

required for formation of the colors. Canback¹⁰ has suggested that the colored species have quinoid-type structure.

DISCUSSION

In discussing the nature of these colored substances, the first possibility to be considered is that of an oxidation-reduction reaction in which the nitro compound would oxidize the iodide, probably to furnish iodine. It appears that the color is not due to molecular iodine, however, for several reasons which are recounted here. First, comparison of a solution of the nitro-iodide color with an iodine solution of equal intensity shows that there is a difference in hue. Second, a positive iodine reaction by the starch-iodide test cannot be obtained from one of the nitroaromatic iodide solutions although a genuine iodine solution of equal intensity does give a positive reaction. Third, though the color intensity of the nitroaromatic-iodide solutions is substantially decreased by the addition of relatively small amounts of water, the color intensity of an iodine solution in acetone is not nearly so drastically reduced by the addition of comparable amounts of water. Fourth, the intensity of color of a solution of DNB and sodium iodide in acetone decreases strikingly on dilution with more acetone, whereas a solution of iodine in acetone undergoes only the "normal" expected decrease in intensity when diluted. Fifth, a dilute aqueous solution of sodium thiosulfate does not bleach the color to any greater extent than does an equal volume of water. Lastly, a concentrated acetone solution of the colored material produced by 1,3-dinitrobenzene and sodium iodide (2.0 g. DNB and 3.6 g. of NaI in 20 ml. acetone) was prepared, allowed to stand for 24 hr., and then poured into a large excess of cold water. Of the original 2.0 g. of DNB, 1.78 g. were recovered unchanged. These observations make it seem very unlikely that the reaction is an oxidation-reduction.

The 1:1 combining ratio for both 1,3-dinitrobenzene and for 2,4,6-trinitrotoluene suggests that the combination may be through the aromatic ring rather than through the nitro group(s). The crystal radius of iodide ion (2.2 Å) is nearly the same as that of the aromatic nucleus, making it seem geometrically plausible for the iodide ion to be involved with the aromatic ring as a whole. (This does not explain why 4,4'-dinitrobiphenyl, with two aromatic rings, should also have a 1:1 combining ratio.) Since the nitro group withdraws electrons from the aromatic nucleus, the aromatic nucleus might then attempt to regain electrons by forming some sort of loose complex with the iodide ion. It is worth noting in this connection that the intensity of color increases with increasing numbers of nitro groups in the aromatic ring. The color produced by TNT is deeper than that produced by

DNB at the same concentration. It would be interesting to see whether aromatic compounds having substituents with electron-attracting power similar to that of nitro group also give this color reaction.

The color is definitely associated with the iodide ion and not the cation, for potassium iodide and ammonium iodide produce the same effect as sodium iodide. Conductivity data¹¹ indicate that sodium iodide in acetone at concentrations of 0.1M or less is appreciably dissociated into the ions, so it is reasonable to assume that iodide ion is acting as an independent species. The color reaction is not restricted to acetone solutions, for methanol solutions have been observed to give similar results.

Acknowledgment. The author would like to express his appreciation to Dr. A. H. Blatt of Queens College, New York, who suggested that this work be done and gave many helpful suggestions and comments.

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(11) J. W. McBain and F. C. Coleman, *Trans. Faraday Soc.*, **15**, 27 (1919).

Studies in the Pyrazole Series. VII.¹ The Base-Induced Scissions of 3,5-Dimethyl-1-carbamylpyrazole and -1-thiocarbamylpyrazole

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We have shown previously^{3a,b} that 1 guanyl- and 1-nitroguanylpyrazoles, Ia and Ib, respectively, deguanylate under aminolytic conditions with the formation of substituted guanidines and a 1-unsubstituted pyrazole. The corresponding 1-carbamyl- and 1-thiocarbamylpyrazoles, Ic and Id, respectively, have now been shown to behave similarly. Thus the reactions of Ic with amines formed a variety of substituted ureas, as well as 3,5-dimethylpyrazole (II). While the expected thioureas were analogously obtained from the reactions of Id with such bases as aniline, benzylamine, 4,4-diphenylsemicarbazide, hydrazine hydrate, and phenylhydrazine, the corresponding ammonium thiocyanates were isolated from its reactions with cyclohex-

(1) Part VI, F. L. Scott, A. Ahearne, and J. Reilly, *Rec. trav. chim.*, **76**, 190 (1957).

