 209–211° to 181–191°; it was not investigated further.

In a second experiment, starting with 6.00 g. of amide, the crude imidyl chloride (a solid) was completely freed of phosphoryl chloride by solution in xylene and distillation to dryness under aspirator vacuum. The residual solid was dissolved in 50 ml. of warm, dry benzene; a small precipitate appeared on cooling. A solution of hydrogen azide in 60 ml. of benzene, prepared from 2.64 g. of sodium azide, was added, and the precipitate dissolved. There was no visible gas evolution, but a new solid began to form after a day. After five days the mixture was poured into excess sodium hydroxide solution. More benzene was added until all solids dissolved, and the benzene layer was separated, washed with water and evaporated in an air stream. Recrystallization of the residue from about 100 ml. of absolute alcohol gave 3.14 g. (48%) of 1,5-di-(2-naphthyl)-tetrazole, m.p. 157–158.5°.

One ml. of concd. hydrochloric acid was added to the filtrate, and the solvents were evaporated. The residue was recrystallized from absolute alcohol giving 1.51 g., m.p. 130–200°, in two crops. This solid was pulverized, wet with a little alcohol, and triturated with sodium hydroxide solution. The resulting slightly sticky solid was washed with water, and then thoroughly with benzene until no more would dissolve. There remained 0.07 g. (1%) of β-naphthoyl-β-naphthylamide, m.p. 236.5–237.5°, not depressed by mixture with an authentic sample. Evaporation of the benzene filtrates and recrystallization of the residue from absolute alcohol gave an additional 0.69 g. (11%) of 1,5-di-(2-naphthyl)-tetrazole, m.p. 157–158.5°. When attempts to obtain a second crop gave only a gummy substance, a little concd. hydrochloric acid was added, after which 0.42 g. of a yellow solid, m.p. 270–280° dec., was obtained. Treatment with base reconverted it to the gum, which was not investigated further.

In a third experiment, otherwise identical with the foregoing one, 9.29 g. (0.0606 mole) of phosphoryl chloride was added to the benzene solution of the imidyl chloride before addition of hydrogen azide. The total yield of 1,5-di-(2-naphthyl)-tetrazole, m.p. 157.5–159.5°, was 61%; neither amide nor urea was isolated.

In a fourth and otherwise similar experiment, the crude imidyl from which most of the phosphoryl chloride had been removed was mixed with about 5 ml. of commercial polyphosphoric acid and warmed slightly with a small flame. The resulting spongy mass was cooled and mixed with hydrogen azide (from 2.64 g. of sodium azide) in benzene; a very slow evolution of gas began from the surface of the lower layer. The addition of 20 ml. of phosphoryl chloride in an attempt to increase the mobility of the lower layer had no visible effect. The mixture was allowed to stand for five days, during which the lower layer was stirred with a glass rod several times a day. Treatment with excess sodium hydroxide solution caused slow formation of a solid from the polyphosphoric acid layer. It was collected after four hours; wt. 0.92 g., m.p. 270–274° dec. Recrystallization from nitrobenzene gave 0.77 g. (13%) of N,N′-di-(2-naphthyl)-urea, m.p. 297° dec., undepressed when mixed with an authentic sample. Evaporation of the benzene filtrate and recrystallization of the residue from absolute alcohol gave 3.08 g. (47%) of 1,5-di-(2-naphthyl)-tetrazole in two crops, m.p. 159–159.5°, with gas evolution from the melt near 200°; m.p. when mixed with an authentic sample, 158.5–159.5°.

By the Aqueous Sodium Azide Method.—The crude imidyl chloride from 5.00 g. (0.0168 mole) of β-naphthoyl-β-naphthylamide was stirred with a solution of 2.19 g. (0.0337 mole) of sodium azide and 4.78 g. (0.0337 mole) of disodium hydrogen phosphate in 40 ml. of water and 50 ml. of acetone. After one hour, the solvents were evaporated in an air stream, and the residue was triturated first with water and then with 125 ml. of hot benzene. The residue, 1.49 g., m.p. 221–223° dec., yielded 1.24 g. (28%) of β-naphthoyl-β-naphthylamide, m.p. 236–238° (undepressed by mixture with an authentic sample), by recrystallization from alcohol. Evaporation of the benzene filtrate and recrystallization of the residue from alcohol gave 2.00 g. (37%) of 1,5-di-(2-naphthyl)-tetrazole, m.p. 156–158°, with gas evolution from the melt near 200°. Two more recrystallizations from alcohol raised the m.p. to 159–159.5° (*cf.* Table I). A second crop, wt. 0.47 g., m.p. 145–160°, yielded 0.07 g. more β-naphthoyl-β-naphthylamide and 0.27 g. (5%) of tetrazole by alternate crystallization from benzene and alcohol.

