carbon tetrachloride or dioxane produced in almost quantitative yield 4,4'-dichlorodiphenyldisulfide (XIV) as yellow plates from petroleum ether, m.p. 72–73°.

Anal. Calcd. for $C_{12}H_8Cl_2S_2$: C, 50.30; H, 2.82. Found: C, 50.58; H, 3.03.

2'-Aminophenyl-3-nitro-4-pyridyl sulfide (X). The reaction between the anhydrous salt of *o*-aminothiophenol and V was conducted in the same manner as described above for VIII. The sulfide X was obtained in 52% yield as yellow needles, m.p. 146–147°, after two recrystallizations from ethanol. Comparable yields were obtained with 1,4-dioxane as the reaction solvent.

Anal. Calcd. for $C_{11}H_9N_3O_2S$: C, 53.42; H, 3.67. Found: C, 53.57; H, 3.90.

2'-Formamidophenyl-3-nitro-4-pyridyl sulfide (XI). The above amino-sulfide (5.0 g., 0.02 mole) was refluxed for several hours with 10 times its weight of 90% formic acid. The solution upon dilution with water did not precipitate the formamido derivative. Neutralization of the mixture with sodium bicarbonate produced a gum. Recrystallization of the latter from benzene and then absolute ethanol yielded the formamido derivative (XI) (2.5 g., 45.5%), m.p. 146–147.5°. A mixture melting point with an authentic sample of the free amino-compound gave a large depression.

Anal. Calcd. for $C_{12}H_9N_3O_3S$: C, 52.35; H, 3.30. Found: C, 52.13; H, 3.12.

Attempted Smiles rearrangement of 2'-formamidophenyl-3-nitro-4-pyridyl sulfide (XI). An acetone solution of the formamido derivative was refluxed with a solution of potassium hydroxide in absolute ethanol for 2 hr. The reddish-brown solution was brought to dryness under vacuum. The residue was not soluble in most organic solvents. However, it was very soluble in alcohol and acidification of its aqueous solution produced a crude precipitate. No test for nitrite ion was obtained nor was 3-azaphenothiazine (XII) isolated. Indications seem to support the fact that a possible rearrangement to the potassium salt of the thiol may have occurred without the elimination of potassium nitrite.

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PHILADELPHIA, PA.

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

The Effect of Some Substituents on the Thermal Breakdown of Diaryltetrazoles[1]

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Nine tetrazoles containing substituted phenyl, pyridyl, or quinolyl groups have been prepared from imidyl chlorides and aqueous sodium azide. All lost nitrogen when heated at 220–250°, to yield carbodiimides accompanied in some cases by benzimidazoles. The Schmidt reaction on acetophenone catalyzed by aluminum chloride in nitrobenzene solution gave 5-methyl-1-phenyltetrazole accompanied irreproducibly by large amounts of *N*-methyl-*N'*-phenylurea.

Tetrazoles have recently been found to break up when strongly heated to give carbodiimides accompanied in some cases by significant amounts of 2-arylarimidazoles.[2] If the reaction leading to imidazole could be made to occur more efficiently, it would be a useful synthetic route to benzimidazoles and perhaps their heterologs, such as the purine ring system. The reaction has now been explored with some representative tetrazoles bearing *p*-substituted phenyl, pyridyl, and quinolyl groups.

The required tetrazoles were prepared by a recently reported[2] modification of the von Braun-Rudolf synthesis from imidyl chlorides, using buffered aqueous sodium azide instead of anhydrous hydrogen azide solutions. This method was found to be generally successful, and to have some advantages in handling and in freedom from rearrangement products, but entailed separating the tetrazoles, formed in about 60% yields, from large amounts of the amides corresponding to the imidyl chlorides. Attempts to prepare 1-(8-quinolyl)-5-phenyl- and 1-(2,6-dimethyl-4-pyrimidyl)-5-*p*-chlorophenyltetrazole failed; this appeared to be due to difficulty in the reaction of the corresponding amides with phosphorus pentachloride.[3]

1,5-Diphenyltetrazole has already been found to give 12–14% of 2-phenylbenzimidazole when pyrolyzed, the remainder going to diphenylcarbodiimide; these results have now been confirmed. Since the two reactions occurring embody competition between one involving migration of a group from carbon to nitrogen, and one involving cyclization to a benzene ring without migration, it is of interest to examine the effect of substituents on the group that might migrate. A *p*-chloro substituent retards the migration of phenyl from C to N in the Beckmann rearrangement[4]; as would be expected from this, it also retarded carbodiimide formation relative to cyclization, and 1-phenyl-5-

