

sharp rap against the side of the bottle was sufficient to break the bulb and release the liquid.

The table below contains the results of a series of determinations made with this method on samples of aliphatic mercaptans, and the last two columns contain, for comparison, figures by Klason and Carlson on the aromatic mercaptans. The extreme and average variations are also shown.

TABLE I.

No.	Methyl.	Ethyl.	Propyl.	<i>n</i> -Butyl.	<i>Sec.</i> Butyl.	<i>Iso</i> - butyl.	<i>Iso</i> - amyl.	Phenyl.	<i>p</i> -Cresol.	$\beta$ -Naph- thol.
1	100.03	98.69	98.79	99.69	98.33	98.55	71.27	99.21	99.89	100.35
2	100.21	98.57	98.55	99.57	98.47	98.35	71.11	99.01	100.22	100.18
3	100.03	98.73	98.79	99.56	98.44	98.48	71.51	99.19	99.89	100.00
4	100.18	98.50	98.50	99.57	98.44	98.46	71.44	98.90	100.22	100.47
5	100.07	98.52	98.82	99.73	98.55	98.64	71.33	98.94	100.01	99.64
6	....	...	...	...	...	...	...	...	99.77	99.48
Av.	100.10	98.60	98.69	99.62	98.44	98.50	71.33	99.05	100.00	100.06
Ex. var.	0.17	0.23	0.32	0.17	0.22	0.29	0.40	0.31	0.45	0.99
Av. var.	0.07	0.08	0.13	0.07	0.05	0.08	0.11	0.12	0.15	0.31

The fact that most of the analyses are a little low shows the difficulty of preparing mercaptans in perfectly pure condition. The methyl mercaptan may have contained traces of hydrogen sulfide, though it had been refractionated. The propyl, *iso*-amyl and phenyl mercaptans were imported preparations purchased a number of years ago. The *iso*-amyl mercaptan appears to have been purified by fractionation only. The other mercaptans had been prepared and purified with care in this laboratory at various times in the past. The butyl mercaptan had been purified with the greatest care.

The excellent agreement of the determinations among themselves establishes the method for aliphatic mercaptans and shows also that the water removes the hydriodic acid sufficiently from the disulfide layer to make the reaction quantitative.

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**THE REACTIONS OF THE FORMAMIDINES. IX. THE SYN-  
 THESIS OF 5-PHENYL-4-PYRAZOLE CARBOXYLIC ACID.**

By F. B. DAINS AND W. S. LONG.

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It has been shown in earlier papers that the amino-methylene derivatives of ethyl benzoylacetate, ethyl aceto-acetate, and acetyl acetone react with phenylhydrazine with the formation of substituted pyrazole derivatives.<sup>1</sup>

These syntheses gave a pyrazole with the carboxyl group in Position 4 and an alkyl group in Position 5 of the ring.

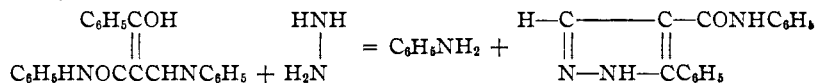
<sup>1</sup> THIS JOURNAL, 31, 1155 (1909); 38, 1516 (1916); 40, 563 (1918).

It seemed now of interest to ascertain whether the further application of this method would lead to the isolation of the unknown 5(3)-phenyl-4-pyrazole carboxylic acid, of which the other two possible isomers with unsubstituted nitrogen were known, *viz.*, 5-phenyl-3-pyrazole carboxylic acid (m. p. 233–4°)<sup>1</sup> and the 4-phenyl-5(3)-pyrazole carboxylic acid (m. p. 233–4°).<sup>2</sup>

### Experimental.

Seven g. of anilino-methylene-benzoyl-aceto-acetanilide,<sup>3</sup> 11.09 g. hydrazine sulfate, dry sodium carbonate (one equivalent) and 75 cc. of ethyl alcohol were boiled for 5 hours under a reflux condenser. The contents of the flask were then evaporated to dryness and the residue extracted with methyl alcohol.

Investigation showed that the reaction had proceeded as follows, with the loss of aniline and the formation of the anilide of 5-phenyl-4-pyrazole carboxylic acid, which melted at 182°.



The analysis and tests indicated that the new pyrazole had crystallized with one mol of methyl alcohol.

Calc. for  $\text{C}_{16}\text{H}_{15}\text{ON}_3\text{CH}_3\text{O}$ : N, 14.25. Found: 14.29, 14.34.