Treatment of 1,5-Di-(2-naphthyl)-tetrazole with Phosphoryl Chloride.—A mixture of 2.00 g. of 1,5-di-(2-naphthyl)-tetrazole, 1.90 g. of phosphoryl chloride and 25 ml. of dry benzene was refluxed for two hours while protected from moisture. The cooled mixture was treated with excess 10% sodium hydroxide solution, and the benzene layer was washed with water and evaporated. Trituration of the residue with alcohol left 1.92 g. (96%) of unchanged tetrazole, m.p. 158.5–160°.

Pyrolysis of 1,5-Diphenyltetrazole: Diphenylcarbodiimide and 2-Phenylbenzimidazole. A. Isolation by Distillation.—A small flask containing 4.50 g. (0.0203 mole) of 1,5-diphenyltetrazole was heated in a Woods metal-bath at 210–220° until gas evolution ceased (about four hours), and the residual liquid was distilled at atmospheric pressure. The first fraction, b.p. 329–333° (752 mm.), was diphenylcarbodiimide, wt. 2.73 g. (70%) (reported[21] b.p. 330–331° (760 mm.)). During one week it gradually became completely solid. Trituration with 100 ml. of boiling benzene left 1.27 g. of amorphous diphenylcarbodiimide trimer, m.p. 145.5–158° (reported 160–161°,[22] 168–170°[23]). It was analyzed without further purification for confirmation of identity.

Anal.[15] Calcd. for $(C_{13}H_{10}N_2)_x$: C, 80.38; H, 5.19; N, 14.42. Found: C, 80.22; H, 5.22; N, 14.59.

After a second fraction, b.p. 333–360°, wt. 0.43 g., was collected, a small amount of solid, m.p. 289–290°, sublimed; it showed no m.p. depression when mixed with 2-phenylbenzimidazole. The diphenylcarbodiimide trimer was subsequently converted into *sym*-diphenylurea, m.p. 238–239°, in 86% yield by treatment with oxalic acid in dioxane.

B. Isolation by Treatment with Acid.—The brown, liquid residue obtained by heating 3.00 g. of 1,5-diphenyltetrazole at 200–220° for three hours was dissolved in 40 ml. of dioxane and treated with 30 ml. of concd. hydrochloric acid on a steam-bath for one hour. Evaporation of the solvents in a stream of air and recrystallization of the residue from alcohol gave two crops of *sym*-diphenylurea, m.p. 235–237.5° (undepressed when mixed with an authentic sample), wt. 1.56 g. (65%). Evaporation of the mother liquors and trituration of the residue with benzene containing a little alcohol gave 0.43 g. (14%) of 2-phenylbenzimidazole hydrochloride, m.p. 325° dec. (reported m.p. 303°,[24] 343°[25]). Treatment with aqueous sodium hydroxide gave the free base, wt. 0.31 g., m.p. 290–292° alone and when mixed with an authentic sample (reported[26] m.p. 291°). Evaporation of the benzene filtrate from the isolation of the hydrochloride and recrystallization of the residue from aqueous alcohol gave 0.50 g. of recovered 1,5-diphenyltetrazole, m.p. 142–143.5°. (The yields of the other products are corrected for this recovery.)

Pyrolysis of 1-(2-Naphthyl)-5-phenyltetrazole. 2-Phenylnaphth[1,2]imidazole.—The dark brown residue from heating 3.00 g. of 1-(2-naphthyl)-5-phenyltetrazole for about two hours at 200–230° was dissolved in 40 ml. of dioxane

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[20] R. Walther and S. Wlodowski, *J. prakt. Chem.*, [2] **59**, 279 (1899).

[21] W. Weith, *Ber.*, **7**, 1307 (1874).

[22] W. von Miller and J. Plöchl, *ibid.*, **28**, 1010 (1895).

