

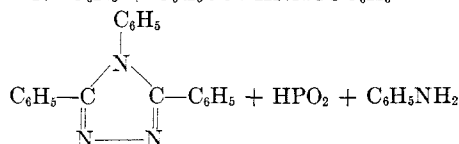
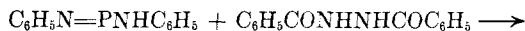
### Preparation of Triaryl-s-triazoles from Diaroylhydrazines<sup>1</sup>

ERWIN KLINGSBERG

Received February 6, 1958

Although the formation of 3,4,5-triaryl-s-triazoles from diaroylhydrazines and primary amines is a well-known "textbook" reaction, it has been little used and its preparative value is dubious. Busch,<sup>2</sup> for example, recommends phosphorus pentoxide as a catalyst, but in our hands this gave only a 20-30% yield of partially purified triphenyl-triazole. Bhagat and Rây<sup>3</sup> prepared several triaryl-triazoles by fusing dibenzoylhydrazine with the amine in the presence of zinc chloride, but they give no yield data, and the reaction does not seem to have been investigated since.

In the search for a good way to carry out this reaction, it seemed that phenylphosphazoanilide might be suitable. Grimmel, Guenther, and Morgan<sup>4</sup>



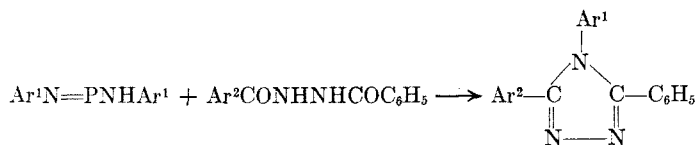
It was in fact found that phenylphosphazoanilide can be prepared in *o*-dichlorobenzene and used *in situ* at reflux to convert *N,N'*-dibenzoylhydrazine to a good yield of the desired triazole.

The scope of the reaction was then explored in a series of experiments, and it appears to be fairly general within certain limits.

All experiments were carried out on a 0.010 mole scale by the general procedure described below. No experiment was repeated. It will be seen that 85-95% yields of product were obtained from dibenzoylhydrazine and the phosphazo derivatives of aniline, *p*-toluidine, *m*-toluidine, and *p*-chloroaniline. *o*-Toluidine and 2-naphthylamine gave distinctly inferior results, although there was no difficulty in obtaining the triazole. *N*-Benzoyl-

TABLE I

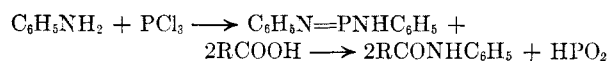
ARYLPHOSPHAZOARYLIDE TRIAZOLE SYNTHESIS



Ar <sup>1</sup> =	Ar <sup>2</sup> =	Crude Product		Pure Product M.P.	Literature M.P.
		M.P.	Yield		
C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	299.5°-300.5°	95%	299-300 <sup>a</sup>	292° <sup>2,5</sup>
<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	301-2°	88%	301-302 <sup>b</sup>	296-7° <sup>3</sup>
<i>o</i> -MeC <sub>6</sub> H <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	159-179°	72%	191-192 <sup>c</sup>	184° <sup>5</sup>
<i>m</i> -MeC <sub>6</sub> H <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	254.5°-255.5°	83%	256-257°	250° <sup>3</sup>
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	260.5°-262°	88%	261.5-262°	New cpd. <sup>d</sup>
C <sub>6</sub> H <sub>5</sub>	4-pyridyl <sup>i</sup>	262-8°	95%	268-269° <sup>e</sup>	New cpd. <sup>f</sup>
2-C <sub>10</sub> H <sub>7</sub>	C <sub>6</sub> H <sub>5</sub>	252-6°	52%	275.5-276.5° <sup>g</sup>	New cpd. <sup>h</sup>

<sup>a</sup> Anal. Calcd. for C<sub>20</sub>H<sub>15</sub>N<sub>3</sub>: C, 80.9; H, 5.1; N, 14.1. Found: C, 80.8; H, 5.2; N, 14.4. <sup>b</sup> Anal. Calcd. for C<sub>21</sub>H<sub>17</sub>N<sub>3</sub>: C, 81.1; H, 5.5; N, 13.5. Found: C, 81.0; H, 5.5; N, 13.3. <sup>c</sup> Crystallized from dil. acetic acid followed by methylenecyclohexane. <sup>d</sup> Anal. Calcd. for C<sub>20</sub>H<sub>14</sub>N<sub>3</sub>Cl: C, 72.3; H, 4.2; N, 12.7; Cl, 10.7. Found: C, 72.3; H, 4.0; N, 12.5; Cl, 10.3. <sup>e</sup> Crystallized from xylene. <sup>f</sup> Anal. Calcd. for C<sub>15</sub>H<sub>14</sub>N<sub>4</sub>: C, 76.5; H, 4.7; N, 18.8. Found: C, 76.6; H, 5.0; N, 18.7. <sup>g</sup> Crystallized from dil. acetic acid followed by xylene. <sup>h</sup> Anal. Calcd. for C<sub>24</sub>H<sub>17</sub>N<sub>3</sub>: C, 83.0; H, 4.9; N, 12.1. Found: C, 83.1; H, 4.6; N, 12.0. <sup>i</sup> *N*-benzoyl-*N'*-isonicotinoylhydrazine, m.p. 226.5-228.5°, prepared according to U.S. Patent 2,689,852.

have reported that this substance, which is readily prepared from phosphorus trichloride and aniline, converts acids to their anilides:



A reaction with dibenzoylhydrazine can be formulated as follows:

(1) Presented at the ACS Meeting-in-Miniature of the North Jersey Section at Seton Hall University on January 27, 1958.