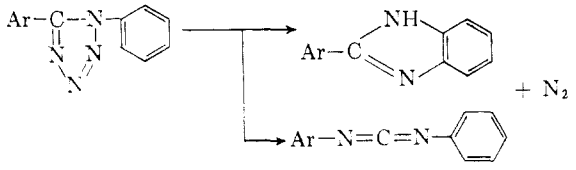
(1) This work was supported by the U. S. Public Health Service, Contract No. C-2613.

(2) P. A. S. Smith and E. Leon, *J. Am. Chem. Soc.*, **80**, 4647 (1958).

(3) *Cf.* D. M. Hall, *J. Chem. Soc.*, 1603 (1948), for a report of similar difficulty.

(4) A. W. Chapman and F. A. Fidler, *J. Chem. Soc.*, 448 (1936).

p-chlorophenyltetrazole gave a significantly higher yield (19%) of benzimidazole. Conversely, a *p*-methyl substituent, which accelerates the migration of a phenyl group in the Beckmann rearrangement,[4] would be expected to promote carbodiimide formation at the expense of benzimidazole, as was confirmed by the formation of no more than 8% of 2-*p*-tolylbenzimidazole from 1-phenyl-5-p-tolyltetrazole. A *p*-nitro group, which would be expected to have a similar effect to *p*-chloro, brought about more deep-seated decomposition on pyrolysis, and no definite products could be characterized. 1-*p*-Tolyl-5-(β-pyridyl)tetrazole showed similar behavior.



The unsymmetrical carbodiimides derived from diaryltetrazoles have been shown[2] to disproportionate under the conditions of the pyrolysis, giving mixtures containing appreciable amounts of the two related symmetrical carbodiimides. It is for this reason that the carbodiimides obtained in the present work were not isolated. However, the disproportionation phenomenon was confirmed in the case of 1-phenyl-5-*p*-chlorophenyltetrazole by hydrating the carbodiimides and separating the mixture of *sym*-diphenyl-, di-*p*-chlorophenyl- and phenyl-*p*-chlorophenyl-urea by fractional crystallization.

For the attempted preparation of pyridimidazole derivatives, four tetrazoles were prepared bearing α-pyridyl or β-quinolyl groups on the 1-position and phenyl or *p*-chlorophenyl groups on the 5-position. All decomposed in the usual temperature range, but only black tars were obtained, from which no pure substances could be isolated.

In addition to the diaryltetrazoles, 1-phenyl-5-methyltetrazole was investigated. It was prepared as reported[5] by the Schmidt reaction with acetophenone using aluminum chloride in nitrobenzene as catalyst. However, the first attempt gave rise to no tetrazole, but to *N*-methyl-*N'*-phenylurea (50% yield). This type of product has been encountered occasionally in other examples of the Schmidt reaction[2,5,6] and presumably arises by hydration of a carbodiimide first formed. The reaction was attempted twelve times, with some small, controlled variations, but the formation of a urea was encountered in only two experiments. There was no apparent correlation of the formation of a urea with temperature, rate of addition of hydrogen azide, exposure to moisture, or the presence of hydrogen chloride. The use of trifluoroacetic acid in place of aluminum chloride failed to bring about either reaction.

1-Phenyl-5-methyltetrazole decomposed on heating like the diaryltetrazoles, but the product was a dark sirup. 2-Methylbenzimidazole could be extracted from this in 7 to 8% yields, but ureas derived from hydration of the expected carbodiimides could not be crystallized.

Since the deep-seated decompositions occurring in so many of the pyrolyses were probably due to secondary reactions brought about by the high temperatures required, means were sought to catalyze the release of nitrogen. It has already been shown[5] that strong acid accomplishes this, but it also alters the course of the reaction. Copper powder was found to lower the decomposition temperature of 1,5-diphenyltetrazole by about 60°, silver appeared to have some effect, while manganese, iron, soft glass, and alumina were ineffective. Unfortunately, the product from the use of copper as catalyst was a black mass, from which no pure substance could be isolated.

