several days in the icebox, a small amount of light tan granular crystals; m. p. 234–235° dec.

Anal. Calcd. for $C_{10}H_6N_4OS$: C, 51.7; H, 3.45; N, 24.1. Found: C, 52.4; H, 3.61; N, 23.08.

In spite of the analysis, the compound gave derivatives which analyzed correctly.

(2) **By Means of β-Cyanoacetyl-2-benzothiazolylhydrazine.**—To a solution of 5.5 g. of cyanoacetazide[15] in 200 ml. of dioxane was added in small portions, with stirring, 8.25 g. of 2-benzothiazolylhydrazine.[17] After standing at room temperature overnight, the solution was filtered, yielding 7.7 g. (67%), m. p. 198–200°. It was recrystallized from dioxane, forming fine white granular crystals, m. p. 200–201°.

Anal. Calcd. for $C_{10}H_{13}N_4OS$: C, 51.7; H, 3.45; N, 24.1. Found: C, 51.70; H, 3.35; N, 24.25.

The compound, refluxed in two equivalents of sodium methylate solution for one hour, gave 1-(2-benzothiazolyl)-3-hydroxy-5-pyrazolone imide, isolated as previously described for this compound. The identity of the two was established by the m. p. and mixed m. p. of the parent substances and of the mono acetyl derivatives obtained therefrom.

1-(2-Benzothiazolyl)-3-acetoxy-5-pyrazolone Acetylimide.—A mixture of 3.4 g. of 1-(2-benzothiazolyl)-3-hydroxy-5-pyrazolone imide in 15 ml. of acetic anhydride was heated on the steam-bath for one hour after solution was complete. Then, 7 ml. of glacial acetic acid was added, followed by 6 ml. of water, to give, on cooling, 2.7 g. (58.5%), m. p. 181–182°. Recrystallized from methanol it gave white needles; m. p. 182–183°.

Anal. Calcd. for $C_{14}H_{12}N_4O_3S$: N, 17.7. Found: N, 17.57.

The compound is insoluble in 3% sodium carbonate and 2% sodium hydroxide.

1-(2-Benzothiazolyl)-3-hydroxy-5-pyrazolone Acetylimide.—To a solution of 2 g. of 1-(2-benzothiazolyl)-3-acetoxy-5-pyrazolone acetylimide in 20 ml. of absolute ethanol, plus 10 ml. of dioxane, was added 0.55 g. of piperidine. After refluxing for one hour, the mixture was cooled to give 1 g. (58%); m. p. 250–252°. Recrystallized from 10 ml. of absolute ethanol, plus 3 ml. of dioxane, it gave 0.75 g. of white microcrystals; m. p. 252–253°.

Anal. Calcd. for $C_{12}H_{10}N_4O_2S$: N, 20.4. Found: N, 20.15.

The compound is soluble in 3% sodium carbonate.

Summary

When *m*-tolylhydrazine, *m*-chlorophenylhydrazine, *p*-methoxyphenylhydrazine, *p*-sulfamylphenylhydrazine, 3-pyridylhydrazine, and 4-pyridylhydrazine are condensed with ethyl cyanoacetate in the presence of sodium ethylate, they, like phenylhydrazine, form the respective 3-amino-5-pyrazolones substituted in position 1.

2-Pyridylhydrazine, 2-quinolylhydrazine, and 2-benzothiazolylhydrazine under the same conditions yield the 3-hydroxy-5-pyrazolone imides substituted in position 1.

The structures of the pyrazolones were established by color tests and by synthesis of the 3-hydroxy-5-pyrazolone imides by means of the β-cyanoacetyl derivatives of the respective hydrazines.

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[COMMUNICATION NO. 981 FROM THE KODAK RESEARCH LABORATORIES]

Investigation of Pyrazole Compounds. VII.[1] The Reaction of Some Hydrazines with Ethyl Malonate Monoimidoester

BY A. WEISSBERGER, H. D. PORTER AND W. A. GREGORY

The condensation of ethyl cyanoacetate with phenylhydrazine in sodium ethylate results in the formation of 1-phenyl-3-amino-5-pyrazolone I.[2] With other monosubstituted hydrazines, the corresponding 3-amino-5-pyrazolone, I, is not always obtained. No defined product was isolated from reaction mixtures with *p*-nitrophenylhydrazine or *p*-cyanophenylhydrazine. 2-Pyridylhydrazine, 2-quinolylhydrazine, and 2-benzothiazolylhydrazine yielded the respective 3-hydroxy-5-pyrazolone imides, II,[1] and not I, while 2-benzoxazolylhydrazine formed unidentified compounds which are neither I nor II.