[23] W. Weith, *ibid.*, **7**, 11 (1874).

[24] H. Franzen, *ibid.*, **40**, 911 (1907).

[25] I. C. Gastaldi and F. Cherchi, *Gazz. chim. ital.*, **43I**, 302 (1913).

[26] K. Auwers and F. von Meyenburg, *Ber.*, **24**, 2386 (1891).

and treated with 2 ml. of concd. hydrochloric acid for one hour on a steam-bath and overnight at room temperature. The yellowish precipitate so formed, wt. 0.76 g., m.p. 312–313° dec., was recrystallized from absolute alcohol, giving 0.70 g. (23%) of 2-phenylnaphth[1,2]imidazole hydrochloride, m.p. 314–315° dec., alone and when mixed with an authentic sample (reported[27] m.p. 310°). The free base monohydrate was prepared by treatment with aqueous sodium hydroxide; it melted at 118–120° with loss of water, resolidified and melted anew at 215–215.5°, alone or when mixed with an authentic[27] sample.

The dioxane filtrates from the first isolation of the hydrochloride were evaporated to dryness and the residue was recrystallized from absolute alcohol. Two crops were collected, wt. 0.38 g., m.p. 284–289°, and were combined and recrystallized from nitrobenzene, giving 0.31 g. of white needles, m.p. 285–286° dec., unchanged by two more recrystallizations from nitrobenzene or by dissolving in alcoholic sodium hydroxide and precipitation with water. It is believed to be a near-eutectic mixture of about three moles of *sym*-di-β-naphthylurea per mole of N-phenyl-N′-β-naphthylurea.

Anal. Calcd. for $C_{21}H_{16}ON_2$: C, 80.75; H, 5.16; N, 8.97. Calcd. for $C_{17}H_{14}ON_2$: C, 77.84; H, 5.38; N, 10.68. Calcd. for $3(C_{21}H_{16}ON_2) + C_{17}H_{14}ON_2$: C, 80.02; H, 5.17; N, 9.62. Found[16]: C, 79.84; H, 5.12; N, 9.55.

The alcoholic filtrates from the isolation of the original 0.38 g. were evaporated, leaving a tar, which was mixed with 10% sodium hydroxide solution and extracted with ether. Evaporation of the ether and recrystallization from alcohol gave a total of 1.35 g. in four crops, all showing wide melting ranges in the region 195–240°. No apparent purification could be obtained by further recrystallizations from alcohol or benzene. A 0.200-g. portion of the most soluble of the crops was hydrolyzed by heating with 5 ml. of 85% orthophosphoric acid at 170–180° until gas evolution (carbon dioxide) ceased. Nothing precipitated on dilution with 25 ml. of water, but sodium hydroxide precipitated 0.094 g. of crude β-naphthylamine, m.p. 105–107°; recrystallization from aqueous alcohol gave 0.089 g. (0.00062 mole), m.p. 109–111°, undepressed when mixed with an authentic sample. Treatment of the basic, aqueous filtrate with benzoyl chloride gave 0.120 g. (0.00061 mole) of benzanilide, m.p. 159–160.5°; when mixed with an authentic sample, m.p. 163.5–164°, the m.p. was 160–163.5°.

Pyrolysis of 1-(1-Naphthyl)-5-phenyltetrazole. A. Isolation of 2-Phenylnaphth[1,2]imidazole.—The dark brown residue obtained by heating 3.00 g. of 1-(1-naphthyl)-5-phenyltetrazole at 200–230° for about two hours was dissolved in 40 ml. of dioxane containing 3 ml. of concd. hydrochloric acid and allowed to stand overnight. The resulting precipitate weighed 0.98 g. after washing with fresh dioxane; m.p. 265–285° dec. After wetting with alcohol and treating with 10% sodium hydroxide, the altered solid was triturated with absolute alcohol; a small residue was left (0.18 g., m.p. 289–290° dec.). The alcoholic solution was evaporated and the resulting solid recrystallized from aqueous alcohol to obtain 0.72 g. (25%) of 2-phenylnaphth[1,2]imidazole hydrate, m.p. 120° with gas evolution, followed by resolidification and melting anew at 215–216°, undepressed by mixture with an authentic sample. Evaporation of the dioxane filtrate from the naphthimidazole hydrochloride and recrystallization from alcohol and benzene gave various crops, total wt. 1.14 g., of apparently mixed ureas, m.p. ranging from 193 to 275°.

