benzene solution left an oil which was crystallized slowly from ligroin to give 0.21 g. (15%) of *o*-phenylbenzanilide, m.p. 110–111° alone and when mixed with authentic material, depressed when mixed with 9-phenylphenanthridine. A repetition of this experiment gave substantially the same results. In another experiment where sulfuric acid (15 ml.) was used in place of trichloroacetic acid, none of the insoluble material was formed, and there was obtained 1.13 g. (89.5%) of pale yellow 9-phenylphenanthridine which melted at 104–108°, and 107–108.5° after recrystallization from methanol and ligroin. It was isolated by extraction into 10% hydrochloric acid from a benzene solution of the reaction products. Evaporation of the benzene solution left only a small amount of yellow oil which resisted all attempts to induce crystallization. Unless the reaction mixture was alkalized with ammonia, most of the product precipitated as its sulfate.

Beckmann Rearrangement of *o*-Phenylbenzophenone Oxime.—*o*-Phenylbenzophenone (5.16 g.) was converted to its oxime by refluxing with 1.6 g. of hydroxylamine hydrochloride in 7 ml. of pyridine and 9 ml. of absolute ethanol for 24 hours. A viscous oil separated on dilution with water, and solidified slowly during six days while covered with dilute acetic acid; wt. 5.3 g., m.p. 94–113°. It was dissolved in 40 ml. of benzene; exactly half of this solution was taken and 3.0 g. of phosphorus pentachloride was added; the temperature rose slightly but remained below 35°. After 7.5 hours the mixture was decomposed with ice-water, the benzene was evaporated, and the residue was alkalized with ammonia. The cream colored, gummy product was completely insoluble in concd. hydrochloric acid, as shown by alkalizing the decanted acid. It crystallized from ethanol as white needles, m.p. 107–110°, wt. 1.11 g. (41%), undepressed when mixed with *o*-phenylbenzanilide, markedly depressed when mixed with *o*-benzamidobiphenyl or 9-phenylphenanthridine.

The mother liquors were evaporated and refluxed with acetic–hydrochloric acid mixture for six days. The acidic products were isolated in customary fashion (wt. 0.85 g.) and were separated by digestion with 100 ml. of warm water. The residue of *o*-phenylbenzoic acid, m.p. 111–113°, weighed 0.35 g. (17.5%); the extracts on neutralization with sodium bicarbonate, concentration to a small volume, and reacidification gave 0.29 g. of crude benzoic acid, m.p. 110–117°, which could not readily be separated from accompanying traces of *o*-phenylbenzoic acid. The corresponding amines were not separated quantitatively, but *o*-aminobiphenyl was isolated as water-insoluble *o*-acetamidobiphenyl, wt. 0.12 g., m.p. 121–122° and aniline was isolated by precipitation as *p*-bromoacetanilide, wt. 0.31 g., m.p. 164–166°, after recrystallization from benzene.

The benzene solution of the other half of the oxime was evaporated, and 70 g. of preheated polyphosphoric acid was poured on the residue. After 15 minutes at 110–130°, the mixture was diluted with 350 ml. of water and alkalized with ammonia. The bright yellow oil which separated was taken up in two portions of benzene, and the extracts were washed first with dilute, then concd. hydrochloric acid, and finally with water. Neutralization of the acid washings precipitated 0.42 g. (16.5%) of 9-phenylphenanthridine, m.p. 105–107°. The benzene was then evaporated and the residue was extracted with warm ligroin. The residue of fluorenone after evaporation of the ligroin was crystallized from methanol in several crops; wt. 0.95 g. (53%), m.p. 82.5–84.5°.

Schmidt Reaction on Fluorenone Anil.—Fluorenone anil[34] (1.27 g.) in 25 g. of trichloroacetic acid and 0.75 ml. of concd. sulfuric acid at 55–60° was treated with 0.5 g. of sodium azide added over one hour. After 5 hours the mixture was poured on ice, and the red oil which separated changed to yellow crystals overnight; wt. 1.07 g., m.p. 67–190°. Extraction of the solid with hot ligroin left 0.09 g. (9%) of phenanthridone, m.p. 286–288° with sublimation. The extracts were evaporated, and the residue of fluorenone was crystallized from methanol in several crops; wt. 0.68 g. (76%), m.p. 82–84°. The original acidic solution gave only a faint opalescence when excess sodium hydroxide was added, and presumably contained only aniline from hydrolysis of unreacted fluorenone anil.

Cyclization of *o*-Phenylbenzanilide.—*o*-Phenylbenzanilide (0.25 g.) was allowed to stand with 1 ml. of phosphorus oxychloride for 1 hour, and then refluxed for 1 hour. Hydrolysis with cold water gave an orange oil which slowly turned to a bright yellow solid, wt. 0.15 g., m.p. 65–75°. Extraction of the solid with hot petroleum ether (b.p. 60–75°) and evaporation of the solvent gave 0.12 g. (79%) of fluorenone, m.p. 79–82°. The original acid filtrate did not precipitate any 9-phenylphenanthridine when excess potassium hydroxide was added, but only became cloudy.

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[34] G. Reddelien, *Ber.*, **43**, 2476 (1910).