All these hydrazines have now been converted to I by a new method of synthesis. In this the hydrazine is condensed with ethyl malonate monoimidoester, III, either directly to the respective 3-amino-5-pyrazolone, I, or with isolation of the intermediate ethyl β-(β-R-hydrazino)-β-iminopropionate, IV. The latter, on treatment with alkali, closes the ring, eliminating ethanol. The structure of the resulting pyrazolones was determined by their dye formation with *p*-nitrosodimethylaniline[3] and the film-strip test.[4] The reaction of 2-pyridylhydrazine with the imidoester was attempted several times but yielded only sporadically very small amounts of an impure product. This, by its dye formation with *p*-nitrosodimethylaniline, was also shown to be essentially I. With those hydrazines which gave I in the condensation with ethyl cyanoacetate, the new method also yielded I.

The pyrazolone derivatives of type I are colorless or pale tan in the solid state, as melts, and in any organic solvent. An exception is 1-(2-quinolyl)-3-amino-5-pyrazolone, which is obtained almost colorless by addition of water to its colorless solution in pyridine, but is bright yellow in glacial acetic acid. The latter solution becomes colorless upon addition of a little hydrogen chloride or of much pyridine. Water precipitates bright yellow microcrystals from the yellow solution. Both the white and the yellow modifications

(1) Investigation of Pyrazole Compounds, VI, THIS JOURNAL, **66**, 1849 (1944.)

(2) Weissberger and Porter, *ibid.*, **64**, 2133 (1942).

(3) Weissberger and Porter, *ibid.*, **65**, 732 (1943).

(4) Weissberger and Porter, *ibid.*, **65**, 1495 (1943).

fuse to a yellow melt. However, neither of them can be obtained analytically pure by recrystallization from pyridine or acetic acid. When 1-(2-quinolyl)-3-amino-5-pyrazolone is treated with benzoyl chloride and pyridine, a carbonate-insoluble dibenzoyl derivative results. The monobenzoyl derivative, obtained by partial deacetylation, forms a dye with *p*-nitrosodimethylaniline. The benzoyl derivatives are therefore considered to be 1-(2-quinolyl)-3-benzoylamino-5-benzoyloxypyrazole, V, and 1-(2-quinolyl)-3-benzoylamino-5-pyrazolone, VI, respectively.[2,4] V is colorless as a solid, when molten, and in glacial acetic acid, but VI behaves like 1-(2-quinolyl)-3-amino-5-pyrazolone. The colorless and the yellow modifications of VI, were obtained in a pure state by recrystallization from dilute pyridine and acetic acid, respectively. Both analyze correctly and have the same melting point of 187–188°. We are indebted to Dr. E. E. Jelley, of these Laboratories, for the following information: "The colorless and the yellow crystals were fused on an object slide under a cover slip and the two melts allowed to come in contact. It was found that they have the same refractive index. Allowed to crystallize at 80°, they formed the same yellow crystals as shown by their birefringence and optical orientation." The yellow modifications of 1-(2-quinolyl)-3-amino-5-pyrazolone and of 1-(2-quinolyl)-3-benzoylamino-5-pyrazolone, VI, appear to be distinguished from the colorless by chelation, VII, the inner hydrogen bridge being broken by excess protons or by proton acceptors.

The purification of some of the pyrazolones, particularly of 1-(*p*-nitrophenyl)-3-amino-5-pyrazolone and of 1-(2-benzothiazolyl)-3-amino-5-pyrazolone, is tedious. From the latter, 1-(2-benzothiazolyl)-3-benzoylamino-5-benzoyloxypyrazole, V (R = 2-benzothiazolyl), and 1-(2-benzothiazolyl)-3-benzoylamino-5-pyrazolone, VI (R = 2-benzothiazolyl), were prepared and, like V and VI, identified by their solubility in carbonate and their dye formation with *p*-nitrosodimethylaniline. Both are readily purified by recrystallization. They are colorless, form colorless melts, and form colorless solutions in glacial acetic acid and other solvents.