B. Isolation of N-Phenyl-N′-(1-naphthyl)-carbodiimide.—The residue from pyrolysis of 3.00 g. of 1-(1-naphthyl)-5-phenyltetrazole was mixed with about 3 ml. of benzene. The successive addition of 15-ml. portions of methanol precipitated a solid in several crops, which were combined and recrystallized from benzene–ethanol mixture to yield 0.83 g. (31%) of N-phenyl-N′-(1-naphthyl)-carbodiimide, apparently as its trimer, m.p. 130–132°. An analytical sample prepared by three more recrystallizations from benzene-methanol mixtures had m.p. 130.8–132°.

Anal.[15] Calcd. for $C_{17}H_{12}N_2$: C, 83.58; H, 4.95; N, 11.47. Found: C, 83.19; H, 5.30; N, 11.46.

When a sample was heated for 15 minutes on a steam-bath with 85% orthophosphoric acid and then diluted with water, a solid, m.p. 200° dec., was obtained, which was recrystallized three times from alcohol to yield N-phenyl-N′-(1-naphthyl)-urea, m.p. 222°, followed by resolidification and melting anew at 242–244°, both m.p.'s being undepressed by mixture with an authentic sample (reported[15] m.p. 222–223° and 244°).

An attempt to isolate the monomeric carbodiimide by distillation of the pyrolysis product at 190–200° (1.5 mm.) gave an oil, whose analysis (C, 80.97; H, 5.27; N, 13.18) indicated that it was a mixture, presumably of diphenyl- and N-phenyl-N′-(1-naphthyl)-carbodiimides. On standing it became viscous and eventually solidified.

Pyrolysis of 1-Phenyl-5-(2-naphthyl)-tetrazole.—The brown residue obtained by heating 3.00 g. of 1-phenyl-5-(2-naphthyl)-tetrazole at 200–220° for about three hours was dissolved in 40 ml. of dioxane containing 2 ml. of concd. hydrochloric acid, heated on a steam-bath for 15 minutes, and allowed to stand overnight. No precipitate formed so the solvents were evaporated in an air stream and the residue was extracted with 40 ml. of absolute alcohol, leaving a residue of wt. 0.53 g., m.p. 288–290°, unchanged by washing with sodium hydroxide solution. When this solid was washed with warm absolute alcohol and warm benzene, there was left 0.34 g., m.p. 297° dec. Analysis was roughly consistent with a composition of about two moles of *sym*-di-2-naphthylurea per mole of N-phenyl-N′-(2-naphthyl)-urea; so was the infrared spectrum (Nujol mull) in relation to the spectra of the pure components.

Anal.[16] Calcd. for $C_{21}H_{16}ON_2$: C, 80.75; H, 5.16; N, 8.97. Calcd. for $C_{17}H_{14}ON_2$: C, 77.84; H, 5.38; N, 10.68. Calcd. for $2(C_{21}H_{16}ON_2) + C_{17}H_{14}ON_2$: C, 79.77; H, 5.25; N, 9.54. Found: C, 79.23; H, 5.28; N, 9.13.

Evaporation of the combined warm alcohol and benzene washings and recrystallization of the residue from alcohol gave 0.02 g., m.p. 285–287° dec., and 0.11 g., m.p. 254° dec. with sintering at 230°. When this material was placed in a bath preheated to 230°, it melted completely, then resolidified and melted anew at 254°. These temperatures were not altered by mixture with an authentic sample of N-phenyl-N′-(2-naphthyl)-urea.

Evaporation of the original alcohol extracts and recrystallization of the residue from benzene containing some alcohol gave 0.52 g. of solid, m.p. 220–250° dec. with prior sintering. Additional fractions were obtained from this material and from its mother liquor. All appeared to be mixtures by their melting behavior, and their infrared spectra could be accounted for in terms of different proportions of *sym*-di-1-naphthyl-, N-phenyl-N′-(1-naphthyl)- and *sym*-diphenylurea, the more soluble fractions being richer in the lower molecular weight compounds. No evidence could be found for the presence of a significant amount of 2-(2-naphthyl)-benzimidazole, although the infrared spectrum of the most benzene-soluble fraction (wt. 0.10 g., m.p. 214–226°) indicated some non-urea contamination.