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(3) (a) F. L. Scott, D. G. O'Donovan, and J. Reilly, *J. Am. Chem. Soc.*, **75**, 4053 (1953); (b) F. L. Scott, M. T. Kennedy, and J. Reilly, *J. Am. Chem. Soc.*, **75**, 1294 (1953).

(10) T. Canback, *Farm. Revy*, **48**, 153 (1949); *Chem. Abstr.*, **43**, 4650 (1949).

ylamine, morpholine, and piperidine. In addition II was isolated in good yield from each of these aminolyses. Some evolution of hydrogen sulfide was also detected in the aminolyses of Id effected with benzylamine, pyrrolidine, pyrrolidone, and phenylhydrazine.

With regard to the mechanism of these reactions three points require comment. First the detected lability of the 1-acylpyrazoles must be attributed primarily to the anionic stability of pyrazolide ion.⁴ Secondly, while some of the reaction products obtained with Id suggest elimination processes,⁵ the bulk of the present data and other related evidence,⁶ suggest that the most probable mechanism for these and similar^{3a,b} aminolyses is a carbamyl addition-elimination process as seen in Figure 1.

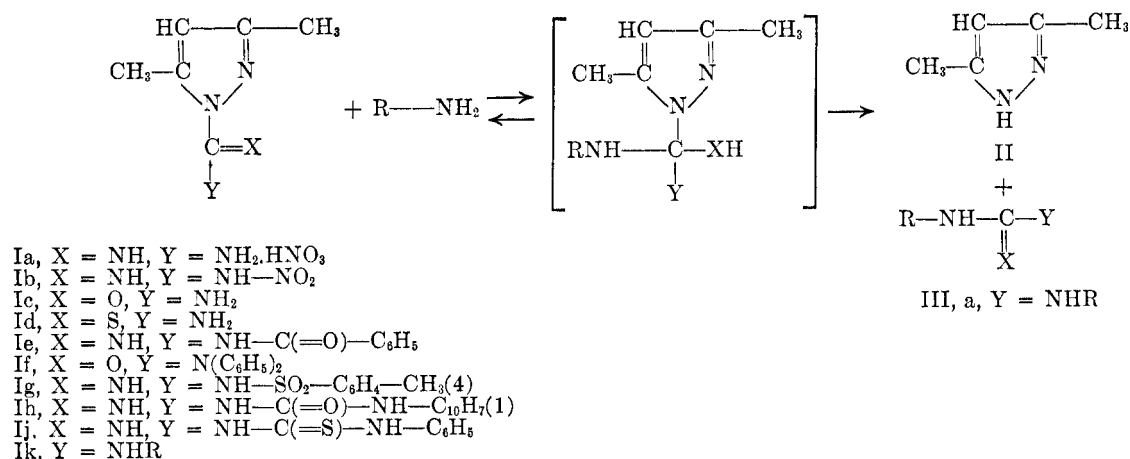


FIG. 1

Thirdly, the normal elimination of pyrazolide ion from the intermediary adduct of this latter reaction may receive competition under certain conditions from the expulsion of anion (Y⁻) therefrom. This latter event would then result in the formation of

(4) This has not been made explicit in our earlier papers. To support the present statement the following factors may be cited: (a) similar leaving groups have been encountered in related situations, see *e.g.*, H. A. Staab, *Chem. Ber.*, **89**, 2088 (1956), and J. Baddiley, J. G. Buchanan, and R. Letters, *J. Chem. Soc.*, 2812 (1956); (b) increasing the electrophilicity of the pyrazole moiety increases its rate of solvolytic 1-deganylation, see F. L. Scott, *Chimia*, in press, and F. L. Scott and R. Rubin, forthcoming paper in this series; (c) a similar displacement of pyrazolide ion from 1-(2',4'-dinitrophenyl) pyrazole by base has been recently described, by H. P. Crocker and R. H. Hall, *J. Chem. Soc.*, 4489 (1955); (d) finally the stability of the 1-guanylpyrazolines (F. L. Scott, unpublished data) wherein the acidic character of the pyrazole ring is totally inhibited, also supports this concept.