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF MICHIGAN]

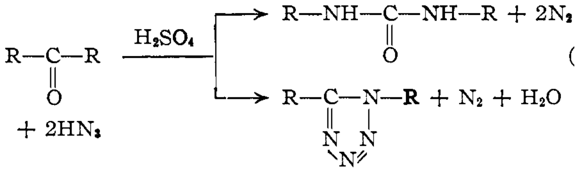
Observations on the Formation and Breakdown of Tetrazoles[1]

BY PETER A. S. SMITH

RECEIVED JULY 14, 1953

The formation of ureas in the Schmidt reaction on certain diaryl ketones has been related to the non-cyclic imidyl azide I precursor of tetrazoles, which is capable of undergoing a Curtius-like rearrangement. Carbodiimides are suggested to be the intermediate products capable of hydration to ureas, and in one case a carbodiimide has been isolated from a tetrazole preparation. The cyclization of imidyl azides to tetrazoles has been shown to be probably reversible, and in strong acid at temperatures above 160° the complete disruption of 1,5-diaryltetrazoles to two moles of amines can be accomplished. This has been applied to the conversion of 1-benzoylphenanthrene through the oxime, Beckmann rearrangement, and formation and disruption of the tetrazole, to 1-phenanthrylamine in 82% over-all yield. The von Braun and Rudolf method for preparing tetrazoles from imidyl chlorides and anhydrous hydrogen azide solutions has been shown to proceed with some success in aqueous sodium azide solutions.

The recent discovery of two cases of the formation of a urea from a monoketone during the course of a Schmidt reaction[2,3] calls for explanation. The usual side-products in Schmidt reactions on ketones are 1,5-disubstituted tetrazoles (equation 1); it therefore seemed that further investigation of the factors governing the formation and breakdown of tetrazoles might elucidate the occasional formation of ureas.



(1)

From *o*-methoxybenzophenone, one of the ketones observed to give a urea, two isomeric tetra-

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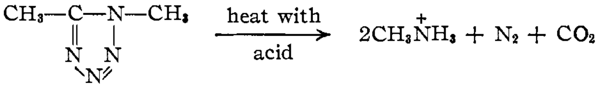
[1] Presented at the National Meeting of the Am. Chem. Soc., Los Angeles, 1953.

[2] P. A. S. Smith and T.-Y. Yu, *J. Org. Chem.*, **17**, 1281 (1952).

[3] P. A. S. Smith, THIS JOURNAL, **76**, 431 (1954).

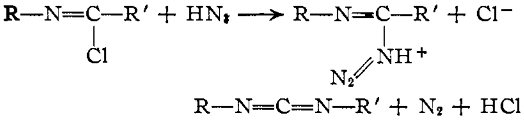
zoles can be derived: 1-*o*-anisyl-5-phenyl- and 1-phenyl-5-*o*-anisyltetrazole. These substances have been prepared from *o*-anisanilide and benzo-*o*-anisidide, respectively, by conversion to the imido chloride with phosphorus pentachloride, followed by reaction with hydrogen azide. They were exposed to concentrated sulfuric acid and trichloroacetic acid under the conditions of the Schmidt reaction, with and without the addition of sodium azide, and found to be essentially unaffected. 1,5-Diphenyltetrazole was similarly inert. The N-phenyl-N'-*o*-anisylurea obtained from the ketone could not therefore have arisen principally by the breakdown of tetrazoles first formed. The corresponding amides are also not the precursors of the ureas, for they, too, were recovered unchanged from exposure to Schmidt reaction conditions.

Some tetrazoles have been reported to break down under the influence of strong acids under more drastic conditions, such as fuming hydrochloric acid in a sealed tube at 200°.[4] Such a breakdown is accompanied by migration from C to N of the substituent originally in the 5-position; for example, 1,5-dimethyltetrazole gives two moles of methylamine.[5]


$$CH_3{-}C{-}N{-}CH_3\ (\text{tetrazole ring } N{=}N) \xrightarrow[\text{acid}]{\text{heat with}} 2CH_3\overset{+}{N}H_3 + N_2 + CO_2$$

Some further observations of the acid-catalyzed breakdown of tetrazoles have now been made, for which a technique more convenient than fuming hydrochloric acid in sealed tubes at 200° has been developed. Sirupy 85% orthophosphoric acid is very suitable; the reactions can be run in open beakers, and little if any discoloration results. Several 1,5-diaryltetrazoles were examined, and all dissolved in the hot phosphoric acid and decomposed smoothly in the range 165–205°. Only amines were formed from diphenyl- and the two phenyl-*o*-anisyltetrazoles; even when the decompositions were quenched short of completion, no ureas could be found. When N,N'-diphenylurea was exposed to the same conditions, it was found to be completely hydrolyzed in a few minutes. This fact may be of practical value, since the hydrolysis of diarylureas is usually a tedious process.

In order to detect the possible formation of ureas from tetrazoles, a compound so constituted as to be unusually resistant to hydrolysis was desired. Since the amides derived from 1-benzoylphenanthrene show such resistance,[6] an attempt was made to prepare the corresponding tetrazoles from the mixed imidyl chlorides prepared by the Beckmann rearrangement of the oxime with phosphorus pentachloride. The substance found in major amount in some experiments, at first assumed to be 1-phenyl-5-(1-phenanthryl)-tetrazole, unexpectedly turned out to be N-phenyl-N'-1-phenanthrylcarbodiimide (or its trimer). This substance presumably arose in the manner indicated in equation 2. This appears to be the first example of such a side reaction in the usually reliable tetrazole synthesis de-


$$R{-}N{=}\underset{Cl}{C}{-}R' + HN_3 \longrightarrow R{-}N{=}\underset{N_2{=}NH^+}{C}{-}R' + Cl^- \longrightarrow R{-}N{=}C{=}N{-}R' + N_2 + HCl \quad (2)$$

veloped by Von Braun and Rudolf.[7] Its significance with respect to the formation of ureas in the Schmidt reaction is brought out further on.