When heated at 120°, the alcohol was driven off.

Calc. for  $\text{C}_{16}\text{H}_{13}\text{ON}_3$ : N, 15.98. Found: 16.08, 16.15.

From ethyl alcohol, the anilide crystallized also with one mol of alcohol, as was shown by the fact that the air-dried sample lost, on heating at 120°, 14.69; the loss calculated for one mol of  $\text{C}_2\text{H}_6\text{O}$  was 14.88.

*Hydrochloride*.—The pyrazole formed in dry benzene an unstable hydrochloride.

**5-Phenyl-4-pyrazole Carboxylic Acid**.—When the anilide was boiled with conc. hydrochloric acid for several hours, aniline and the free acid were obtained. The acid was insoluble in ether, difficultly soluble in hot ethyl alcohol, and slightly soluble in boiling water, from which it crystallized in fine, white silky needles, which melted at 260°.

Calc. for  $\text{C}_{10}\text{H}_8\text{O}_2\text{N}_2$ : N, 14.90. Found: 15.15.

*Salts*.—Its properties as an acid were further confirmed by the preparation and analysis of the silver, copper and barium salts.

**Ethyl Ester, 5-Phenyl-4-carbethoxy-pyrazole**.—This was prepared by the action of hydrazine on the ethyl-*o*-phenetidyl-amino-methylene-benzoyl acetate.<sup>4</sup> Crystallized from dil. alcohol, it formed white needles

<sup>1</sup> *Ber.*, **35**, 36 (1902); **37**, 2204 (1904).

<sup>2</sup> *Ibid.*, **28**, 700 (1895); **33**, 3596 (1900); *Gazz. chim. ital.*, **36**, (2) 55 (1906).

<sup>3</sup> Rugeburg, *Diss.*, Freiburg (1904).

<sup>4</sup> THIS JOURNAL, **38**, 1516 (1916).

which melted at 85–6° and, on hydrolysis, gave the corresponding acid (m. p. 260°).

Calc. for  $C_{12}H_{12}O_2N_2$ : N, 12.97. Found: 13.00.

The ester was unreactive. It did not form a hydrochloride, an acetyl or benzoyl derivative, nor did it add methyl iodide.

**5(3)-Phenyl-pyrazole.**—Further proof of the constitution of the acid and the position of the phenyl group was afforded by the fact that when the acid was heated between 260–70°, carbon dioxide was lost. From the oily residue there was isolated the 5-phenyl-pyrazole which melted at 78°.<sup>1</sup>

Calc. for  $C_8H_8N_2$ : N, 19.52. Found: 19.75, 19.77.

**Action of Aniline.**—The free acid or its ethyl ester failed to react with aniline, even though heated for several hours at 200°. The same remarkable stability had been noted in the case of the corresponding 5-methyl-4-pyrazole carboxylic acid and its ester.<sup>2</sup>

There would seem to be some relationship between this fact and the ease of hydrolysis for, while the anilides of the 5-phenyl-4-carboxylic acids are hydrolyzed only with difficulty, the efforts to decompose the corresponding derivatives of 5-methyl-4-pyrazole carboxylic acid and of 1,5-diphenyl-4-carboxylic acids have met with no success.

The *p*-Anisidide of 5-Phenyl-4-pyrazole Carboxylic Acid was synthesized from hydrazine and *p*-anisidyl-amino-methylene-benzoyl acet-*p*-anisidide. It crystallized from dil. alcohol in long needles, which melted at 161° and on hydrolysis gave the acid (m. p. 260°)

Calc. for  $C_{17}H_{16}O_2N_3$ : N, 14.34. Found: 14.57.

The *o*-Anisidide of 5-Phenyl-4-pyrazole Carboxylic Acid was obtained in an analogous manner.

Calc. for  $C_{17}H_{16}O_2N_3$ : N, 14.34. Found: 14.67.

It was readily soluble in organic solvents and melted at 127°.

The compound is more stable than the *p*-anisidide. Hydrolysis to the acid could be effected only by boiling with conc. hydrobromic acid.

#### Summary.

5-Phenyl-4-pyrazole carboxylic acid and several of its derivatives have been synthesized and their properties and reactions noted

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<sup>1</sup> *Ann.*, 279, 254 (1894).

<sup>2</sup> THIS JOURNAL, 40, 565 (1918).