with the addition of boron fluoride and in nearly every case a spontaneous reaction took place which marked the end of the rearrangement. If the rearrangement was incomplete after the addition of boron fluoride, the mixture was refluxed from one-half to three-quarters of an hour. The purification was the same except that 15% potassium hydroxide was used.

**Preparation of Phenoxyacetic Acid Derivative.**—This preparation was described by Koelsch.<sup>13</sup> He used an alkaline solution and chloroacetic acid, then extracted the phenoxyacetic acid derivative with ether. During this work the ether extraction was eliminated, since it seemed to be unnecessary for the compounds prepared.

Conductivity Measurements.—The usual Kohlrausch assembly was used for conductivity measurements. The phenol had a specific conductivity of  $72.30 \times 10^{-8}$ .

## Summary

The synthesis of the possible substituted phenols and phenyl alkyl ethers up to and including the trialkylphenyl isopropyl ethers has been accomplished by the rearrangement of the isopropyl phenyl or cresyl ether and by the condensation of propylene with phenol or cresol.

Intra- and inter-molecular rearrangements have been shown to take place in the same reaction.

The direct nuclear condensation of propylene with alkyl phenyl ethers has been shown experimentally to be a probable step in condensation reactions.

The conductivities for the system phenol-boron fluoride have been determined.

(13) Koelsch, This Journal, **53**, 304 (1931). Notre Dame, Indiana

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## The p-Xylylmethylpyrazolones and Some Derivatives

By RALPH C. HUSTON, HAROLD M. SELL AND HARLOW R. BRIGHAM

In a study of the p-xylylpyrazolones, the compounds listed in the table have been prepared from p-xylylhydrazine and its acetyl derivative.

The hydrazine was prepared in 68% yield by the method of Demonbreun and Kremer,<sup>1</sup> so modified that exact molecular quantities of reagents were used and the temperature was not allowed to rise above  $-5^{\circ}$  during either the diazotization or the reduction. It boiled at  $120^{\circ}$  (4 mm.) and melted<sup>2</sup> at  $76-77^{\circ}$ .

Acylation of the hydrazine was accomplished by refluxing with glacial acetic acid. When recrystallized from water, N'-acetyl-N-(2,5-dimethyl-phenyl)-hydrazine melted<sup>3</sup> at 104–106°.

Condensation of *p*-xylylhydrazine with ethyl acetoacetate gave 1-*p*-

<sup>(1)</sup> Demonbreun and Kremer, J. Am. Pharm. Assn., 12, 589 (1923).

<sup>(2)</sup> Willgerodt and Lindenberg, J. prakt. Chem., [2] 71, 389 (1905).

<sup>(3)</sup> Willgerodt and Lindenberg, ibid., [2] 71, 408 (1905), give 196° as the melting point.

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xylyl-3-methyl-5-pyrazolone melting at  $164^{\circ}$  together with a small amount<sup>4</sup> of a compound, more soluble in alcohol, melting at  $150-151^{\circ}$ , which showed the same percentage composition but which did not give the pyrazole blue test. It is suggested that this low melting derivative may be the imine<sup>5</sup> form of pyrazolone formed by a reaction of the hydrazine with the enol form of acetoacetic ester.

		М.р.,	Nitrogen, %		
Compound	Crystalline structure	°C.	Calcd.	alcd. Found	
1-p-Xylyl-3-methyl-5-pyrazolone <sup>6</sup>	Needles from alcohol or high test gasoline	164	13.86	13.92	14.05
1-p-Xylyl-2,3-dimethyl-5-pyrazolone <sup>7</sup> (p-xylylantipyrine)	Lustrous plates from high test gasoline	97.5	12.96	13.02	13.22
1 - p - Xylyl - 3 - methyl - 5 - benzoyl - 5-pyrazolone <sup>8</sup>	Colorless needles from alcohol or pet. ether	119	9.15	9.25	9.23
N - Acetyl - N(2,5 - dimethylphenyl) - hydrazine	Leaflets from water	104-106	15.72	15.55	
1-p-Xylyl-5-methyl-3-pyrazolone <sup>9</sup>	Cream-colored plates from alcohol or ligroin	180181	13.86	13.77	13.61
1 - p - Xylyl - 3 - benzoyl - 5 - methyl - 3-pyrazolone <sup>8</sup>	Cream-colored rhom- boids from ligroin	74	9.15	9.17	9.22

(4) In some earlier runs this compound was the only product isolated.

(5) Knorr, Ber., 28, 706 (1895).

(6) Prepared by method of Knorr, *Ber.*, **16**, 2597 (1883). Heated for eight hours at  $150-160^{\circ}$ . A concentrated alcoholic solution of the crude product was boiled with an excess of high test gasoline until solution was complete and then cooled.

(7) Prepared by method of Knorr, Ber., 17, 550, 2037 (1884). Heated for eight hours at  $130^{\circ}$ .

(8) From pyrazolone, benzoyl chloride and pyridine.

(9) Prepared by the method of Michaelis, Ann., 238, 310 (1887).

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## Decomposition of Polyuronides by Fungi and Bacteria. I. Decomposition of Pectin and Pectic Acid by Fungi and Formation of Pectolytic Enzymes<sup>1</sup>

By Selman A. Waksman and Melvin C. Allen

Polyuronides or uronic acid containing complexes are synthesized extensively by higher and lower plants. When the residues of these plants undergo decomposition in the soil, in composts or in the sea, the various carbohydrates, including the polyuronides, are readily decomposed by numerous fungi and bacteria; the rate and nature of the decomposition is not always the same, however. Some of these compounds are utilized by a great variety of microörganisms, while others are highly specific in nature and can be acted upon only by certain limited groups of fungi or bacteria.

Among the various polyuronides so far described, including the polymers of a single uronic acid and combinations of uronic acids with hexose and

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<sup>(1)</sup> Journal Series paper of the New Jersey Agricultural Experiment Station, Department of Soil Microbiology.