Pyrolysis of 1-Phenyl-5-(1-naphthyl)-tetrazole.—The residue from heating 3.00 g. of 1-phenyl-5-(1-naphthyl)-tetrazole at 200–220° for about two hours was dissolved in 40 ml. of dioxane and warmed with 2 ml. of concd. hydrochloric acid; a precipitate began to form after a few minutes. After 30 minutes of heating, and then standing overnight, the precipitate was collected and washed with dioxane. It weighed 0.45 g., m.p. 284–286° dec. (with some prior sublimation), unchanged by washing with benzene or sodium hydroxide solution (reported[17] for *sym*-di-1-naphthylurea, m.p. 286–287° dec.), and its infrared spectrum matched that of an authentic sample. The mother liquor was evaporated and the residue was fractionated from alcohol and benzene into four fractions, each of which appeared from its melting range and infrared spectrum to be a mixture of phenyl- and 1-naphthyldiarylurea. No evidence for a significant amount of imidazole could be obtained.

In another experiment, starting with 0.50 g. of tetrazole, the pyrolysis product was hydrated by warming with oxalic acid in dioxane. Fractional crystallization from benzene and alcohol so as to concentrate the material least soluble in the former and most soluble in the latter gave 0.04 g., m.p. 233–235° dec. Further recrystallization from alcohol and benzene raised this to 236–237° alone, and 237–239° when mixed with an authentic sample of diphenylurea, m.p. 238–239°.

Pyrolysis of 1,5-Di-(2-naphthyl)-tetrazole.—The residue obtained by heating 1.50 g. of 1,5-di-(2-naphthyl)-tetrazole at 200–230° for about two hours was dissolved in 20 ml. of

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[27] L. Hunter, *J. Chem. Soc.*, 809 (1945).

dioxane, then heated on a steam-bath for an hour with 1.5 ml. of concd. hydrochloric acid and allowed to stand overnight. The solvents were evaporated and the residue was triturated with 20 ml. of boiling alcohol, cooled and filtered. This yielded 0.16 g. (11%) of 2-(2-naphthyl)-naphth[1,2]-imidazole hydrochloride, m.p. 332–336°. The free base was liberated with sodium hydroxide in alcohol and isolated by evaporating the alcohol and washing the residue with water. Recrystallization from aqueous alcohol gave 0.13 g. (9% from tetrazole) of 2-(2-naphthyl)-naphth[1,2]imidazole hydrate, m.p. 130–140° with loss of water, followed by solidification and remelting at 261–262°. For analysis the material was recrystallized twice from aqueous alcohol and allowed to dry in air at room temperature; the melting behavior was unchanged.

Anal. Calcd. for $C_{21}H_{16}ON_2$: C, 80.75; H, 5.16; N, 8.97. Found: C, 80.75; H, 5.39; N, 8.95.

The mother liquor of the imidazole hydrochloride yielded only tar in attempts to obtain a solid substance by crystallization from alcohol and benzene, both before and after treatment with sodium hydroxide, and no solid picrate could be obtained.

Disproportionation of N-Phenyl-N′-(1-naphthyl)-carbodiimide.—N-Phenyl-N′-(1-naphthyl)-thiourea was prepared from phenyl isothiocyanate and α-naphthylamine in hot alcohol. It melted at 162–163°, then partially resolidified and melted anew at 169°. The reported m.p.'s are 158–159°[28] and 162–163°,[29] but no mention of the resolidification phenomenon appears to have been made before.

A solution of 10.0 g. (0.036 mole) of the thiourea in 400 ml. of reagent grade acetone was refluxed for 30 minutes with 20 g. (0.0896 mole) of lead oxide, 5 g. of calcium sulfate and 0.4 g. of sulfur. The filtered solution was then distilled to dryness, the residue was taken up in 100 ml. of benzene, 50 ml. of the benzene was removed by distillation, and the cooled mixture was filtered from a small insoluble residue of N-phenyl-N′-(1-naphthyl)-urea, m.p. 225°, followed by resolidification and melting anew at 245°. The resulting clear solution was divided in half, and one portion was examined for disproportionation by hydration to urea by warming with 3 ml. of concd. hydrochloric acid. Evaporation of the solvents and extraction of the residue with 40 ml. of dioxane left 1.50 g. of a solid, m.p. 270–273° dec. with prior sintering and sublimation, unchanged by washing with sodium hydroxide solution. Washing with warm absolute alcohol left 0.68 g., m.p. 285° dec. Two recrystallizations from nitrobenzene gave an analytical sample, m.p. 292–293° dec. (reported[17] for N,N′-di-(1-naphthyl)-urea, 286–287° dec.).

