Similarly 1-p-chlorophenyl-5-m-nitrophenylpenta-1,4-dien-3one was prepared in 67% yield, m.p. 160°.

Anal. Calcd. for C<sub>17</sub>H<sub>12</sub>NO<sub>3</sub>Cl: C, 65.00; H, 3.82. Found: C, 65.31; H, 4.05.

The infrared spectrum was in accord with the assigned structure

Preparation of *p*-Acetamidocinnamoylmethylenetriphenylphosphorane (III).-A mixture of 2.24 g. (0.02 mole) of potassium t-butoxide, 5.89 g. (0.01 mole) of I, and 40 ml. of dimethyl sulfoxide was stirred under nitrogen at 40° for 2 hr. There was added 3.60 g. (0.022 mole) of *p*-acetamidebenzaldehyde in 13 ml. of dimethyl sulfoxide. The mixture was heated at ca. 46° for 8 hr. After cooling, the precipitate was collected to give 3.0 g. of material, m.p. 269-271. Titration with perchloric acid gave equiv. wt., 487; calculated for III, 476.11 Two crystallizations from acetic acid gave material, m.p. 273-274°. Anal. Calcd. for C<sub>30</sub>H<sub>26</sub>O<sub>2</sub>NP: C, 77.75; H, 5.62; N, 3.10.

Found: C, 77.32; H, 5.86; N, 2.98.

The infrared spectrum had N-H and amide carbonyl absorptions. The material gave a positive test for phosphorus.<sup>12</sup>

(11) S. T. Ross and D. B. Denney, Anal. Chem., 32, 1896 (1960). (12) A Vogel, "A Textbook of Practical Organic Chemistry," 3rd Ed., Longmans Green and Co., London, 1957, p. 1043.

# The Cyclization of N-Phenylcinnamamides to 3,4-Dihydro-4-phenylcarbostyrils with **Polyphosphoric Acid**<sup>1</sup>

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Recently, Koo<sup>2</sup> has reported the cyclization of 3anilinopropionic acids to 4-keto-1,2,3,4-tetrahydroquinolines using polyphosphoric acid. A convenient preparation of 2-keto-1,2,3,4-tetrahydroquinolines (3,4dihydrocarbostyrils) was observed by us sometime ago in the preparation of a series of substituted materials for pharmacological evaluation. The procedure reported here is analogous to the cyclization of 3halopropionanilides<sup>3</sup> to 3,4-dihydrocarbostyrils in which typical Friedel-Crafts conditions using aluminum chloride were employed.



phenylcinnamamides were prepared. It was found that the amides could readily be cyclized with polyphosphoric acid to 3,4-dihydro-4-phenyl-6-substituted carbostvrils. N-(p-Nitrophenyl)cinnamamide could not be cyclized in polyphosphoric acid at reaction temperatures as high as  $180^{\circ}$ . In this case, the starting amide was recovered almost quantitatively. The parent amide and the *p*-substituted amides were prepared in benzene solution by reacting cinnamoyl chloride with the desired aniline derivative. The cyclization procedure described in the Experimental was typical and appears quite general for amides which do not have strong electron-deactivating groups on the aromatic ring. The structure of the lactams was confirmed in each case by examination of the infrared spectral characteristics, namely, by the absence of the  $\alpha,\beta$ -unsaturated linkages in conjugation with the amide carbonyl and the amide II linkage of secondary amides which is generally absent in lactams. In the case of the known parent compound of the series, 3,4-dihydro-4-phenylcarbostyril, identity was established by both its characteristic spectrum and mixture melting point determination. The yields and physical properties of the substituted dihydrocarbostyrils are summarized in Table I.