Four of the tetrazoles prepared in this work were tested for *in vivo* inhibition of Sarcoma 180, but showed no activity.[7]

EXPERIMENTAL

Preparation of tetrazoles. The diaryltetrazoles were prepared by heating amides with phosphorus pentachloride until reaction occurred (liquefaction and/or gas evolution observed), removing phosphoryl chloride, treating the remaining imidyl chloride with aqueous sodium azide and sodium acetate, and recrystallizing the precipitated product alternately from benzene (in which the tetrazoles are more soluble) and ethanol or methanol (in which the amides are more soluble). With the pyridyl and quinolyl derivatives, a larger proportion of sodium acetate was used, followed by sodium hydroxide in the work-up. The tetrazoles showed no infrared absorption over the 1600-2400 cm.$^{-1}$ region (where azide would show up), but all showed an absorption band at 1095–1105 cm.$^{-1}$ and one or two other bands in the 1100–1200 cm.$^{-1}$ region, reported to be characteristic of the tetrazole ring.[8] The results are summarized in Table I, and the details of the method are illustrated by the following example.

1-Phenyl-5-p-nitrophenyltetrazole. A mixture of 9.7 g. (0.04 mole) of *p*-nitrobenzanilide and 8.35 g. (0.04 mole) of phosphorus pentachloride was warmed with a heating mantle until liquid, and heating was maintained until visible evolution of hydrogen chloride ceased. Phosphoryl chloride was evaporated under aspirator vacuum. The residue of imidyl chloride was added to a stirred solution prepared from 0.5 g. (0.075 mole) of sodium azide and 1.04 g. (0.08 mole) of sodium acetate trihydrate, 50 ml. of water, 10 to 20 g. of ice, and 75 ml. of acetone. Stirring was continued for 2 hr., during which the crusts which deposited on the

(5) P. A. S. Smith, *J. Am. Chem. Soc.*, **76**, 436 (1954).

(6) P. A. S. Smith and T. Y. Yu, *J. Org. Chem.*, **17**, 1281 (1952); P. A. S. Smith, *J. Am. Chem. Soc.*, **76**, 431 (1954).

(7) Private communication from Drs. Donald A. Clarke and C. Chester Stock of the Sloan-Kettering Institute for Cancer Research. The compounds tested were 5-*p*-nitrophenyl-1-phenyl-, 5-phenyl-1-(α-pyridyl)-, 5-(β-pyridyl)-1-*p*-tolyl-, 5-*p*-chlorophenyl-1-(α-pyridyl)-, and 5-phenyl-1-(β-quinolyl)-tetrazole.

(8) E. Lieber, D. Levering, and L. Patterson, *Anal. Chem.*, **23**, 1594 (1951).

TABLE I

1,5-DIARYLTETRAZOLES

1-Ar	5-Ar	Yield, %	M.P., °C.	Calcd. for	Analysis % C	% H	% N	Found % C	% H	% N
C_6H_5	p-$NO_2C_6H_4$	62	180	$C_{13}H_9O_2N_5$	58.42	3.37	26.22	58.35	3.36	26.24
C_6H_5	p-ClC_6H_4	61–70	155.5	$C_{13}H_9N_4Cl$	60.81	3.51	21.83	60.84	3.51	21.88
C_6H_5	p-$CH_3C_6H_4$	59	133.5	$C_{14}H_{12}N_4$	71.19	5.09	23.73	70.99	5.08	23.88
p-$CH_3C_6H_4$	β-C_5H_4N	38–46	106	$C_{13}H_{11}N_5$	65.83	4.64	29.54	65.84	4.58	29.59
α-C_5H_4N	C_6H_5	58[a]	100–101	$C_{12}H_9N_5$	64.59	4.03	31.39	64.68	3.97	31.54
α-C_5H_4N	p-ClC_6H_4	54[b]	121–121.5	$C_{12}H_8N_5Cl$	55.93	3.11	27.18	55.98	3.10	27.19
β-C_9H_6N	p-ClC_6H_4	47[c]	118	$C_{16}H_{10}N_5$	62.44	3.25	22.77	62.52	3.34	22.74
β-C_9H_6N	C_6H_5	48–55[d]	166.5	$C_{16}H_{11}N_3$	70.33	4.03	25.64	70.40	4.08	25.69