A summary of the results when substituted hydrazines are condensed with ethyl malonate monoimidoester, with cyanoacetazide, with ethyl cyanoacetate, or with α-carbethoxyacetothioacetanilide,[3,5] is given in the table. The compound formed is identified by a Roman numeral. A search for the other respective isomer in the reaction mixtures has hitherto been unsuccessful.

For the reactions with ethyl malonate monoimidoester (A), and with cyanoacetazide (B), numerals IV and VIII are inserted if the respective intermediates were isolated. The structure of these intermediates follows from the nature of the pyrazolone (I or II), obtained by ring closure. The nitrogen at which the hydrazine reacts to form the respective intermediate is indicated in the table by α or β. Where, in reaction A, the intermediate was not isolated, α or β follows directly from the structure of the pyrazolone, assuming that the imidoester always reacts first at the —$C(NH)OC_2H_5$ group. From the assignment of α or β under A and B, it is evident that the intermediates and pyrazolones obtained are those which should be expected in view of the fact that the β-position of the hydrazine is more reactive than the α-position in the aromatic and heterocyclic series.[6]

This rule applies likewise to the reaction of the aromatic and of some of the heterocyclic hydrazines with ethyl cyanoacetate in sodium ethylate (C) if the addition to the cyano group precedes the elimination of ethanol. Whether or not the exception to the rule observed with 2-pyridyl-, 2-quinolyl-, and 2-benzothiazolylhydrazine is related to the ability of these hydrazines to form chelate compounds, IX, cannot be decided at present.

The rule holds also for Worrall's reaction,[3,5] (D), provided that the elimination of ethanol (see X) proceeds more readily than that of hydrogen sulfide. This includes the reaction of 2-pyridylhydrazine, forming 1-(2-pyridyl)-3-hydroxy-5-pyrazolone anil, II, which has not been described previously. The behavior of this compound in the color reactions is noteworthy. While 1-phenyl-3-hydroxy-5-pyrazolone anil, II,[3] gives a weak but unmistakable magenta dye when oxidized in the presence of *p*-aminodimethylaniline,[7] the 2-pyridyl derivative does not show any dye formation at all. It resembles in this respect the 1-acetyl-3-hydroxy-5-anilinopyrazole.[4] Presumably, in both compounds the pyrazole form is strongly stabilized by chelation, XI, so that the reaction of the methylene group of the pyrazolone anil, weak as it is, becomes masked altogether.

Experimental

Ethyl malonate monoimidoester was obtained by adding 50 g. of the hydrochloride[7a] portionwise to a solution of 50 g. of sodium bicarbonate in 300 ml. of water containing ice, filtering, and washing with cold water; 30.5 g. (75%) of fine, white needles, m. p. 42–43°; recrystallized from petroleum ether, m. p. 42–43°.

Anal. Calcd. for $C_7H_{13}NO_3$: N, 8.8. Found: N, 8.75.

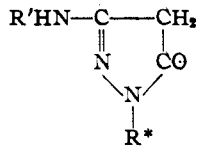
Ethyl β-(β-Phenylhydrazino)-β-iminopropionate Hydrochloride.—A solution of 10.8 g. of phenylhydrazine and 15.9 g. of ethyl malonate monoimidoester in 50 ml. of benzene was refluxed for one-half hour, cooled, 300 ml. of ligroin added, and the solvent decanted from the oil which separated. The oil was dissolved in 100 ml. of absolute alcohol, cooled in ice, and saturated with dry hydrogen chloride. The crystals which separated were combined with those obtained from the filtrate on adding ether (100 ml.); 11.4 g. (44%) of light orange plates, m. p. 185–186°, were formed. A portion recrystallized from *n*-propanol gave white plates, m. p. 185–186°.

(5) Worrall, THIS JOURNAL, **44**, 1551 (1922).

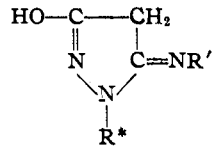
(6) (a) E. Fischer, *Ann.*, **190**, 125 (1878); (b) Fargher and Furness, *J. Chem. Soc.*; **107**, 688 (1915).