This carbodiimide could be converted to N-phenyl-N'-1-phenanthrylurea by brief heating with phosphoric acid, and longer heating hydrolyzed the urea to aniline and 1-phenanthrylamine. The conversion of 1-benzoylphenanthrene to 1-phenanthrylamine by these steps was accomplished in an over-all yield of 40%; when the accompanying tetrazole was also converted to amine, the over-all yield of amine from ketone was 82%. By contrast, the Beckmann or Schmidt rearrangement followed by hydrolysis of the mixed amides can give a maximum yield of only 18%,[6] and is a tedious process. The phenanthryltetrazoles can be disrupted by phosphoric acid under only slightly more severe conditions than suffice for the urea, namely, heating with phosphoric acid for about 30 minutes at 200° in an open vessel. The first attempt to repeat the preparation of the carbodiimide led to the essentially complete conversion of the imidyl chlorides to the tetrazoles, and subsequent experiments sometimes gave the carbodiimide and sometimes did not. It seems probable that higher temperatures favor the loss of nitrogen from the imidyl azide (equation 2) over cyclization; the possible influence of the nature of the reaction medium, as affected by the presence of phosphorus halides, is also being investigated.

In another attempt to obtain a urea, 1-*o*-anisyl-5-phenyltetrazole was heated in polyphosphoric acid, in the hope that the lower availability of water in that solvent would slow hydrolysis. However, no urea was isolated, and the result was in general the same as with orthophosphoric acid.

For comparison with the reactions in acid medium, the purely thermal breakdown of 1-phenyl-5-(1-phenanthryl)-tetrazole was also studied. The scanty reports of the pyrolysis of tetrazoles show only 1,2,4,5-tetrazines and 1,3,4-triazoles as products.[8] The phenanthryltetrazole evolved gas smoothly between 220 and 250°, and produced the carbodiimide previously obtained, together with two other crystalline substances which are neither tetrazoles nor amides. Since this result is sufficient to show that thermal decomposition is of a different nature to the acid-catalyzed reactions, report of this reaction in detail will be withheld until a later communication.

No satisfactory explanation has yet been offered concerning the path by which tetrazoles break up in acid solution; however, it seems probable that the first step is protonation.[9] At sufficiently high temperatures, the protonated tetrazole may reason-

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(4) For a summary of examples, see F. R. Benson, *Chem. Revs.*, **41**, 55 (1947).

(5) K. F. Schmidt, *Friedländer*, **15**, 333 (1930).

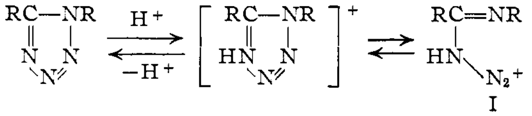
(6) (a) W. E. Bachmann and C. Boatner, THIS JOURNAL, **58**, 2097 (1936); (b) J. R. Dice and P. A. S. Smith, *J. Org. Chem.*, **14**, 179 (1949).

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

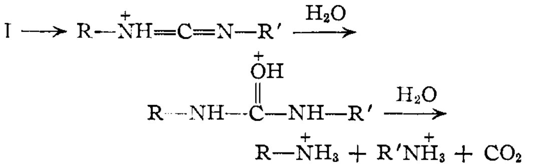
(8) W. Lossen and F. Statius, *Ann.*, **298**, 104 (1897); W. Lossen and J. Colman, *ibid.*, **298**, 107 (1897).

(9) *Cf.* K. F. Schmidt, *Ber.*, **57**, 704 (1924), for a suggestion which ignores acid catalysis.

ably be expected to be in equilibrium with a significant amount of the ring-opened species I, from which at lower temperatures the tetrazoles are believed to be formed[10] (equation 3).


(3)

As a reaction competitive to cyclization to a tetrazole, rearrangement of I with loss of nitrogen may be expected to occur, involving migration of R from C to N, exactly as in the Schmidt[10a] and acid-catalyzed Curtius[11] reactions. The resulting species is a protonated carbodiimide, known to react readily with water to give a urea, which in turn would hydrolyze to amine and carbon dioxide under the conditions used to disrupt tetrazoles (equation 4).

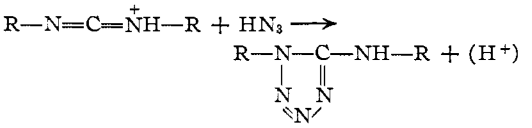


$$\mathrm{I} \longrightarrow \mathrm{R{-}\overset{+}{N}H{=}C{=}N{-}R'} \xrightarrow{H_2O} \mathrm{R{-}NH{-}\overset{\overset{+}{O}H}{\overset{\|}{C}}{-}NH{-}R'} \xrightarrow{H_2O} \mathrm{R{-}\overset{+}{N}H_3 + R'\overset{+}{N}H_3 + CO_2} \quad (4)$$

The postulated ring–chain isomerism is not unusual; among the structurally similar triazoles many examples have been studied where the two forms could actually be isolated.[12] Among tetrazoles the cyclization of isolable guanyl azide to 5-aminotetrazole is perhaps the most clear-cut example, and disubstituted 5-aminotetrazoles display isomerism which is best interpreted as proceeding by ring–chain interconversion.[13]

During a Schmidt reaction, the protonated imidyl azide I may be formed by reaction of the intermediate iminocarbonium ion with excess hydrogen azide[10]; it is then usually found as a tetrazole resulting from cyclization. If the temperature where I begins to rearrange faster than it cyclizes is low enough, then during a Schmidt reaction the same products may arise as are formed from tetrazoles under more drastic conditions. The ureas which are postulated as arising from tetrazoles in equations 3 and 4 are usually hydrolyzed as fast as they are formed under the conditions required to disrupt tetrazoles, but under the mild conditions of the usual Schmidt reaction they are not appreciably affected. The formation of ureas in a Schmidt reaction may therefore be thought of as competitive with tetrazole formation, dependent upon the temperature and the structure of the original ketone.

The reaction scheme by which ureas are formed is also capable of explaining the hitherto anomalous formation of 1-phenyl-5-anilinotetrazole from benzophenone and three moles of hydrogen azide under Schmidt reaction conditions.[5] If there is hydrogen azide present when the carbodiimide is formed, it may react with that instead of with water, giving rise to an aminotetrazole derivative[14] (equation 5).