(5) The isolation of ammonium thiocyanates is not unequivocal evidence for direct eliminations from Id. Such thiocyanic acid derivatives may also arise *via* initial ethanolysis of Id to ethyl thionourea followed by elimination of thiocyanate ion from this latter substance. Compare *e.g.*, M. Battagay and E. Hegazi, *Helv. Chim. Acta*, **16**, 999 (1933).

(6) See Scott, reference 4 (b) and subsequent papers in this series.

pyrazoles of type Ik, and these in turn should readily lead to compounds such as IIIa. We have encountered some products of this type *e.g.*, in the reactions of both aniline and *p*-nitroaniline with Ic, and of aniline and benzylamine with Id. However, in view of the infrequency of IIIa type compounds among the large number of pyrazolyl aminolyses we have examined^{3a,b,6} and their possible and demonstrable origination in other ways,⁷ we attribute the formation of derivatives such as IIIa to further aminolyses of the initially formed monosubstituted ureas and thioureas. The extent of incursion of IIIa type substances appears to increase with increase in reaction temperature.

Some experiments were also performed herein with azide ion as a deacylating entity. In ethanolic

solution the substituted pyrazoles Ie, If, Ig, Ih, and Ij were recovered in *ca.* 80% yields after three hours refluxing with equivalent quantities of sodium azide. After six hours of such treatment, the yield of recovered Ig dropped to 58%. Under the former conditions Ia and Ib were deguanlylated by the azide nucleophile and yielded 5-amino- and 5-nitroaminotetrazoles, respectively. Under different experimental conditions *i.e.*, at room temperature but with a much greater reaction time, Id was also deacylated.⁸

EXPERIMENTAL⁹

3,5-Dimethyl-1-carbamylpyrazole (Ic) was prepared by a modification of Posner's method.¹⁰ To a solution of 11.2 g. of

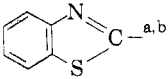
(7) Compare F. L. Scott and M. T. Scott, unpublished results.

(8) Because we have found (F. L. Scott, A. J. Kocjarski, and J. Reilly, to be published) that thiocarbamyl azide, or rather 5-aminothiazotriazole [F. L. Scott, to be published], readily desulfurizes under comparable conditions, and as we encountered no loss of sulfur in the deacylation of Id effected in the presence of sodium azide, we regard this latter deacylation as resulting mainly from ethanolysis.

(9) All melting points are uncorrected. Microanalyses are by Drs. Wieler and Strauss, Oxford, England.

(10) T. Posner, *Ber.*, **34**, 3973 (1901).