Anal.[16] Calcd. for $C_{21}H_{16}ON_2$: C, 80.75; H, 5.16; N, 8.97. Found: C, 80.40; H, 5.21; N, 9.02.

The remainder of the reaction mixture gave various fractions of impure ureas on recrystallization from benzene and alcohol.

Disproportionation of Phenyl-β-naphthylcarbodiimide.—N-Phenyl-N′-(2-naphthyl)-thiourea was prepared from phenyl isothiocyanate and β-naphthylamine in boiling alcohol. It melted sharply at 160°, resolidified and melted anew at 170° (reported m.p.'s: 157°,[28] 165°,[30] 182–182°)[31]; the resolidification phenomenon has not been reported.

To a solution of 10.0 g. of N-phenyl-N′-(2-naphthyl)-thiourea in 400 ml. of boiling acetone were added 30 g. of lead oxide, 2 g. of calcium sulfate and 0.4 g. of sublimed sulfur, and the mixture was refluxed for 45 minutes. After filtering and concentration to 50 ml. by distillation, the solution was chilled to −10°. The resulting precipitate, N-phenyl-N′-(2-naphthyl)-urea, weighed 2.28 g. (28%) after washing with benzene, and had m.p. 226° followed by resolidification and melting anew at 254° dec. The combined filtrate and washings were divided in two equal portions.

One portion was hydrated by adding 3 ml. of concd. hydrochloric acid and evaporating the solvents on a steam-bath. Trituration of the residue with 40 ml. of dioxane left 2.92 g. (82%) of N-phenyl-N′-(2-naphthyl)-urea, m.p. 228–229° followed by resolidification and melting anew at 255° dec.; a second crop, 0.76 g., m.p. 205–207° dec., was obtained from the filtrate. Recrystallization of the combined crops from alcohol gave 3.16 g. (89%), m.p. 226.5–227° followed by resolidification and gradual decomposition with complete melting at 255°, unchanged by treatment with sodium hydroxide solution or by three recrystallizations from acetone (reported m.p. 220–221°[32] and 236–238°,[33] resolidification not mentioned). An authentic sample prepared from phenyl isocyanate and β-naphthylamine had after exhaustive recrystallization m.p. 234.5–235° followed by resolidification a few degrees higher, then gradual decomposition and complete melting at 255° to a liquid that continued to evolve gas. The sample prepared from the carbodiimide was analyzed for confirmation.

Anal. Calcd. for $C_{17}H_{14}ON_2$: C, 77.84; H, 5.38; N, 10.68. Found: C, 77.85; H, 5.56; N, 10.43.

The second portion of the carbodiimide solution was freed of solvents by distillation and then heated at 200° for an hour, becoming dark brown. It was dissolved in 40 ml. of dioxane, 2 ml. of concd. hydrochloric acid was added, and the mixture was allowed to stand overnight. The solvents were removed from the clear solution with an air stream and the residue was triturated with absolute alcohol. There remained 0.08 g. (2%) of *sym*-di-2-naphthylcarbodiimide, m.p. 300° dec. (reported[20] 300° dec.).

Anal. Calcd. for $C_{21}H_{16}ON_2$: C, 80.75; H, 5.16; N, 8.97. Found: C, 80.49; H, 5.24; N, 9.12.

The filtrate was alkalized with sodium hydroxide, the solvents were evaporated, and the residue was washed free of inorganic matter with water. Trituration with benzene containing a little absolute alcohol left 0.27 g., m.p. 267° dec. Concentration of the filtrate from this gave 0.10 g. (3%) of N-phenyl-N′-(2-naphthyl)-urea, m.p. 224–226° and 254° dec. Further concentration gave 0.56 g. of a solid, m.p. 200–212° dec. After two recrystallizations the m.p. was 203° dec., but one more raised it to 209–230° dec.; analysis of the last fraction indicated it to be a mixture of N-phenyl-N′-(2-naphthyl)-urea and *sym*-diphenylurea.