(7) Weissberger and Porter, THIS JOURNAL, **65**, 52 (1943).

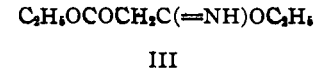
(7a) Pinner and Oppenheimer, *Ber.*, **28**, 478 (1895).



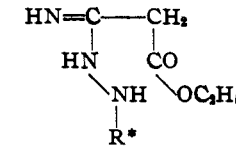
*R = aryl or heterocyclic group
R′ = H or C_6H_5
I



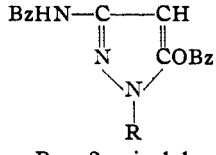
*R = aryl or heterocyclic group
R′ = H or C_6H_5
II



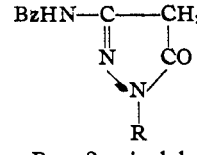
III



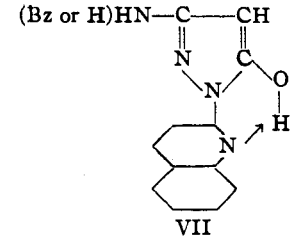
*R = aryl or heterocyclic group
IV



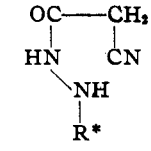
R = 2-quinolyl
V



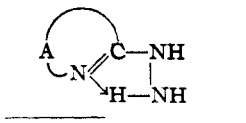
R = 2-quinolyl
VI



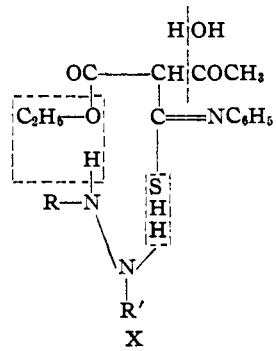
VII



VIII

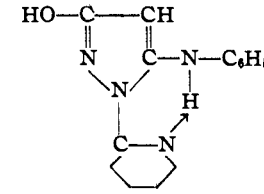


A = atoms to complete the pyridine, quinoline or benzothiazole nucleus
IX



X

RNHNHR′ is a monosubstituted hydrazine, R or R′ may be aryl, or a heterocyclic group, the one other being H.



XI

TABLE I

CONDENSATION OF HYDRAZINES TO PYRAZOLONES

	A			B			C		D	
	Reaction with									
	$C_2H_5OC(=NH)CH_2CO_2C_2H_5$			$NCCH_2CON_2$			$NCCH_2CO_2C_2H_5$ + $2NaOCH_3$		$CH_3COCH(CO_2C_2H_5)$-$C(SNa)=NC_6H_5$	
Hydrazine	Intermediate	Reactivity of hydrazine	Pyrazolone	Intermediate	Reactivity of hydrazine	Pyrazolone	Reactivity of hydrazine	Pyrazolone	Reactivity of hydrazine	Pyrazolone
Phenyl-	IV	β	I	VIII	β	II[7]	β	I[3]	β	II[3]
m-Tolyl-							β	I[1]		
m-Chlorophenyl-							β	I[1]		
p-Methoxyphenyl-							β	I[1]		
p-Sulfamylphenyl-	IV	β	I				β	I[1]		
p-Cyanophenyl-	IV	β	I							
p-Nitrophenyl-		β	I							
2-Pyridyl-		β	I[a]	VIII	β	II[1]	α	II[1]	β	II
3-Pyridyl-		β	I				β	I[1]		
4-Pyridyl-		β	I				β	I[1]		
2-Quinolyl-	IV	β	I	VIII	β	II[1]	α	II[1]		
2-Benzothiazolyl-	IV	β	I	VIII	β	II[1]	α	II[1]		
2-Benzoxazoyl-	IV	β	I							

[a] Minute yield, not quite pure.

Anal. Calcd. from $C_{11}H_{16}N_3O_2Cl$: N, 16.3. Found: N, 16.56.

1-Phenyl-3-amino-5-pyrazolone.[2]—Ethyl malonate monoimidoester (10 g.) was heated with 6.8 g. of phenylhydrazine on the steam-bath for three hours, the resulting mush was slurried with 20 ml. of methanol, cooled, and filtered; 5.5 g. (50%) of short tan needles formed, m. p. 215–216° dec.[8]

(8) Identified by mixed m. p.