TABLE I
 AMINOLYSES OF 3,5-DIMETHYL-1-CARBAMYL- AND -1-THIOCARBAMYLPIRAZOLES

Amine	Product (III), with R==	Molecular Formula	M.P., °C.	Yield, %	Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
2-Aminobenzo- thiazole		C ₈ H ₇ N ₂ SO	337 ^c	40	49.7	50.2	3.6	3.6
Cyclohexylamine	C ₆ H ₁₁ — ^{a,b}	C ₇ H ₁₄ N ₂ O	197 ^d	70	59.2	59.1	9.9	9.7
1-Naphthylamine	1-C ₁₀ H ₇ ^{a,b}	C ₁₁ H ₁₀ N ₂ O	214 ^e	60	71.0	70.8	5.4	5.3
2-Naphthylamine	2-C ₁₀ H ₇ ^{a,b}	C ₁₁ H ₁₀ N ₂ O	219 ^f	57	71.0	70.6	5.4	5.3
4-Nitroaniline	4-NO ₂ —C ₆ H ₄ — ^{a,b,g}	C ₁₃ H ₁₀ N ₂ O ₅	313 ^h	97 ⁱ	51.7	51.3	3.3	3.5
<i>n</i> -Octylamine	<i>n</i> -C ₈ H ₁₇ — ^{a,b}	C ₉ H ₂₀ N ₂ O	100–101 ^j	90	62.8	63.2	11.6	11.6
<i>p</i> -Phenylenedi- amine	4—NH ₂ —C(=O)— NH—C ₆ H ₄ — ^{a,b}	C ₈ H ₁₀ N ₄ O ₂	>360 ^k	45	49.5	49.2	5.2	5.1
Benzylamine ^l	C ₆ H ₅ CH ₂ ^m	C ₁₅ H ₁₈ N ₂ SO ⁿ	146 ^o	56	65.7	66.2	6.6	6.1 ^p
Cyclohexylamine ^l	— ^a	C ₇ H ₁₄ N ₂ S	101	62	53.2	52.7	8.9	8.8
4,4-Diphenyl- semicarbazide ^l	(C ₆ H ₅) ₂ N—C(=O)— NH— ^m	C ₁₄ H ₁₄ N ₂ SO	197	34	58.8	59.2	4.9	4.5 ^r
Morpholine ^{l,s}	— ^t	C ₅ H ₁₀ N ₂ SO	119–120	63	41.1	41.5	6.8	7.2
Phenylhydrazine ^l	C ₆ H ₅ NH ^m	C ₇ H ₉ N ₃ S	202–203 ^u	72	50.3	50.3	5.4	5.0 ^v
Piperidine ^{l,s}	— ^w	C ₆ H ₁₂ N ₂ S	93	67	50.0	49.9	8.3	8.4

^a These are represented by the general formula III, with X = 0 and Y = NH₂. ^b These are reaction products from the appropriate aminolysis of IC in 95% aqueous ethanol, with a 3 hr. reflux period. High yields of II were isolated in each reaction. ^c M.p. >300°, as reported by H. P. Kaufmann, *Arch. Pharm.*, **273**, 22 (1935). ^d J. L. Boivin and P. A. Boivin, *Can. J. Chem.*, **29**, 478 (1951) report this m.p. as 195–196°. ^e Reported^{15b} m.p. 215–220°. ^f Reported^{15b} m.p. 219–220°. ^g This represents 1,3-di-*p*-nitrophenylurea which is formed in nitrobenzene solution from Ic and *p*-nitroaniline. In ethanolic solution *p*-nitrophenylurea was the sole product isolated from these same reactants and it was formed in only 22% yield. Finally, in toluene as solvent, the major product was again the disubstituted urea (in ca. 70% yield), together with ca. 5% of the monosubstituted ureide. Each of these reactions involved a 3-hr. reflux period. ^h M.p. 310°, as reported by G. V. Gadhave, *J. Indian Chem. Soc.*, **10**, 391 (1933). ⁱ This yield is corrected for recovered amine. ^j M.p. 102.5°, reported by J. S. Buck, A. M. Hjort, W. S. Ide, and E. J. de Beer, *J. Am. Chem. Soc.*, **60**, 461 (1938). ^k Previously reported by E. Lellmann, *Ann.*, **221**, 14 (1883) to char without melting. ^l These correspond to aminolyses of Id in ethanolic solution, with a general reflux time of 3 hr. unless otherwise noted. ^m These correspond to III with X = S and in general Y = NH₂. However with benzylamine the product isolated was 1,3-dibenzylthiourea with Y = NHCH₂C₆H₅. ⁿ Physical data correspond to a monohydrate. ^o M.p. 147–148°, reported by G. M. Dyson and H. J. George, *J. Chem. Soc.*, **125**, 1702 (1924). ^p Calcd.: N, 10.2; S, 11.7. Found: N, 10.4; S, 12.1. ^q Apparently, this is cyclohexyl-ammonium thiocyanate; 1-cyclohexylthiourea has been reported to melt at 161–162°, by A. Skita and H. Rolfes, *Ber.*, **53B**, 1242 (1920). ^r Calcd.: N, 19.6; S, 11.2. Found: N, 20.0; S, 11.1. ^s Reflux period: 40 min. ^t This is morpholinium thiocyanate, compare A. Kjaer and K. Rubinstein, *Acta Chem. Scand.*, **7**, 528 (1953). It did not depress on mixture melting point with an authentic sample. This latter sample was prepared by reaction of equimolar quantities of morpholine, potassium thiocyanate, and hydrochloric acid in ethanolic solution at room temperature. The compound thus prepared also had a m.p. 119–120°. ^u Reported^{16c} m.p. 200–201°. ^v Calcd.: N, 25.1; S, 19.2. Found: N, 25.0; S, 19.2. ^w This is piperidinium thiocyanate, m.p. 95°, as reported by H. Lecher and A. Goebel, *Ber.*, **55**, 1483 (1922). Again it did not depress on mixture melting point with an authentic sample, prepared similarly to the morpholine derivative, as described above. The melting point of the isomeric 1-thiocarbamylpiperidine has been reported as 128° by O. Wallach, *Ber.*, **32**, 1872 (1899).