[a] Accompanied in one experiment by a trace of colorless substance, m.p. 171–172°, which may have been impure phenyl-α-pyridylcarbodiimide polymer. *Anal.* Calcd. for $C_{12}H_9N_3$: C, 73.85; H, 4.62; N, 21.54. Found: C, 74.20; H, 5.22; N, 20.14. [b] Prepared from *p-chlorobenzoyl α-pyridylamide* (*ca.* 30% yield from *p*-chlorobenzoyl chloride and α-aminopyridine), m.p. 139°. *Anal.* Calcd. for $C_{12}H_9ON_2Cl$: N, 12.04. Found: N, 12.02. [c] Prepared from *β-(p-chlorobenzamido)quinoline* (60% yield from *p*-chlorobenzoyl chloride and β-aminoquinoline), m.p. 231.5–233.5°. *Anal.* Calcd. for $C_{16}H_{11}ON_2Cl$: N, 9.69. Found: N, 9.80. [d] Prepared from β-benzamidoquinoline (84% yield from benzoyl chloride and β-aminoquinoline), m.p. 196–197°. *Anal.* Calcd. for $C_{16}H_{12}ON_2$: N, 11.29. Found: N, 11.32.

walls of the container were from time to time washed back into the reaction mixture with small portions of acetone. The volume was then reduced to about 50 ml. by evaporation in an air stream and about 100 ml. of water was added. The precipitate was triturated with the mother liquor, filtered and washed with water. Recrystallization from hot benzene gave a fraction containing most of the amide; evaporation of the benzene filtrate gave crude tetrazole, which was further purified by recrystallization from hot methanol. Systematic repetition of this pattern with the different fractions obtained gave an efficient separation; the total yield of tetrazole, m.p. 180°, was 6.62 g. (62%), and that of recovered amide was 8%.

2,6-Dimethyl-4-(p-chlorobenzamido)pyrimidine was prepared in low yield by Schotten-Baumann acylation of 2,6-dimethyl-4-aminopyrimidine. It was apparently accompanied at first by a diacyl derivative, as also seemed to have occurred in the acylations of α-aminopyridine and β-aminoquinoline. This contaminant could be more or less successfully removed by boiling with aqueous alcoholic potassium carbonate. The pure compound had m.p. 101.5° after recrystallization from aqueous alcohol.

Anal. Calcd. for $C_{13}H_{12}ON_3Cl$: N, 16.06. Found: N, 16.17.

An attempt to convert this amide to a tetrazole resulted only in the recovery of amide.

1-Phenyl-5-methyltetrazole. Solutions of about 0.1 mole of acetophenone and 0.25 mole of anhydrous aluminum chloride in 200 ml. of nitrobenzene were treated with benzene solutions of hydrogen azide (0.1–0.15 mole) in the manner already described,[5] with various modifications and results as follows. Work-up was in all cases similar, and consisted of adding some 1:1 hydrochloric acid, steam-distilling to remove acetophenone, and filtering the solid material from the cooled residue. The crude material was usually recrystallized once from methanol incidentally to decolorizing with charcoal.

Experiment 1, in which the reaction mixture was cooled somewhat by a shallow ice bath, gave only *N*-methyl-*N'*-phenylurea, in 12% yield. In Experiment 2, the acetophenone–aluminum chloride solution was treated immediately with hydrogen azide solution, the latter being added in large portions; *N*-methyl-*N'*-phenylurea was formed in 50% yield. Experiment 3 differed from Experiment 2 only in that the reaction mixture was not cooled; 1-phenyl-5-methyltetrazole was formed in 45% yield. Experiment 4 was like 3 except that the hydrogen azide solution was filtered instead of being decanted from the calcium chloride used to dry it, and was added in small portions; 1-phenyl-5-methyltetrazole was formed in 55% yield. In Experiment 5 the acetophenone–aluminum chloride solution was allowed to stand for 4 hr. before use, the filtered azide solution was added in large portions, and there was no cooling; 30% of 1-phenyl-5-methyltetrazole was formed. Experiment 6 was the same as Experiment 5 except that the acetophenone–aluminum chloride solution was used at once; the result was the same. Experiment 7 was like Experiment 5 except that the azide solution was added in small portions and continuous ice bath cooling was used; 37% of 1-phenyl-5-methyltetrazole was formed. In additional experiments, a larger proportion of aluminum chloride was used, or the acetophenone–aluminum chloride solutions were treated with steam to effect some hydrolysis, or dry hydrogen chloride was passed in, or aluminum chloride from a previously unopened bottle was used; in each case, only tetrazole was obtained.