Ethyl β-[β-(*p*-sulfamylphenyl)-hydrazino]-β-iminopropionate.—*p*-Sulfamylphenylhydrazine[9] (4.67 g.) and 4.02 g. of ethyl malonate monoimidoester in 25 ml. of dioxane was heated on the steam-bath for two hours, the solution cooled, and 100 ml. of ethyl ether added. The brown gum, which precipitated, crystallized from its solution in 20 ml. of alcohol, and was washed with alcohol and ether; it gave

(9) Crippa and Maffei, *Gazz. chim. ital.*, **72**, 97 (1942); *C. A.*, **37**, 618 (1943).

2.79 g. (27%), m. p. 167–169°. Recrystallized from ethanol, it gave tan crystals, m. p. 168–169°, the melt resolidifying almost immediately and then decomposing at about 200°.

Anal. Calcd. for $C_{11}H_{16}N_4O_4S$: N, 18.7. Found: N, 17.96.

1-(*p*-Sulfamylphenyl)-3-amino-5-pyrazolone.[1]—To a solution of sodium ethylate (0.3 g. of sodium in 10 ml. of absolute ethanol), was added 0.8 g. of ethyl β-[β-(*p*-sulfamylphenyl)-hydrazino]-β-iminopropionate and the mixture was heated to boiling. After cooling, 5 ml. of water was added and the resulting solution acidified with dilute hydrochloric acid; 0.37 g. (54%) of brown microneedles formed; m. p. 257–260° (dec.).[8]

***p*-Cyanophenylhydrazine.**—*p*-Aminobenzonitrile (50 g.)[10] suspended in 750 ml. of 10% hydrochloric acid was diazotized below 0° with 35 g. of sodium nitrite in 250 ml. of water. The solution was poured slowly, with stirring, into a solution of 250 g. of stannous chloride in 250 cc. of concentrated hydrochloric acid at −10°. After one-quarter of an hour, the heavy cream-colored tin complex was filtered off, suspended in 500 ml. of ice water, and 200 ml. of 40% sodium hydroxide added with stirring. The solid (30 g.), after filtering and washing with water, was recrystallized from 200 ml. of benzene; it gave 24 g. (43%) of orange crystals, m. p. 91–93°.

Anal. Calcd. for $C_7H_7N_3$: N, 31.6. Found: N, 31.46.

Ethyl β-[β-(*p*-Cyanophenyl)-hydrazino]-β-iminopropionate.—A mixture of 2.38 g. of *p*-cyanophenylhydrazine and 3.18 g. of ethyl malonate monoimidoester in 20 ml. of benzene was refluxed for one hour, cooled slowly, filtered, and recrystallized from *n*-butanol; 2.5 g. (51%) of brown microcrystals was formed, m. p. 147–150°; recrystallized from ethanol; light yellow microcrystals, m. p. 153–155°.

Anal. Calcd. for $C_{12}H_{14}N_4O_2$: C, 58.5; H, 5.70. Found: C, 58.64; H, 5.62.

1-(*p*-Cyanophenyl)-3-amino-5-pyrazolone.—To a solution of sodium ethylate (0.23 g. of sodium in 20 ml. of absolute ethanol) was added 2 g. of ethyl β-[β-(*p*-cyanophenyl)-hydrazino]-β-iminopropionate, and the mixture heated to boiling. After cooling, 20 ml. of water was added and the solution acidified with dilute hydrochloric acid; it gave 1.42 g. (93%) of brown crystals, m. p. 226–227° (dec.).

Anal. Calcd. for $C_{10}H_8N_4O$: C, 60.0; H, 4.00. Found: C, 60.24; H, 4.18.

1-*p*-Nitrophenyl-3-amino-5-pyrazolone.—A solution of 50 g. of ethyl malonate monoimidoester and 48 g. of *p*-nitrophenylhydrazine in 50 ml. of pyridine was heated on the steam-bath for two hours, 50 ml. of methanol was added, and the solution was cooled, filtered, and washed with 100 ml. of methanol; it gave 25 g. (36%) of orange powder, m. p. 248–250° (dec.). No solvent was found for satisfactory recrystallization.