semicarbazide hydrochloride in 30 ml. of water was added 10.0 g. of acetylacetone in 10 ml. of absolute ethanol. A vigorous, exothermic reaction resulted and Ic separated in 95% yield. After recrystallization from absolute ethanol or better from benzene-pentane or chloroform-pentane mixtures, it melted at 112°, reported m.p. 111.4–112.4°.

Anal. Calcd. for C₈H₉N₃O: C, 51.8; H, 6.5. Found: C, 51.8; H, 6.3.

Essentially, the same technique was employed in the preparation of Id, which was isolated in 85% yield and after crystallization from benzene had m.p. 98–99°. It was markedly unstable.

Anal. Calcd. for C₈H₉N₃S: C, 46.5; H, 5.8; N, 27.1; S, 20.6. Found: C, 46.1; H, 5.8; N, 27.0; S, 21.0.

Aminolysis experiments. (1) of Ic.¹¹ The following is representative of the reactions effected. To a solution of 2.39 g. of Ic dissolved in 30 ml. of 95% ethanol was added a slight excess, 1.8 g., of aniline. The solution was then refluxed for 4 hr. On cooling and diluting the solution with an excess of

water a white flocculent precipitate (0.20 g., 5.5% yield)¹² of 1,3-diphenylurea was obtained. This after recrystallization from aqueous ethanol melted at 239–240°, reported¹³ m.p. 238–239°.

Anal. Calcd. for C₁₃H₁₂N₂O: C, 73.6; H, 5.7. Found: C, 73.4; H, 5.8.

The filtrate on further work-up gave 0.90 g. (37.7% yield) of phenylurea m.p. 146–147°, reported¹³ m.p. 144.5–145.6°, which did not depress the melting point of an authentic sample. In addition a quantitative yield of 3,5-dimethylpyrazole (II), m.p. 105–106°, reported^{14a} m.p. 107–108°, was isolated and identified by mixture melting point with an authentic sample, and *via* its picrate m.p. 166°, reported^{14b} m.p. 166–167°.

(12) These yields are based on the quantity of amine employed when diureas are isolated as aminolysis products of Ic (or Id) but on the quantity of substituted pyrazole used when the reaction product is a monosubstituted urea.

(13) D. G. Crosby and C. Niemann, *J. Am. Chem. Soc.*, **76**, 4458 (1954).

(14) (a) R. H. Wiley and P. E. Hexner, *Org. Syntheses*, **31**, 43 (1951); (b) R. V. Rothenburg, *J. prakt. Chem.*, **52**, 45 (1895).

(11) We are indebted to Miss M. M. Hearn, M.Sc., for assistance with these experiments.

Anal. Calcd. for $C_{11}H_{11}N_3O_7$: C, 40.6; H, 3.4; N, 21.5
Found: C, 41.1; H, 3.7; N, 21.5.

It is to be understood that II was similarly isolated and identified in all the pyrazolyl aminolyses effected. The yields of II throughout averaged between 75–85%.