(5)

The formation of tetrazoles in the Schmidt reaction is seen to be in all cases competitive with the reaction of an intermediate with water instead of hydrogen azide. It would therefore appear that if the Schmidt reaction could be run in a solvent incapable of furnishing the elements of water, tetrazole formation should be greatly favored. In the customary medium for the Schmidt reaction, concentrated sulfuric acid, tetrazole formation does not always compete successfully with amide formation, even when a large excess of hydrogen azide is present.[15] Nitrobenzene will dissolve hydrogen azide, most ketones, and aluminum chloride. Such a solution was found to evolve nitrogen rapidly at room temperature when the ketone was acetophenone or 2-acetonaphthone. Even when the hydrogen azide was added in less than an equivalent amount or at a slow rate, 1-aryl-5-methyltetrazoles predominated over the amides. On the other hand, in a single experiment the use of phosphoryl chloride in benzene–chloroform solution led only to amide formation; in hindsight, this result was probably due to phosphoric acid in the reagent. Stannic chloride was ineffective, since in the examples studied it precipitated the ketones as insoluble complexes. Further examples are seen in the successful use of stannic chloride in anhydrous medium to cause tetrazole formation from camphor and thujone,[16] and in the improved procedure for making pentamethylenetetrazole with the aid of ferric chloride.[17]

While hydrogen azide may not be able to compete satisfactorily with water in tetrazole *vs.* amide formation, azide ion might be expected to be more successful. It is not possible to test this by suitably altering the conditions of the Schmidt reaction, due to the requirement of high acidity in order to initiate any reaction at all. However, the preparation of tetrazoles from imido chlorides offers a practical means. This preparation is commonly carried out by reaction with hydrogen azide in an inert solvent; use of solid sodium azide under such conditions is only occasionally successful, presumably due to its insolubility.[12,18] It has now been found that a tetrazole can be made from an imido chloride and *aqueous* sodium azide (equation 6); this may be due to the expected faster reaction of azide ion competing with hydrolysis. This technique has the considerable practical value that

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(10) (a) P. A. S. Smith, THIS JOURNAL, **70**, 320 (1948); (b) E. K. Harvill, C. W. Roberts and R. M. Herbst, *J. Org. Chem.*, **15**, 58 (1950).

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

(12) O. Dimroth and H. Aikelin, *Ber.*, **39**, 4390 (1906).

(13) Literature summarized by E. Lieber and G. B. L. Smith, *Chem. Revs.*, **25**, 213 (1939); *cf.* also E. Lieber, R. A. Henry and W. G. Finnegan, THIS JOURNAL, **75**, 2023 (1953); and W. L. Garbrecht and R. M. Herbst, *J. Org. Chem.*, **18**, 1269 (1953).

(14) E. Oliveri-Mandala, *Gazz. chim. ital.*, **52**, **II**, 139 (1922); R. Stolle, *Ber.*, **55**, 1289 (1922); R. Stolle and F. Henke-Stark, *J. prakt. Chem.*, **124**, 261 (1930).

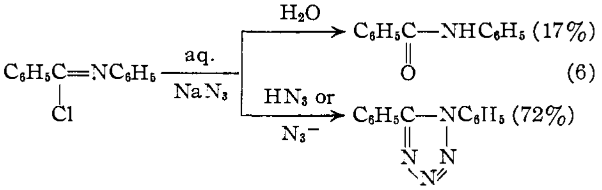
(15) E. K. Harvill, R. M. Herbst, E. C. Schreiner and C. W. Roberts, *J. Org. Chem.*, **15**, 662 (1950).

(16) K. F. Schmidt, U. S. Patent 2,029,799 (1936); *C. A.*, **30**, 1950 (1936); *Frdl.*, **211**, 675 (1937).

(17) N. B. Chapman, H. McCombie and B. C. Saunders, *J. Chem. Soc.*, 929 (1945).

(18) G. Schoerter, *Ber.*, **42**, 2336 (1909).

the preparation of solutions of anhydrous hydrogen azide, with the attendant danger and inconvenience, is avoided; on the other hand, the tetrazole must be separated by crystallization or hydrolysis from the considerable amounts of amide simultaneously formed.



(6)

When the preparation of 1-phenyl-5-*o*-anisyltetrazole was first attempted by the interaction of N-phenyl-*o*-anisoimidyl chloride with hydrogen azide, the product could not be made to crystallize. An alternative synthesis was attempted starting with *o*-anisoyl hydrazide and benzenediazonium sulfate, according to the method used by Dimroth and Montmollin[19] to prepare some tetrazoles. Although this method has recently been shown to be useful when starting with fatty acid hydrazides,[20] in the present case it led only to the diacyl hydrazide and *o*-anisamide. An attempt to reproduce Dimroth and Montmollin's preparation of 1,5-diphenyltetrazole by this method likewise led only to benzamide and dibenzhydrazide. Starting with di-*o*-anisoyl hydrazide, only unreacted starting material was obtained. Its failure is perhaps due to unexpectedly great sensitivity to temperature. When the original preparation *via* the imido chloride finally crystallized after four months, further investigation of the diazonium method was abandoned; the incomplete results obtained are reported here because they include the preparation of some new compounds.

Experimental[21]

1-Phenyl-5-*o*-anisyltetrazole.—A mixture of 1.06 g. of *o*-anisanilide and 1.05 g. of phosphorus pentachloride was warmed on a steam-bath until it melted and the subsequent gas evolution had ceased. Most of the phosphoryl chloride was removed under aspirator vacuum, and the residue was taken up in benzene and added to a dry benzene solution of hydrogen azide prepared from 1.0 g. of sodium azide.[22] Lively gas evolution continued for several hours; after 20 hours, the yellow solution was washed with sodium carbonate solution, then water, and evaporated to a yellow sirup. Attempts to induce crystallization from numerous organic solvents led only to a few milligrams of unidentified colorless material which melted at 189.5–191°. *Anal.*[23] Found: C, 62.71; H, 4.72; ash (non-alkaline), 2.87.