It also should be noted that both N-phenylcrotonamide and N-(*p*-methoxyphenyl)crotonamide could not be cyclized to the 3,4-dihydro-4-methylcarbostyrils by this technique, thus presently limiting the synthetic applicability of this method to 4-phenyl-substituted

R	Yield, %	M.p., °C.	Calcd			Found		
			С	Н	N	С	н	N
Н	<b>94</b>	177-178 <sup>a</sup>						
Br	83	188 - 190	59.62	4.00	4.63	59.40	3.79	4.5
CH₃	83	164 - 165	80.98	6.37	5.90	81.22	6.51	5.9
OCH3	90	110-111	75.86	5.96	5.53	75.84	5.72	5.2

TABLE I SUMMARY OF N-PHENYL-a, &-UNSATURATED AMIDE CYCLIZATIONS

<sup>a</sup> Ref. 4 reports 177-178°.

It was reasoned that N-phenylcinnamamide (I) should readily protonate in hot polyphosphoric acid to give an intermediate (II) capable of undergoing a Friedel-Crafts cyclization to 3,4-dihydro-4-phenylcarbostyril (III). In an effort to confirm this proposal and to evaluate the synthetic value and general applicability of the reaction, a series of N-(4-substituted)

(1) This work was supported by the Division of Neurological Disease and Blindness, National Institutes of Health under Grant No. NB-03628. (2) J. Koo, J. Org. Chem., 28, 1134 (1963).

(3) F. Mayer, L. van Zutphen, and M. Philipps, Ber., 60, 858 (1927).

carbostyrils. Apparently this failure is due to the instability of the intermediate alkyl carbonium ion.

#### Experimental

All melting points are corrected. The infrared comparisons were determined on the solid samples in potassium bromide wafers using a Beckman IR-5A infrared spectrophotometer.

3,4-Dihydro-4-phenylcarbostyril.--A mixture of 1.00 g. of Nphenylcinnamamide and 20 g. of polyphosphoric acid was heated to 120°. After 10 min., the reaction mixture was cooled and hydrolyzed over crushed ice. The reaction products were extracted with three 125-ml. portions of chloroform. The extracts were combined, dried over anhydrous magnesium sulfate, filtered, and evaporated to yield, after two recrystallizations from ethanol-water, 0.94 g. (94%) of 3,4-dihydro-4-phenylcarbostyril, m.p. 177-178°, lit.<sup>4</sup> m.p. 177-178°.

(4) E. F. M. Stephenson, J. Chem. Soc., 2557 (1956).

## Dicyanomethylene-1,3-dithietane

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Dicyanomethylene-1,3-dithietane (I) is akin to the desaurins  $(II)^1$  but differs from them in having only one exocyclic methylene group and in being much more reactive.



This new dithietane is prepared in yields of 65%from dipotassio-1,1-dimercapto-2,2-dicyanoethylene and excess diiodomethane in refluxing acetonitrile. These conditions are similar to those used in the preparation of simple dialkyl derivatives.<sup>2</sup> The dithietane must be handled with great care because it causes severe itching and skin lesions.

$$(NC)_2C = C(SK)_2 + CH_2I_2 \xrightarrow{CH_2CN} (NC)_2C = C \xrightarrow{S} CH_2 + 2KI$$

Conceivably, the methylene hydrogens of I might be acidic, especially since a  $6-\pi$ -electron system could result on loss of a proton. In accordance with this hypothesis, a nearly quantitative yield of hydrogen is obtained when I reacts with sodium hydride in dimethoxyethane; however, dithietane was not recovered upon acidification. A stable sodium salt could not be isolated nor could any alkylation products be observed under these conditions. No deuterium exchange occurred when dithietane was heated in refluxing deuterium oxide. It appears that the anion of I forms only with strong base and, if it possesses unusual stability,<sup>3</sup> it is at the same time very reactive.

**Ring-Opening with Pyridine.**—The ring itself proved to be remarkably labile, being opened by nucleophilic reagents.<sup>4</sup> When the dithietane in hot benzene is treated with pyridine, the initially clear solution rapidly

(4) Cyclic acetals of dicyanoketene are attacked by nucleophilic reagents to give ring-opened products: W. J. Middleton and V. A. Engelhardt, J. Am. Chem. Soc., **80**, 2788 (1958).