Pyrolysis of tetrazoles. A 2.0-g. sample of tetrazole was heated in a small Erlenmeyer flask in a Wood's metal bath to a temperature at which steady gas evolution occurred (between 220° and 250°). After about 2 hr. the gas evolution had entirely ceased, and the mixture was then heated on a steam bath for 1 hr. with 30 ml. of dioxane and 10 ml. of concentrated hydrochloric acid. After about 12 hr. the solvents were evaporated in an air stream, and the residue was extracted repeatedly with hot water containing a little hydrochloric acid and a little alcohol, until the cooled extracts no longer deposited solid. The product (arimidazole hydrochloride) was filtered from the cooled extracts, and a further crop was obtained by concentration of the filtrates. The free base was obtained by treating an aqueous alcoholic solution of the hydrochloride with sodium hydroxide solution; partial evaporation of the solution while hot led to crystallization on cooling.

In this manner 1,5-diphenyltetrazole yielded 12% of 2-phenylbenzimidazole hydrochloride. 1-Phenyl-5-*p*-chlorotetrazole yielded 19% of 2-*p*-chlorophenylbenzimidazole hydrochloride, m.p. 308–310° with prior darkening and sublimation. Free 2-*p*-chlorophenylbenzimidazole obtained from this had m.p. 297°.

Anal. Calcd. for $C_{19}H_9N_2Cl$: C, 68.26; H, 3.94; N, 12.26. Found: C, 68.32; H, 3.89; N, 12.35.

1-Phenyl-5-*p*-tolyltetrazole yielded 7–8% of 2-*p*-tolylbenzimidazole hydrochloride, m.p. 264–266°, from which free base of m.p. 268–269° was obtained (reported m.p. 266–269°[9]). 1-Phenyl-5-methyltetrazole yielded about 7% of quite impure 2-methylbenzimidazole hydrochloride, m.p. 265–270° (reported m.p. 300°[10]), from which a picrate, m.p. 210–212° was obtained (reported m.p. 214°[10]).

(9) E. L. Holljes and E. C. Wagner, *J. Org. Chem.*, 9, 31 (1944).

(10) M. A. Phillips, *J. Chem. Soc.*, 172 (1928).

The other tetrazoles all gave black tars on pyrolysis, from which identifiable samples of arimidazoles could not be obtained. However, 1-phenyl-5-*p*-nitrophenyltetrazole did yield a trace of solid of indefinite m.p. above 230°, but the amount was too small for further purification. The tar from 1-(3-quinolyl)-5-phenyltetrazole yielded a small amount of a mixture of basic solids, which was chromatographed on an alumina column with chloroform-alcohol mixture as eluent. A trace of an unidentified white solid was thus obtained, m.p. 288–290°.

Anal. Found: C, 67.24, 69.91; H, 5.61, 5.90; N, 17.35, 17.41.

Pyrolysis products of 1-phenyl-5-(p-chlorophenyl)tetrazole and 1-phenyl-5-p-tolyltetrazole. In additional experiments, the nature of all the pyrolysis products was examined, without special reference to yield. A 3.5-g. sample of 1-phenyl-5-*p*-chlorophenyltetrazole was heated for 5 hr. at 230–235° and worked up as previously described. The cooled dioxane–hydrochloric acid solution deposited 0.1 g. of solid, m.p. 305° dec., undepressed by mixture with an authentic sample of *p,p'*-dichlorocarbanilide (reported m.p. 305–306° dec.[11]). The filtrate was evaporated and the residue recrystallized from ethanol, giving a further quantity (0.35 g.), m.p. 300–301° dec. The filtrate was acidified with a little hydrochloric acid and enough water was added to cause crystallization. The precipitate (1.15 g.) melted at 235° after gradual shrinkage, and showed no melting point depression when mixed with authentic *p*-chlorocarbanilide.[12] The filtrate deposited more solid on standing; this proved to be 2-(*p*-chlorophenyl)benzimidazole, wt. 0.15 g., m.p. 305°. The filtrate from this substance gave only small amounts of impure material on further treatment.