The oil from the evaporation of the mother liquors partly solidified after four months of exposure to laboratory dust. Trituration with ether left about 100 mg. of 1-phenyl-5-*o*-anisyltetrazole as a white powder, readily soluble in methanol, from which it crystallized in prisms, m.p. 102–103°. *Anal.* Calcd. for $C_{14}H_{12}ON_4$: C, 66.65; H, 4.79. Found: C, 66.57; H, 4.93.

1-*o*-Anisyl-5-phenyltetrazole.—A mixture of 1.13 g. of benzo-*o*-anisidide and 1.1 g. of phosphorus pentachloride was treated as in the previous example. The sirupy product crystallized in a few minutes when rubbed with 2–3 ml. of methanol, and was collected in three crops, total wt. 1.11 g. (89%), m.p. 117–120°. Recrystallization from methanol gave 1-*o*-anisyl-5-phenyltetrazole as colorless rods, m.p. 119–120.5°. *Anal.* Calcd. for $C_{14}H_{12}ON_4$: C, 66.65; H, 4.79. Found: C, 66.49; H, 4.88.

***o*-Anisoyl Hydrazide.**—The crude methyl ester made from 5.0 g. of *o*-anisic acid *via* the acid chloride was heated with 4.5 ml. of 85% hydrazine hydrate and a few drops of methanol until homogeneous. After the volatile materials had been distilled under aspirator vacuum, the residue crystallized on scratching; after trituration with benzene it weighed 3.6 g. (66%), m.p. 77–87°. One recrystallization from benzene gave 3.29 g. of clear prisms, m.p. 83–86°, unchanged on further recrystallization. *o*-Anisoyl hydrazide is very soluble in both water and alcohol and slightly soluble in benzene. *Anal.* Calcd. for $C_8H_{10}O_2N_2$: C, 57.82; H, 6.07. Found: C, 57.96; H, 6.12.

***sym*-Di-*o*-anisoyl hydrazide** was prepared by shaking 5 ml. of 85% hydrazine hydrate with a benzene solution of the acid chloride from 5.0 g. of *o*-anisic acid. By filtration there was obtained 4.3 g. (87%) of colorless crystals, m.p. 195–199°. A sample for analysis recrystallized twice from methanol formed platelets, m.p. 202–203°. *Anal.* Calcd. for $C_{16}H_{16}O_4N_2$: C, 63.99; H, 5.37. Found: C, 63.87; H, 5.36.

Reaction with Benzenediazonium Sulfate.—To an ice-cold solution prepared from 1.93 ml. of aniline, 1.93 ml. of concentrated sulfuric acid and 1.55 g. of sodium nitrite in *ca.* 10 ml. of water, in which excess nitrous acid had been destroyed with a little sulfamic acid, was added 3.29 g. of *o*-anisoyl hydrazide dissolved in *ca.* 3 ml. of water. A pale yellow precipitate formed at once. A cold solution of 4 g. of sodium hydroxide in *ca.* 25 ml. of water containing some ice was added, and the resulting foamy mixture of yellow solution and dark gum was allowed to stand for an hour at 0°. The gum was separated by filtration, washed with water and recrystallized from 10 ml. of benzene; the resulting yellow, cottony solid weighed 0.83 g., m.p. 127–130°. Recrystallization from benzene with charcoal gave a colorless product, m.p. 130–132°, undepressed when mixed with *o*-anisamide prepared *via* the acid chloride.

The aqueous solution filtered from the gum was treated with *ca.* 5 g. of solid ammonium chloride, which precipitated 0.46 g. of pale yellow solid, m.p. 187–189°. Careful solution in benzene separated the bulk of the material from a few unidentified pinkish needles, m.p. 199–200°, unchanged by recrystallization from ethanol, in which they were difficultly soluble. They were not investigated further. *Anal.* Calcd. for $C_{14}H_{14}O_2N_4$(?): C, 62.21; H, 5.22. Found: C, 62.34; H, 5.19.

The benzene-soluble material melted at 202–203° after several recrystallizations from methanol, and gave no melting point depression when mixed with *sym*-di-*o*-anisoyl hydrazide.

Benzhydrazide and Benzenediazonium Sulfate.—By the procedure described for the case of *o*-anisoyl hydrazide, 2.7 g. of benzhydrazide gave 0.5 g. of *sym*-dibenzoyl hydrazide, m.p. 241–243°, and 0.12 g. of benzamide, m.p. 128–129°. There may have been traces, but not more, of 1,5-diphenyltetrazole in the mother liquors from the crystallization of benzamide; phenyl azide appeared to be present. The actual amount of benzamide formed was undoubtedly much larger since no attempt was made to recover that part which must have been dissolved in the aqueous phase from which it was filtered.

Schmidt Reaction Conditions on Anilides from *o*-Methoxybenzophenone.—The conditions used were 15 g. of trichloroacetic acid and 0.8 ml. of concentrated sulfuric acid at 50–60° for two hours, during which 0.5 g. of sodium azide was added in portions. From 1.13 g. of benzo-*o*-anisidide (m.p. 67–68.5°) there was recovered 0.98 g. of crude starting material, m.p. 64.5–65.5°, as obtained from the reaction mixture by dilution with water. Recrystallization from petroleum ether, which should concentrate the less soluble N-phenyl-N′-*o*-anisylurea if present, only raised slightly and sharpened the melting point. Similarly, from 1.13 g. of *o*-anisanilide (m.p. 76–78°) there was recovered 0.98 g. which melted at 76–78° as obtained by dilution with water.