Anal. Calcd. for $C_9H_8N_4O_3$: N, 25.4. Found: N, 24.81.

1-(2-Pyridyl)-3-amino-5-pyrazolone.—A mixture of 1.1 g. of 2-pyridylhydrazine,[6b] and 1.6 g. of ethyl malonate monoimidoester was heated on the steam-bath for two hours. A solution of sodium methylate (0.5 g. of sodium in 10 ml. of methanol) was then added and the solution refluxed for one hour, and concentrated to dryness; the residue was dissolved in 15 ml. of water and acidified with glacial acetic acid. The small tan precipitate was recrystallized three times from a large volume of 95% ethanol, to give a minute amount of fine, ivory crystals, m. p. 277–279°.

Anal. Calcd. for $C_8H_8N_4O$: C, 54.5; H, 4.55; N, 31.8. Found: C, 56.43; H, 4.16; N, 29.86.

1-(3-Pyridyl)-3-amino-5-pyrazolone.[1]—3-Pyridylhydrazine (2.18 g.)[11] and 3.18 g. of ethyl malonate monoimido ester in 25 ml. of benzene was refluxed for one hour. The dark brown solid, which separated, was filtered and washed with benzene; 0.37 g., m. p. 196–200° (dec.). Recrystallized from water; 0.1 g., m. p. 215–216° dec.[8]

1-(4-Pyridyl)-3-amino-5-pyrazolone.[1]—A mixture of 2.4 g. of 4-pyridylhydrazine hydrochloride[12] in sodium methylate solution (0.4 g. of sodium in 5 ml. of methanol) was refluxed for five minutes, 2.6 g. of ethyl malonate monoimidoester was added, and the solvent allowed to distill off and heating of the residual mixture continued for two hours. After cooling, it was triturated with 15 ml. of water, filtered, and recrystallized twice from 95% ethanol; it gave 0.5 g. (17%) of light yellow crystalline powder, sintered 234°, m. p. 238–239° (dec.).[8]

Ethyl β-[β-(2-Quinolyl)-hydrazino]-β-iminopropionate.—2-Quinolylhydrazine[13] (29.0 g.) and 31.8 g. of ethyl malonate monoimidoester in 125 ml. of benzene was refluxed for one hour on the steam-bath, let stand at room temperature for one hour, filtered, and washed with ether; it gave 38 g. (70%) of bright yellow crystals, m. p. 123–124°; recrystallized from benzene, m. p. 123–124°.

Anal. Calcd. for $C_{14}H_{16}N_4O_2$: N, 20.6. Found: N, 20.63.

1-(2-Quinolyl)-3-amino-5-pyrazolone.—To a solution of sodium ethylate (4.35 g. of sodium in 280 ml. of absolute ethanol) was added 93 g. of ethyl β-[β-(2-quinolyl)-hydrazino]-β-imiopropionate, and the mixture refluxed for half an hour. After cooling, a clear solution formed upon addition of 130 ml. of water, and acidification with glacial acetic acid gave 38 g. (86%) of light tan flakes, m. p. 196–197°; recrystallized from *n*-butanol, m. p. 196–197°.

Anal. Calcd. for $C_{12}H_{10}N_4O$: C, 63.7; H, 4.42; N, 24.8. Found: C, 63.36; H, 4.22; N, 24.56.

1-(2-Quinolyl)-3-benzoylamino-5-benzoyloxypyrazole.—To a suspension of 3 g. of 1-(2-quinolyl)-3-amino-5-pyrazolone in 16 ml. of dry pyridine was added dropwise, with stirring, 3.7 g. of benzoyl chloride, while cooling in a water bath at 30°. After the addition was complete, the mixture was warmed to 45° for one hour. It was then cooled to room temperature, 4 ml. of water added and crystallization induced by scratching, and the mixture cooled in an ice-bath. The filtered residue was washed with methanol and recrystallized from 16 ml. of 1:1 95% ethanol–pyridine, giving 2.05 g. (36%) of short white needles, m. p. 203–204°.

Anal. Calcd. for $C_{26}H_{18}N_4O_3$: N, 12.9. Found: N, 13.12.