Anal.[16] Calcd. for $C_{17}H_{14}ON_2$: C, 77.84; H, 5.38; N, 10.68. Calcd. for $C_{13}H_{12}ON_2$: C, 73.56; H, 5.70; N, 13.20. Calcd. for $3(C_{17}H_{14}ON_2) + C_{13}H_{12}ON_2$: C, 76.75; H, 5.46; N, 11.31. Found: C, 76.92; H, 5.62; N, 11.06.

Mixture with N-phenyl-N′-(2-naphthyl)-urea raised the m.p. to 225–227° and 253° dec., while mixture with *sym*-diphenylurea lowered it to 204–210° dec. From the combined mother liquors of the several recrystallizations of the 0.56-g. fraction, a second crop was obtained by concentration and cooling; it had m.p. 221–231° dec., raised to 225–235° dec. by mixture with *sym*-diphenylurea, and lowered to 213–223° dec. by N-phenyl-N′-(2-naphthyl)-urea. Analysis indicated a mixture rich in the former component.

Anal.[16] Calcd. for $6(C_{13}H_{12}ON_2) + C_{17}H_{14}ON_2$: C, 74.17; H, 5.65; N, 12.84. Found: C, 74.23; H, 5.60; N, 13.20.

A eutectic mixture of roughly equimolar amounts of authentic samples of the foregoing two ureas could be approached from either side, and had m.p. 203° dec.

Pyrolysis of 1-Phenyl-5-(1-phenanthryl)-tetrazole.—An 0.80-g. sample of this tetrazole[5] was heated at 220–250° until gas evolution ceased (about 0.5 hour); only slight discoloring occurred. When the cooled melt was stirred with *ca.* 5 ml. of benzene, crystallization occurred, yielding 0.16 g. of colorless solid, m.p. 200–205°, sharply depressed when mixed with the starting tetrazole. A second crop, 0.03 g., was obtained by concentrating the filtrate. Recrystallization from benzene gave colorless crystals of di-1-phenanthrylcarbodiimide, m.p. 206–208°. It showed a strong infrared absorption band at 4.62 μ (C=N=C).

Anal. Calcd. for $C_{29}H_{18}N_2$: C, 88.30; H, 4.60; N, 7.10. Found: C, 87.88; H, 4.55; N, 7.28.

Treatment of 0.0156 g. dissolved in 2 ml. of dioxane with 0.0176 g. of oxalic acid on a steam-bath overnight gave a precipitate. Dioxane was evaporated without filtration, and the colorless, crystalline residue was washed well with water; the *sym*-di-1-phenanthrylurea remaining weighed 0.0141 g. (86%), m.p. 323° dec.

Anal. Calcd. for $C_{29}H_{20}ON_2$: C, 84.44; H, 4.89; N, 6.79. Found: C, 84.57; H, 4.77; N, 6.74.

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(28) K. Mainzer, *Ber.*, **15**, 1414 (1882).

(29) F. Foerster, *ibid.*, **21**, 1869 (1888).

(30) M. Freund and H. Wolf, *ibid.*, **25**, 1468 (1892).

(31) H. L. Wheeler, THIS JOURNAL, **23**, 226 (1901).

(32) H. Goldschmidt and E. Molinari, *Ber.*, **21**, 2567 (1888).

(33) P. P. T. Sah, *J. Chinese Chem. Soc.*, **5**, 100 (1937).

Another sample of the carbodiimide, wt. 0.0337 g., was hydrolyzed by heating with 1 ml. of 85% orthophosphoric acid for two hours at 170–180°. Dilution of the cooled mixture with water gave a precipitate of 1-phenanthrylamine phosphate,[5] which was washed with sodium hydroxide solution and then water to convert it to 0.0286 g. of 1-phenanthrylamine, m.p. 142–144° (reported[34] 145–146°), undepressed when mixed with an authentic sample. Alkalizing the acidic mother liquor gave a second crop, wt. 0.0012 g., making the total yield 90%.

The benzene mother liquor from the crude carbodiimide was evaporated to a sirupy semi-solid, from which by trituration with absolute alcohol containing a little benzene a small amount of crude phenyl-1-phenanthrylcarbodiimide was obtained, m.p. 105–110°, raised to 111–113° when mixed with an authentic sample. The mother liquors yielded more solid on concentration, showing the characteristics of impure diphenylcarbodiimide polymer.