(2) M. Busch, *J. Prakt. Chem.*, **89**, 552 (1914).

(3) K. L. Bhagat and J. N. Rây, *J. Chem. Soc.*, 2357 (1930).

(4) H. W. Grimmel, A. Guenther, and J. F. Morgan, *J. Am. Chem. Soc.*, **68**, 539 (1946).

*N'*-isonicotinoylhydrazine and aniline gave excellent results.

A limitation on the reaction is its apparent inapplicability to triazoles with aliphatic substituents. Thus no product was obtained from *N*-acetyl-*N'*-benzoylhydrazine and aniline, while dibenzoylhydrazine and cyclohexylamine gave diphenyloxadiazole.

## EXPERIMENTAL

*General procedure.* To a solution or suspension of 0.060 mole of the amine in 20-30 ml. of *o*-dichlorobenzene was slowly added, with shaking, 0.96 ml. (1.51 g.; 0.011 mole) of

(5) R. Stollé, *J. Prakt. Chem.*, **73**, 288 (1906).

phosphorus trichloride. Reaction was immediate, and could be completed by gentle warming on the steam bath for a few moments.

After the addition of 0.010 mole of the diacylhydrazine, the mixture was stirred and refluxed for 3 hr. in an oil bath at 190–200°. Efficient stirring is desirable. In an occasional experiment, trace amounts of byproducts were found to undergo spontaneous ignition in the condenser. This does no harm on the 0.010 mole scale, but can be prevented by operating in a nitrogen atmosphere. After cooling, the product was collected and digested in hot water or dilute hydrochloric acid. It was purified by crystallization from glacial or dilute acetic acid.

*Acknowledgments.* The author wishes to express his gratitude to Eugene R. Klim for technical assistance and to Oliver E. Sundberg and his staff for microanalyses.

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## 1-Phenylpropyne

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*Received March 24, 1958*

1-Phenylpropyne,  $C_6H_5C\equiv CCH_3$ , has been synthesized in a number of ways including (a) methylation of phenylacetylene with methyl iodide,<sup>1</sup> methyl sulfate,<sup>2</sup> or methyl toluenesulfonate,<sup>3</sup> (b) dehydrobromination of 2-bromo-1(or -3)-phenylpropene by fused<sup>4</sup> or alcoholic<sup>5</sup> potassium hydroxide, or by

(1) J. U. Nef, *Ann.*, **310**, 333 (1900).

(2) M. Bourguet, *Compt. rend.*, **186**, 1212 (1928).

(3) R. Truchet, *Ann. chim.*, [10] **16**, 309 (1931).

(4) M. Tiffeneau, *Compt. rend.*, **135**, 1347 (1902); *Ann. chim.*, [8] **10**, 169 (1907).

(5) R. Lespieau and Garreau, *Compt. rend.*, **171**, 112 (1920); R. Lespieau, *Bull. soc. chim.*, [4] **29**, 533 (1921); M. Bourguet, *Ann. chim.*, [10] **3**, 350 (1925).

magnesium<sup>6</sup> in ether, and (c) an approach<sup>7</sup> from benzaldehyde and methyl ethyl ketone involving steps of condensation, oxidation, bromination, and dehydrobromination.

It seemed to us that dehydrochlorination of 2-chloro-1(or -3)-phenylpropene offered possibilities of a better synthesis. Zaki and Iskander<sup>8</sup> prepared this equilibrium mixture of chlorides by treating phenylacetone with phosphorus pentachloride in hot benzene solution, then distilling the product and washing it with ice water.

We found that benzene (solvent) could be omitted with no loss of yield. The reactants (110 g. of phenylacetone and 208 g. of phosphorus pentachloride) were mixed directly and heated for an hour at 100°. Then the phosphoryl chloride was distilled off under diminished pressure and the two desired chlorides in the residue were collected by distillation 105–125° (25 mm.); the yield was 110 g. (88%), which is the same as that reported by Zaki and Iskander.

The 110 g. of product was refluxed for 3 hr. with 55 g. of sodium hydroxide pellets in 120 ml. of absolute ethyl alcohol. Decomposition with water, extraction with benzene, drying, and distillation yielded 70 g. of 1-phenylpropyne boiling at 90° and 20 mm. This represents an 84% yield based on the last step, or a 74% yield based on the phenylacetone.

In another similar run, 164 g. of 1-phenylpropyne (88% yield) was obtained from 245 g. of the mixture of 2-chloro-1-phenylpropene and 2-chloro-3-phenylpropene.

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(6) C. D. Hurd and C. N. Webb, *J. Am. Chem. Soc.*, **49**, 557 (1927).

(7) M. T. Bogert and D. Davidson, *J. Am. Chem. Soc.*, **54**, 334 (1932).

(8) A. Zaki and Y. Iskander, *J. Chem. Soc.*, 68 (1943).