1-(2-Quinolyl)-3-benzoylamino-5-pyrazolone.—To a solution of 2 g. of 1-(2-quinolyl)-3-benzoylamino-5-benzoyloxypyrazole in 8.5 ml. of dioxane, heated on the steam-bath, 0.4 g. of piperidine was added, drop by drop, with stirring. After heating for fifteen minutes, 5 ml. of hot water was added, and the mixture was cooled, and filtered, giving 1.45 g. (93%) of light yellow crystals, m. p. 186–187°. Recrystallized from glacial acetic acid, it gave bright yellow needles, m. p. 187–188°.

Anal. Calcd. for $C_{19}H_{14}N_4O_2$: N, 17.0. Found: N, 16.88.

Recrystallized from a 1–1.5–1:5 mixture of water, 95% ethanol, and pyridine, it gave fine ivory crystals, m. p. 187–188°.

Anal. Found: N, 16.69.

Ethyl β-[β-(2-Benzothiazolyl)-hydrazino]-β-iminopropionate.—An intimate mixture of 41 g. of powdered 2-benzothiazolylhydrazine[14] and 41 g. of ethyl malonate monoimidoester was heated on the steam-bath for three hours. The solid cake formed after partial melting was broken up in 50 ml. of ethyl ether, filtered, and washed with 50 ml. of 95% ethanol, yielding 61 g. (87%) of light yellow crystals, m. p. 178–180°; recrystallized from dioxane, it gave white needles, m. p. 181–182°.

Anal. Calcd. for $C_{12}H_{14}N_4O_2S$: C, 51.8; H, 5.03; N, 20.1. Found: C, 51.91; H, 4.81; N, 19.68.

1-(2-Benzothiazolyl)-3-amino-5-pyrazolone.—To a solution of sodium ethylate (2.3 g. of sodium in 50 ml. of abso-

(10) Bogert and Kohnstamm, THIS JOURNAL, **25**, 481 (1903).

(11) Räth, *Ann.* **486**, 95 (1931).

(12) Koenigs, Weiss and Zscharn, *Ber.*, **59**, 316 (1926). Methanol instead of ethanol was used for the recrystallization.

(13) Perkin and Robinson, *J. Chem. Soc.*, **103**, 1978 (1913).

(14) German Patent 614,327 (1935).

lute ethanol) was added 27.8 g. of finely powdered ethyl β-[β-(2-benzothiazolyl)-hydrazino]-β-iminopropionate. The mixture was refluxed for one hour, 30 ml. of hot water was added, and the hot solution was acidified with glacial acetic acid, cooled, and filtered; it gave 22.3 g. (96%) of tan microcrystals, m. p. 252–254°; recrystallized from dioxane, the m. p. was 254–256°.

Anal. Calcd. for $C_{10}H_8N_4OS$: C, 51.7; H, 3.45; N, 24.1. Found: C, 52.42; H, 3.84; N, 24.59.

1-(2-Benzothiazolyl)-3-benzoylamino-5-benzoyloxypyrazole.—To a suspension of 11.6 g. of 1-(2-benzothiazolyl)-3-amino-5-pyrazolone in 125 ml. of dry pyridine, heated on the steam-bath, was added, drop by drop with stirring, 15 g. of benzoyl chloride. The resulting solution was heated for one hour longer and allowed to cool to 40°, and after addition of 80 ml. of water, cooled in an ice-bath, and filtered. The crude product was recrystallized twice from a mixture of 100 ml. of 95% ethanol and 40 ml. of dioxane; it gave 6 g. (27%) of fine white needles, m. p. 202–203°.

Anal. Calcd. for $C_{24}H_{16}N_4O_3S$: N, 12.7. Found: N, 12.73.

1-(2-Benzothiazolyl)-3-benzoylamino-5-pyrazolone.—To a solution of 4.4 g. of 1-(2-benzothiazolyl)-3-benzoylamino-5-benzoyloxypyrazole in 10 ml. of dioxane on the steam-bath was added, drop by drop, 0.85 g. of piperidine. After heating for fifteen minutes, the solution was cooled, filtered, and the product (3 g., m. p. 220–222°) recrystallized from 40 ml. of glacial acetic acid gave 2.3 g. (68.5%), of ivory needles, m. p. 225–226° (dec.).