ANN ARBOR, MICH.

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(34) W. E. Bachmann and C. H. Boatner, THIS JOURNAL, **58**, 2099 (1936).

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Debenzylation of S-Benzyl-N-phthaloyl-L-cysteinyl Chloride with Aluminum Halides. Preparation of L-α-Phthalimido-β-propiothiolactone[1]

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S-Benzyl-N-phthaloyl-L-cysteinyl chloride gave with two moles of aluminum halide L-α-phthalimido-β-propiothiolactone (I), while with one mole of aluminum halide a polythioester II was obtained. The structure of I and II was proved by conversion into cystine and cysteine derivatives. A mechanism for the formation of I and II is suggested.

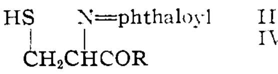
In the course of our studies on the configuration of chloramphenicol[2] and nor-pseudo-ephedrine,[3] we have correlated the configurations of these compounds with D-serine and D-alanine by means of chemical interconversion. The key intermediates in these syntheses were the optically active α-phthalimido-β- substituted propiophenones, prepared from the corresponding phthalimido-propionyl chlorides using the usual Friedel–Crafts reaction.

Incidental to this investigation it was observed that formation of propiophenone *via* Friedel–Crafts reaction largely depended on the character of the β-substituent. When O-ethyl-N-phthaloyl-DL-seryl chloride was subjected to the Friedel–Crafts reaction, the corresponding ketone was obtained in a 25% yield,[4] while the same reaction gave a yield of 63% with O-methyl-N-phthaloyl-DL-seryl chloride[5] and a yield of over 90% with N-phthaloyl-L-alanyl chloride.[3]

In continuation of this work with the idea of correlating the configuration of cysteine to chloramphenicol and nor-pseudo-ephedrine, we subjected S-benzyl-N-phthaloyl-L-cysteinyl chloride to the usual Friedel–Crafts reaction. At first it was expected that S-benzyl-N-phthaloyl-L-cysteinyl chloride would react in the normal way giving the corresponding propiophenone which upon debenzylation with aluminum halide would give rise to a ketone related to cysteine or cystine. During attempts to purify the reaction products, it was observed that no ketonic material was present in the reaction mixture. However, two different products could be obtained depending on the amount of aluminum halide used in the reaction. With two moles of aluminum halide the α-phthalimido-β-propiothiolactone(I) was obtained, while with one mole of aluminum halide a polymeric compound II was isolated. In a series of experiments it was found that the formation of I was independent of the concentration of aluminum halide as long as at least two moles was used.

The propiothiolactone ring was first prepared by Lin'kova, Kil'disheva and Knunyants[6] in 1955. By condensing the ethylchloro carbonate with the triethylamine salt of β-mercaptoisovaline the Russian authors prepared β,β-dimethylpropiothiolactone. In a similar way N-formyl-, N-acetyl-, N-phenacetyl- and N-phenaceturyl-β,β-dimethylpropiothiolactones also were prepared.[7]

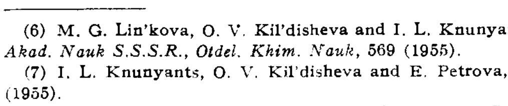
The structure of the compound I was proved by several routes. Hydrolysis of I with hydriodic acid in glacial acetic acid afforded L-cystine and phthalic acid. The acid-catalyzed reaction with ethanol gave an almost quantitative yield of N-phthaloyl-L-cysteine ethyl ester (III). It is interesting to note that in the propiolactone series the acid-catalyzed reaction with strong acids afforded ether rather than ester.[8] The ester III is an oily product which can be distilled in high vacuum without decomposition and significant racemization. Upon hydrolysis with hydriodic acid, the ester III gave cystine and phthalic acid. Benzyla-



I

$$(SCH_2CHCO)_x \cdot H_2O, \quad CH-N{=}\text{phthaloyl}$$

II



$$HS-CH_2CH(N{=}\text{phthaloyl})COR$$

III $R = OC_2H_5$

IV $R = NHCH(CH_2CH_2SCH_3)CO_2C_2H_5$

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(1) Presented before XVIth International Congress of Pure and Applied Chemistry, Paris, July, 1957; Congress Handbook (Division of Organic Chemistry), p. 41.

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