(2) of *Id*. To 2.0 g. of *Id* dissolved in the minimum quantity of ethanol was added 1.2 ml. of aniline. The mixture was refluxed for 3 hr., during which time it developed a yellow coloration. On standing overnight, 0.76 g. (52% yield)¹² of white flakes, m.p. 148–150° settled out. After crystallization from ethanol these had a m.p. of 152° and corresponded to 1,3-diphenylthiourea, reported^{16a} m.p. 154°.

Anal. Calcd. for $C_{13}H_{12}N_2S$: C, 68.4; H, 5.3; N, 12.3; S, 14.0. Found: C, 68.0; H, 5.3; N, 12.2; S, 13.6.

The alcoholic filtrate was allowed to evaporate in a stream of air and the residual solid was then washed with 6×20 ml. portions of ether. A further quantity, 0.15 g. (10.3%) of 1,3-diphenylthiourea remained behind, as essentially ether-insoluble. The ethereal liquor on work-up yielded 82% of II, identified as previously described. Most of the remaining aminolyses of both *Ic* and *Id* are summarized in Table I.

Some related observations. When treated with *Ic* under the general conditions described above the following bases were carbamylated: dimethylamine yielded 1,1-dimethylurea, m.p. 182°, reported¹³ m.p. 182°, in 64% yield; phenylhydrazine afforded 1-phenylsemicarbazide, m.p. 172°, reported^{16a} m.p. 172°, in 90% yield; 4-nitrophenylhydrazine resulted in 1-(4'-nitrophenyl)semicarbazide, m.p. 215°, reported¹⁷ m.p. 211–212°, in 95% yield; and thiosemicarbazide yielded 2-thiobiurea, m.p. 216–218°, reported¹⁸ m.p. 220°, in 82% yield.¹⁹ When the base employed was either diphenylamine, lysine hydrochloride, nitroaminoguanidine, or phthalimide, *Ic* completely decarbamylated under the usual reaction conditions without forming any appreciable quantities of the corresponding ureides and thus the deacylation encountered was purely solvolytic in origin. A series of experiments were run to put this on a semiquantitative basis. These consisted of refluxing measured quantities of *Ic* for varying periods of time in 95% ethanol solution, then rapidly cooling the reaction sample and analyzing the liquor for both II and unchanged *Ic*. From these, a rough rate constant for the solvolytic deacylation of *Ic* was derived, viz. $k_1 = 1.2(\pm 0.2) \times 10^{-3}$ sec.⁻¹ This accounts for the non-survival of *Ic* even with the weakest nucleophiles employed and is in reasonable accord with the more precise rate value as determined by spectrophotometric means.^{4b} Incidentally, in the sample analyzed after a minute reflux period, the presence of cyanic acid was suggested in the cooled reaction liquor by means of its $[Co(CNO)_2 \cdot 2 KCNO]$ complex.²⁰ A similar complex was not formed from a cold solution of pure *Ic* or II. When *Id* was refluxed with 1 equivalent of either pyrrolidone or pyrrolidine for 40 min., hydrogen sulfide was vigorously evolved; however only 3,5-dimethylpyrazole, in 60% yield, was identified, as before, on work-up of the reaction liquor. Similarly treated with hydrazine hydrate, with 1 hr. refluxing, *Id* afforded II in 77% yield and 51% thiosemicarbazide m.p. 181–182°, reported^{15b} m.p. 181–183°. Semioxamazide analogously treated, save

with a 20-min. reflux period, resulted in a 90% recovery of starting hydrazide, no detectable evolution of either sulfur or hydrogen sulfide, and an 11% yield of II. All the substituted ureides described above were identified by mixture melting point with authentic samples, which were either already available or prepared by standard methods from the literature. Finally, while benzylamine and phenylhydrazine afforded simple displacement products with *Id*, see Table I, their aminolyses were accompanied by a faint evolution of hydrogen sulfide from the reaction liquor.