Schmidt Reaction Conditions on 1,5-Diaryltetrazoles.—1,5-Diphenyltetrazole (m.p. 144–146°) was exposed to the following conditions: 0.22 g. of tetrazole in 10 g. of trichloroacetic acid plus 0.3 ml. of concentrated sulfuric acid for 4.5

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[19] O. Dimroth and G. de Montmollin, *Ber.*, **43**, 2904 (1910).

[20] D.-Y. Wu and R. M. Herbst, *J. Org. Chem.*, **17**, 1216 (1952).

[21] Melting points are corrected. Analyses are by Mr. Goji Kodama of this Department unless otherwise indicated.

[22] The method of J. von Braun, *Ann.*, **490**, 125 (1931), was modified by using 50% sulfuric acid in place of concentrated.

[23] This analysis by Clark Microanalytical Laboratories, Urbana, Ill.

hr. at 50–60° gave 0.20 g. of recovered tetrazole, m.p., 143.5–146°, on dilution with water; 0.20 g. of tetrazole heated slowly to 160° in 5 ml. of concentrated sulfuric acid gave 0.18 g. of recovered tetrazole, m.p. 143–145°; 0.18 g. of tetrazole in 5 ml. of concentrated sulfuric acid at 50° for three hours during which 0.10 g. of sodium azide was added gave 0.17 g. of recovered tetrazole, m.p. 143–145.5°.

Under the first set of conditions, 0.2 g. of 1-*o*-anisyl-5-phenyltetrazole gave 0.19 g. of recovered material, m.p. 116–119°, and 0.06 g. of 1-phenyl-5-*o*-anisyltetrazole gave 0.045 g. of recovered tetrazole, m.p. 99–101°.

Phosphoric Acid Treatment of Tetrazoles.—When 0.17 g. of 1,5-diphenyltetrazole was heated in 5 ml. of 85% orthophosphoric acid for 1.25 hr., during which the temperature rose to 155°, there was active boiling above 125°. Dilution of the cooled mixture with water precipitated 0.15 g. of recovered tetrazole, m.p. 142–144°, with prior softening. The clear filtrate gave a strong opalescence with potassium bromide–bromate mixture, indicating that some aniline had been formed. When the experiment was repeated with an increase in temperature to 175°, maintained for 2.5 hours, no starting material was precipitated on dilution with water. Treatment of the clear solution with bromide and bromate gave an immediate precipitate of tribromoaniline, m.p. 117–119°, wt. 0.37 g., from 0.15 g. of tetrazole. The substitution of polyphosphoric acid for orthophosphoric acid in the first of these experiments did not change the results.

To a preheated 5-ml. portion of phosphoric acid at 150° was added 0.19 g. of 1-*o*-anisyl-5-phenyltetrazole. The resulting clear solution began to evolve small bubbles above 160°. After 10 min. between 160 and 170°, the mixture was quenched and diluted with water. The precipitated tetrazole weighed 0.12 g., m.p. 116.5–118.5°. The clear filtrate was neutralized with sodium carbonate, treated with 2 ml. of acetic anhydride, and extracted with chloroform. Evaporation of the extracts left a crystalline cake of mixed acetanilides melting over a range below 100°.

From these experiments it was concluded that decomposition of diaryltetrazoles takes place in phosphoric acid conveniently at 160–170° and requires perhaps one hour for completion. Treatment of diphenylurea under these conditions resulted in complete hydrolysis; no starting material was precipitated on dilution with water, but aniline could be isolated by customary procedures in 80% yield as *p*-bromoacetanilide.

1-Phenyl-5-(1-phenanthryl)-tetrazole and N-(1-Phenanthryl)-N′-phenylcarbodiimide.—To a suspension of 2.0 g. of unrecrystallized 1-benzoylphenanthrene oxime[6a] in 25 ml. of reagent grade benzene was added 1.5 g. of phosphorus pentachloride, and the mixture was heated to boiling for a few minutes. After decantation from some particles of unreacted phosphorus pentachloride, the clear solution was mixed with a benzene solution (*ca.* 20 ml.) of hydrogen azide prepared from 1.0 g. of sodium azide. Slow steady gas evolution began in a few minutes, and the precipitation which began in about an hour appeared to be completed in five hours. After 20 hours the mixture was heated to boiling for 15 minutes, chilled and filtered. The solid was washed with sodium carbonate solution and with water; wt. 0.88 g., m.p. 112–114°. Recrystallization from 5 ml. of hot benzene gave a white product, m.p. 113–114°, presumed to be N-phenyl-N′-(1-phenanthryl)-carbodiimide. *Anal.* Calcd. for $C_{21}H_{14}N_2$: C, 85.69; H, 4.79; N, 9.52. Found: C, 85.57; H, 4.83; N, 9.60.

The original benzene filtrate was evaporated to dryness and crystallized in several crops from methanol; total wt. 0.85 g. The first crop (0.55 g., m.p. 168–187°) was recrystallized twice from ethanol–benzene mixture, giving colorless prisms of 1-phenyl-5-(1-phenanthryl)-tetrazole, m.p. 197–198°. This structure assignment is made in view of the demonstrated preponderance of phenyl migration in the Beckmann rearrangement of 1-benzoylphenanthrene oxime.[6a] *Anal.* Calcd. for $C_{21}H_{14}N_4$: C, 78.24; H, 4.38. Found: C, 78.40; H, 4.30.