In an analogous manner, 2.0 g. of 1-phenyl-5-*p*-tolyltetrazole yielded 0.2 g. of carbo-*p*-toluidide, m.p. 260–261°, 0.2 g. of 2-*p*-tolylbenzimidazole, and 0.65 g. of mixed ureas, from which repeated recrystallization from ethanol produced a pure sample of *p*-methylcarbanilide, m.p. 212°.

Catalyzed pyrolysis of 1,5-diphenyltetrazole. Samples of approximately equal volume each of 1,5-diphenyltetrazole and the potential catalytic agent were carefully mixed, and the behavior of the mixtures was observed while they were heated in melting point capillaries. Ground soft glass, alumina, silver powder, iron powder, and manganese powder did not alter the decomposition temperature (*ca.* 240°) significantly. Copper powder lowered the decomposition temperature to 175–180°. A 2.0-g. sample of 1,5-diphenyltetrazole was then mixed with 1.0 g. of copper powder and and heated at 190–200° for 2.25 hr. We could extract no 2-phenylbenzimidazole from the resulting black mass by the usual means, however, and the experiment was therefore abandoned.

ANN ARBOR, MICH.

(11) C. Manuelli and E. Ricca-Rossellini, *Gazz. chim. ital.*, **29II**, 124 (1899).

(12) H. Goldschmidt and B. Bardach, *Ber.*, **25**, 1364 (1892).

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

Acetylation of Aryl Aminotetrazoles

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Acetylation of both 1-aryl-5-aminotetrazoles and 5-arylaminotetrazoles with boiling acetic anhydride leads to 1-aryl-5-acetamidotetrazoles. Acetylation of 5-arylaminotetrazoles in the cold with acetic anhydride in the presence of aqueous alkalies leads to 1-acetyl-5-arylaminotetrazoles that rearrange on heating to the 1-aryl-5-acetamidotetrazoles. Prolonged treatment of either 1-*p*-nitrophenyl-5-aminotetrazole, its acetyl derivative or 5-*p*-nitrophenylaminotetrazole with boiling acetic anhydride causes loss of nitrogen and rearrangement to 2-methyl-5-*p*-nitrophenylamino-1,3,4-oxadiazole. The latter was identified by degradation and by independent synthesis.

After it had been shown that 5-alkylaminotetrazoles undergo rearrangement on heating to form 1-alkyl-5-aminotetrazoles[2,3] and on acetylation to give 1-alkyl-5-acetamidotetrazoles,[4] it became of interest to investigate the behavior of arylaminotetrazoles under similar conditions. The formation of 1-phenyl-5-acetamidotetrazole on acetylation of 1-phenyl-5-aminotetrazole had been observed.[5] Since many 1-aryl-5-aminotetrazoles can be converted easily into 5-arylaminotetrazoles on heating near their melting points or even in refluxing xylene,[2,3] it was of particular interest to determine whether this rearrangement could be reversed by acetylation.

For reference 1-phenyl-5-acetamidotetrazole (Ia) was prepared from 1-phenyl-5-aminotetrazole (IIa) in boiling acetic anhydride. The same product (Ia) was obtained from 5-phenylaminotetrazole (IIIa) in boiling acetic anhydride. Hydrolysis of Ia with concentrated hydrochloric acid regenerated IIa. As already noted by von Braun and Keller[5] the acetyl derivative (Ia) is acidic and dissolves easily in aqueous alkalies or alkali carbonates. It is precipitated unchanged from these solutions on acidification. It resists hydrolysis in boiling, dilute, aqueous alkalies.

When IIIa was acetylated in cold, aqueous, alkaline solution by treatment with acetic anhydride, a different acetyl derivative (IVa) was obtained. IVa is not readily soluble in aqueous alkalies or alkali carbonates. Although IVa can be dissolved in aqueous potassium carbonate on pro-

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(2) W. G. Finnegan, R. A. Henry, and E. Lieber, *J. Org. Chem.*, **18**, 779 (1953).

(3) W. L. Garbrecht and R. M. Herbst, *J. Org. Chem.*, **18**, 1269 (1953).

(4) R. M. Herbst and W. L. Garbrecht, *J. Org. Chem.*, **18**, 1283 (1953).

(5) J. von Braun and W. Keller, *Ber.*, **65**, 1677 (1932).