Anal. Calcd. for $C_{17}H_{12}N_4O_2S$: N, 16.7. Found: N, 16.70.

Ethyl β-[β-(2-Benzoxazolyl)-hydrazino]-β-iminopropionate.—2-Benzoxazolylhydrazine[14] (1.0 g.) and 1.5 g. of ethyl malonate monoimidoester in 5 ml. of benzene was refluxed for thirty minutes, cooled, filtered, and washed with benzene; the yield was 1.28 g. (72%), m. p. 120–121°; when recrystallized from 95% ethanol, it formed white crystals, m. p. 120–121°.

Anal. Calcd. for $C_{12}H_{14}N_4O_3$: N, 21.4. Found: N, 20.85.

1-(2-Benzoxazolyl)-3-amino-5-pyrazolone.—To a solution of sodium ethylate (0.13 g. of sodium in 10 ml. of absolute ethanol), was added 1.5 g. of ethyl β-[β-(2-benzoxazolyl)-hydrazino]-β-iminopropionate in 10 ml. of methanol. The mixture was warmed to 50° for two minutes. The sodium salt of the pyrazolone which began to separate was dissolved by adding 25 ml. of water, and the solution was acidified to litmus with dilute hydrochloric acid. The crystalline precipitate was filtered, and washed with water; the yield was 1.18 g. (96%), m. p. 220–221° dec.; recrystallized from *n*-propanol, it gave very fine white needles, m. p. 226–227° dec.

Anal. Calcd. for $C_{10}H_8N_4O_2$: C, 55.5; H, 3.70; N, 25.9. Found: C, 55.87; H, 3.79; N. 25.68.

1-(2-Pyridyl)-3-hydroxy-5-pyrazolone Anil.—To a solution of sodium methylate (1.1 g. of sodium in 15 ml. of methanol) was added 6.25 g. of ethyl acetoacetate and then 6.5 g. of phenyl isothiocyanate. After refluxing for half an hour, 5.5 g. of 2-pyridylhydrazine[6b] was added, and the mixture was refluxed for twenty-four hours. After cooling, the sodium salt of the product was precipitated by the addition of 10 ml. of water. This was dissolved in 25 ml. of methanol and upon acidification with glacial acetic acid, the product crystallized out; the yield was 2 g. (16%), m. p. 201–202°; recrystallized from absolute ethanol, it gave white microcrystals, m. p. 201–202°.

Anal. Calcd. for $C_{14}H_{12}N_4O$: C, 66.7; H, 4.76; N, 22.2. Found: C, 66.34; H, 4.57; N, 22.03.

Summary

1. Condensation of ethyl malonate monoimidoester with phenylhydrazine, substituted phenylhydrazines, the three pyridylhydrazines, 2-quinolylhydrazine, 2-benzothiazolylhydrazine and 2-benzoxazolylhydrazine produces the corresponding 3-amino-5-pyrazolones.

2. In some of the reactions, the intermediate ethyl β-hydrazino-β-iminopropionates were isolated.

3. Condensation of α-carbethoxyacetothioacetanilide with 2-pyridylhydrazine yields 1-(2-pyridyl)-3-hydroxy-5-anilinopyrazole.

4. The reactions of hydrazines with ethyl malonate monoimidoester, cyanoacetazide, ethyl cyanoacetate, and α-carbethoxyacetothioacetanilide are discussed with respect to the preferential reactivity of the hydrazines at the α or β nitrogen.

5. Mono and dibenzoyl derivatives of 1-(2-quinolyl)-3-amino-5-pyrazolone and of 1-(2-benzothiazolyl)-3-amino-5-pyrazolone were prepared.

6. 1-(2-Quinolyl)-3-amino-5-pyrazolone and 1-(2-quinolyl)-3-benzoylamino-5-pyrazolone exist in a colorless and in a yellow form. A 5-hydroxypyrazole structure, stabilized by chelation, is suggested for the yellow compounds.

7. Stabilization of a corresponding anilinopyrazole form appears to be responsible for the lack of dye formation observed with 1-(2-pyridyl)-3-hydroxy-5-pyrazolone anil.

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