1-Aminophenanthrene from the Carbodiimide.—A mixture of 0.44 g. of crude N-phenyl-N′-(1-phenanthryl)-carbodiimide and 10 ml. of 85% orthophosphoric acid was heated slowly to 170° and kept at 170–180° until all solid had dissolved (*ca.* 1 hr.). On cooling and dilution with water there was precipitated a nearly white solid, wt. 0.40 g. (100%), m.p. 260–265° after charring at 225°, insoluble in all ordinary solvents. When 0.2 g. of this material, believed to be 1-aminophenanthrene phosphate, was digested with sodium carbonate solution, there was obtained by filtration 0.13 g. (100%) of crude 1-aminophenanthrene, m.p. 141–144°.[6a] From 0.065 g. of this there was obtained by treatment with acetic anhydride 0.05 g. of 1-acetamidophenanthrene, m.p. 222–224°.[6a]

In another experiment, 0.27 g. of the carbodiimide was heated with 5 ml. of phosphoric acid at 170° for about ten minutes, at which time there was much undissolved solid. The solids obtained by dilution with water were washed with sodium carbonate solution, water and then dilute hydrochloric acid and ethanol. The solid remaining undissolved weighed 0.10 g. (39%), m.p. 323–325°[6a] alone and when mixed with N-phenyl-N′-(1-phenanthryl)-urea. The ethanol filtrates on evaporation left 0.09 g. (47%) of 1-aminophenanthrene hydrochloride, m.p. 249–252°.[6a]

1-Aminophenanthrene from the Tetrazole.—Ten ml. of 85% orthophosphoric acid was heated to 205° in an open vessel to allow the escape of excess moisture. To the hot liquid was added 0.10 g. of 1-phenyl-5-(1-phenanthryl)-tetrazole, which immediately melted and slowly evolved gas as it dissolved. After 25 min. at 205°, solution was complete, and the mixture was allowed to cool. Dilution with water caused no immediate precipitation, but after 12 hr. bunches of needles of 1-aminophenanthrene phosphate separated, wt. 0.08 g. after washing with water and a very little ethanol. Digestion with an excess of dilute ammonium hydroxide converted this to 0.055 g. (89%) of 1-aminophenanthrene, m.p. 144–145°. (Initial isolation as the phosphate in such preparations is recommended over direct neutralization, in order to achieve a sharp separation from aniline, and to avoid the formation of large amounts of inorganic phosphates which may crystallize.)

1-Aminophenanthrene from 1-Benzoylphenanthrene.—From 1.0 g. of 1-benzoylphenanthrene there was obtained 1.03 g. of crude oxime after 45 hours heating with hydroxylamine hydrochloride in 1:1 pyridine–ethanol solution.[6a] A suspension of the oxime in benzene was warmed with 0.9 g. of phosphorus pentachloride, filtered through cotton from some curds, and combined with a dry benzene–chloroform solution of hydrogen azide prepared from 1 g. of sodium azide. After 22 hr. the precipitate was collected by pressure-filtration (to avoid evaporation of hydrogen azide), rinsed with benzene and washed with aqueous sodium carbonate and with water; wt. 0.50 g. (48%), m.p. 108–110° (crude carbodiimide). The benzene filtrates were allowed to stand for an additional 18 hr., then heated to near boiling for 4 hr., cooled, washed with aqueous sodium carbonate and with water and evaporated to a yellow solid. After washing with a small volume of methanol, this weighed 0.485 g. (42.5% as tetrazole), m.p. 165–195°.

By the phosphoric acid treatment already described the carbodiimide fraction gave 0.275 g. of 1-aminophenanthrene, m.p. 143–145° (40% from ketone; 84% from carbodiimide). The aqueous phosphoric acid filtrate on neutralization gave an additional 30 mg. (4.4%), m.p. 133–138°. Acidification with hydrobromic acid and treatment with potassium bromate gave 0.51 g. (43.5% from ketone) of 2,4,6-tribromoaniline, m.p. 117–120°. Similarly, the "tetrazole" fraction (which undoubtedly contained some carbodiimide) gave 0.215 g. of 1-aminophenanthrene, m.p. 143–145 (31.5% from ketone, 74% from "tetrazole") plus a further 45 mg. (6.6%) from the phosphoric acid filtrate. Bromination then gave 0.42 g. (36%) of tribromoaniline. The methanol washings from the tetrazole fraction left a gum on evaporation which gave only dark material in the phosphoric acid treatment. The over-all total yield of 1-aminophenanthrene was thus 82.5%, and that of aniline 79.5%. The separate handling of the two fractions is not essential for synthetic purposes, but appears to give a purer product. In some runs little or no carbodiimide appeared to be formed, but the over-all conversion to amine was similar. In runs where insufficient time, reagent, or heat prevented complete interaction of the imido chloride and hydrogen azide, amides were formed from unreacted imido chloride and precipitated during the sodium carbonate washing; in the phosphoric acid treatment these gave rise to dark decomposition products and very impure amine.

Schmidt Reaction on β-Acetonaphthone.—To a solution of 1.7 g. of β-acetonaphthone and 3 g. of anhydrous aluminum chloride in 20 ml. of nitrobenzene was added 10 ml. of 1.4 *N* hydrogen azide in benzene; there was lively gas evolution. After three hours, a little dilute hydrochloric acid was added and the mixture was steam distilled to remove solvents. The residual oil solidified on cooling. After recrystallization from *ca.* 30 ml. of hot benzene it weighed 0.97 g., m.p. 153–157°; an additional 0.18 g., m.p. 153–159°, was obtained by concentrating the benzene filtrate; total yield 55%. Recrystallization once from ethanol and once from acetone gave colorless plates, m.p. 167°. *Anal.* Calcd. for $C_{12}H_{10}N_4$: C, 68.55; H, 4.79. Found: C, 68.74; H, 4.48.

In a similar experiment in which 2.3 ml. of stannic chloride was substituted for aluminum chloride, a heavy, yellow precipitate formed immediately, and no gas evolution was detectable. The addition of 15 ml. of chloroform appeared to dissolve some of the solid, and started gas evolution. No crystalline product could be isolated by the foregoing work-up procedure, except for a small amount of unreacted ketone.