Notes

$$(NC)_{2}C = C \xrightarrow{S} CH_{2} + C_{5}H_{5}N \xrightarrow{(NC)_{2}C} = C - S - CH_{2} - N \xrightarrow{+} N$$

becomes turbid, and a pyridinium zwitterion is obtained in 80% yield.

Elemental analysis, molecular weight, proton magnetic resonance, and ultraviolet spectral data were in agreement with the zwitterion structure. The ultraviolet spectrum of the pyridinium zwitterion,  $\lambda_{\text{max}}$  338 m $\mu$  ( $\epsilon$  19,300) and 263 (9860), compares favorably with that of tetraethylammonium 2,2-dicyano-1-ethylthioethylene-1-thiolate,  $\lambda_{\text{max}}$  342 m $\mu$  ( $\epsilon$  21,800) and 285 (10,000), prepared by the pyrolysis of bis(tetraethylammonium) 2,2-dicyanoethylene-1,1-dithiolate.

Treatment of the pyridinium zwitterion with methyl *p*-toluenesulfonate gave an S-methyl derivative whose ultraviolet spectrum is virtually identical with that of

$$(NC)_{2}C = C - SCH_{2}N + C_{7}H_{7}SO_{3}CH_{3} \rightarrow$$

$$SCH_{3}$$

$$(NC)_{2}C = CSCH_{2}N + C_{7}H_{7}SO_{3}^{-}$$

1,1-dicyano-2,2-bis(methylthio)ethylene when allowance is made for the pyridinium and p-toluenesulfonate absorptions.

**Ring-Opening with Triphenylphosphine.**—Triphenylphosphine does not remove sulfur from the dithietane ring as it does readily with episulfides<sup>6</sup> and slowly with thietanes.<sup>6</sup> The reaction of I with triphenylphosphine opens the dithietane ring to give a phosphonium zwitterion. No reaction was observed with the weaker nucleophile triphenylarsine. Elemental analysis, molecular weight determination, and spectral data again supported the zwitterionic structure.



#### Experimental

**Dipotassio-1,1-dimercapto-2,2-dicyanoethylene** was prepared from carbon disulfide, malononitrile, and 2 moles of potassium hydroxide.<sup>7</sup> The salt was prepared earlier by Kendall and Edwards but was not isolated.<sup>2</sup>

Bis(tetraethylammonium) 2,2-Dicyanoethylene-1,1-dithiolate. —Dipotassio-1,1-dimercapto-2,2-dicyanoethylene (56 g., 0.26 mole) was dissolved in 290 ml. of methanol. Tetraethylammonium chloride (100 g., 0.6 mole) in 135 ml. of methanol was added. The reaction mixture was stirred for 15 min. and filtered to remove 31 g. of potassium chloride. The filtrate was evaporated on a rotary evaporator, and the yellow solid which remained was dried in a vacuum oven at 50° (18 mm.). The crude tetraethyl-

(7) W. R. Hatchard, to be published.

P. Yates and D. R. Moore, J. Am. Chem. Soc., 80, 5577 (1958), references cited therein; A. Schönberg, L. Vargha, and H. Kaltschmitt, Ber., 64, 2581 (1931); A. Schönberg, A. Stephenson, H. Kaltschmitt, E. Petersen, and H. Schulten, *ibid.*, 66, 243 (1933).

<sup>(2)</sup> H. D. Edwards and J. D. Kendall, U. S. Patents 2,533,233 and 2,493.071 (1950).

<sup>(3)</sup> The methylene protons in the diethylmercaptal of formaldehyde are acidic enough to give an anion which can be alkylated: J. F. Arens, M. Fröhling, and A. Fröhling, *Rec. trav. chim.*, **78**, 663 (1959).

<sup>(5)</sup> R. E. Davis, J. Org. Chem., 23, 1767 (1958); C. C. J. Culvenor, W. Davies, and N. S. Heath, J. Chem. Soc., 282 (1949).

<sup>(6)</sup> S. M. Kotin, Ph.D. thesis, University of Pennsylvania, 1963.