Displacements with azide ion. The reaction with *Id* was as follows: To 5.0 g. of *Id* dissolved in 200 ml. of cold ethanol was added 2.05 g. of sodium azide dissolved in 20 ml. of water. The mixture was continuously mechanically agitated. At 24-hr. intervals, 44 ml. aliquots were withdrawn. Each aliquot was evaporated to dryness in a stream of air, the residual solid was then dissolved in water and the aqueous liquor extracted with ether. The quantities of II thus isolated from the ethereal extracts and identified as before corresponded to: 0.34 g. (after 24 hr.); 0.40 g. (48 hr.); 0.42 g. (72 hr.); 0.44 g. (96 hr.) and 0.56 g. (120 hr.). Total yield of II obtained, 2.16 g. (71.5%). No other material was isolated (this includes sulfur).⁸ The above figures result in a rough rate of deacylation for *Id* of 7×10^{-3} l. mole⁻¹ sec.⁻¹ Of the remaining pyrazoles studied only with *Ia* was a comparable series of experiments run. With this latter pyrazole the solvent employed was water and the reactions were run at reflux temperature. After 1 hr. of such treatment of *Ia* with an equivalent quantity of sodium azide, 17% *Ia* was recovered, 34% II was isolated, *via* ether extraction, etc, and 22% of 5-aminotetrazole, m.p. 205°, reported^{21a} m.p. 203°, was also obtained.

Anal. Calcd. for CH_3N_3 : C, 14.1; H, 3.5; N, 82.4. Found: C, 14.4; H, 3.8; N, 81.9.

After 3 hr. of such refluxing the respective percentages isolated were 13, 39, 35; after 6 hr. they consisted of 10, 51, and 36 and after 9 hr. they corresponded to 7, 52, and 44. These data yielded an approximate value for the second-order rate constant of the azide induced deacylation of *Ia* in aqueous solution, at 100°, viz. $k_2 = 5 \times 10^{-5}$ l. mole⁻¹ sec.⁻¹ From *Ib* after 3 hr. refluxing in aqueous solution with 1 equivalent of sodium azide was isolated either the sodium salt of 5-nitraminotetrazole, m.p. >360° with very violent explosion, in 46% yield, or, after acidification of the mother liquor, 5-nitraminotetrazole itself, m.p. 137° (with explosion), reported^{21b} m.p. ca. 140°, in 26% yield.

Anal. Calcd. for $CH_3N_6O_2$: C, 9.2; H, 1.6. Found: C, 10.0; H, 2.1.

The yield of II from both experiments with *Ib* was 32 and 18% respectively. When the pyrazoles *Ie*, *If*, *Ig*, *Ih*, and *Ij* were refluxed for 3 hr. in aqueous ethanolic solution with 1 equivalent of sodium azide they were recovered unchanged in 80, 85, 84, 75, and 82% yields respectively. After 6 hr. refluxing, *Ig* was recovered in only 58% yield, and II was isolated in 11% yield. However, no tetrazolyl by-products were identified in the reaction with *Ig*. Finally when *Ic* was stirred for 24 hr. in aqueous ethanol with an equimolar quantity of azide ion it was recovered in 70% yield without the detection of any formation of substance II.

(15) *Organic Reagents for Organic Analysis*, 2nd Edition, Hopkin and Williams, Essex, England, 1950; (a) p. 178; (b) p. 122.

(16) I. Heilbron and H. M. Bunbury, *Dictionary of Organic Compounds*, 4th Edition, Eyre and Spottiswoode, London, 1953; (a) Vol. IV, p. 173; (b) Vol. III, p. 592; (c) Vol. IV, p. 179.

(17) E. Hyde, *Ber.*, **32**, 1812 (1899).

(18) S. L. Ganniah and P. C. Guha, *J. Indian Inst. Sci.*, **16A**, 11 (1933).

(19) This percentage has been corrected for recovered amine.

(20) H. E. Williams, *Cyanogen Compounds*, 2nd Edition, p. 400, Arnold and Co., London, 1948.

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(21) (a) J. Thiele, *Ann.*, **270**, 54 (1892); (b) see E. Lieber, C. C. Herrick, and E. Sherman, *J. Am. Chem. Soc.*, **74**, 2684 (1952) and previous papers.