In an experiment with quantities identical to the successful one, the hydrogen azide solution was added to the solution of ketone and aluminum chloride at the rate of one drop in four seconds, with motor stirring. When worked up as before, there was obtained a crystalline solid, which when recrystallized from absolute ethanol gave 0.39 g. (19%) of crude tetrazole, m.p. 150–152°. Evaporation of the filtrate gave 1.14 g. of sticky, brown solid, which by recrystallization from benzene gave 0.2 g. (11%) of β-acetamidonaphthalene, m.p. 127–129° alone, and 130–132° when mixed with an authentic sample.

In an experiment identical with the first one except for the use of half the quantity of hydrogen azide (5 ml. of 1.4 *N*), there was obtained 0.47 g. (73% based on HN_3) of tetrazole, m.p. 158–159°.

1-Phenyl-5-methyltetrazole.—The first experiment described under β-acetonaphthone was repeated using 1.2 g. of acetophenone and the hydrogen azide obtained from 1.0 g. of sodium azide. There was obtained 0.54 g. (34% based on ketone; 42% based on NaN_3) of 1-phenyl-5-methyltetrazole, silky needles, m.p. 98–99° (reported[24] 98–99°).

To determine whether the tetrazole may have resulted from a secondary reaction induced by aluminum chloride on acetanilide first formed, 1.35 g. of acetanilide was treated in nitrobenzene solution with 2.7 g. of aluminum chloride and the hydrogen azide from 1.0 g. of sodium azide. After two hours the solvents were removed by steam distillation. The homogeneous, aqueous residue deposited no tetrazole on cooling; 0.32 g. of the characteristic leaves of crude acetanilide, m.p. 106–107°, was obtained by seeding. At the most, tetrazole could only have been present in the small amount necessary to lower the melting point to this extent.

[24] A. G. Knoll, *Chem. Fabriken*, German Patent 540,409 (Feb. 12, 1927); *C. A.*, **26**, 3263⁸ (1932).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF BOSTON UNIVERSITY]

Preparation and Reactions of Bis-diazoalkanes

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Bis-nitrosoureido alkanes, bis-nitrosocarbamates and dinitroso diaza diketones have been made and decomposed to form bis-diazoalkanes which were not isolated, but were allowed to react with carboxylic acids, aldehydes, acetone, phenol and ethyl acetoacetate.

Bis-diazoalkanes have been reported by Petersen,[3] by Lieser and Beck[4a] and by Lettré and Brose,[4b] although none of these reports were available when our work was started.

Lieser and Beck prepared several bis-diazoalkanes by the treatment of an ethereal solution of the bisnitrosoureides, $NH_2CON(NO)(CH_2)_xN(NO)CONH_2$, where $x = 2–6$ and of the bis-nitrosocarbamates, $EtOOCN(NO)(CH_2)_xN(NO)COOEt$, where $x = 3–8$, with 40% aqueous potassium hydroxide at 0°. Ethereal solutions of the bis-diazoalkanes were allowed to react with phenol, β-naphthol or catechol, but neither yields nor analyses were given.

Lettré and Brose prepared ether solutions of bis-diazoalkanes from the bis-nitrosoureides, $H_2NCON(NO)(CH_2)_xN(NO)CONH_2$ where $x = 3–6$ and allowed these bis-diazoalkanes to react with benzoic acid and *p*-nitrobenzoic acid.

We have made bis-diazoalkanes not only from bis-nitrosoureido alkanes[3,4a,4b] and bis-nitrosocarbamates[3,4] but also from dinitroso diaza diketones which were made by a modification of the method used by Berenbom and Fones[5] for the preparation of diazomethane. It was hoped to make a bis-nitroso derivative of 1,6-bis-nitroguanidinohexane but this latter compound was so insoluble in concentrated acids at low temperature that the idea was abandoned.

The properties of the bis-nitroso compounds are listed in Table I.

The ultraviolet absorption spectra of three N,N'-dinitrosocarbamates and N,N'-dinitroso-1,2-diureidoethane were determined. The extinction coefficients of the dinitrosocarbamates (240–242) were very close to that of N,N'-dinitro-N,N'-dicarbethoxy-1,6-diaminohexane (238),[6] but appreciably lower than that for N,N'-dinitroso-1,2-eidoethane.

Bis-nitrosocarbamates and bis-nitrosoureido alkanes have been decomposed to form bis-diazo alkanes by treatment of a cold ether solution with solid potassium carbonate[3] or with a concentrated aqueous solution of potassium hydroxide.[4] The catalytic decomposition of nitroso-β-alkylamino ketones by means of sodium ethoxide in ethyl alcohol has been reported by Jones and Kenner.[7] We have found that the reaction with solid potassium carbonate is very slow in a cold room at 5,5°, requiring more than two weeks to go to completion, as evidenced by the cessation of the evolution of nitrogen.[8] The best method of decomposing the

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[1] Abstracted from a portion of the dissertation submitted by Carlos M. Samour in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Armstrong Cork Company Research Fellow, 1947–1949.

[3] Petersen, ORTS Report No. 694.

[4] (a) T. Lieser and G. Beck, *Ber.*, **83**, 137 (1950); (b) H. Lettré and U. Brose, *Naturwissenschaften*, **36**, 57 (1949).

[5] M. Berenbom and W. S. Fones, THIS JOURNAL, **71**, 1629 (1949).

[6] H. M. Curry and J. P. Mason, *ibid.*, **73**, 5449 (1951).

[7] E. C. Jones and J. Kenner, *J. Chem. Soc.*, 363 (1933).

[8] In this experiment, treating an absolute ethyl alcohol solution of N,N'-dinitroso-N,N'-dicarbethoxy-1,6-diaminohexane and benzaldehyde with solid potassium carbonate, we have made the assumption that the slow reaction is the decomposition of the bis-nitroso compound. This assumption appears to be justified by the fact that the same reaction is complete within 20 minutes when sodium hydroxide is used to decompose the bis-nitroso compound and also by the fact that, whenever the bis-diazoalkane was prepared in alcohol (or ether) solution and then added to the reactant, the reaction was rapid.