The yields of pyridine, when phenyl(trichloromethyl)-mercury was employed as the carbene precursor, were from 63% (based on the carbene precursor when its mole ratio to pyridine N-oxide was 1:3) to 25% (when the ratio was 1:1). When methyl trichloroacetate[7] was used as the carbene precursor the yields of pyridine were 40%, 28%, and 18% (when the haloacetate to pyridine ratios were 3:1, 2:1, and 1:1, respectively). The reaction of potassium *t*-butoxide and chloroform with pyridine N-oxide gave trace amounts of pyridine.

The usefulness of pyridine N-oxide and dimethyl sulfoxide as oxygen-donating species with a number of nonhalocarbenes[6] is being explored also.

Experimental

Materials.—Powdered sodium methoxide[8] and potassium *t*-butoxide[9] are always transferred in a drybox under an atmosphere of dry nitrogen. The methyl trichloroacetate[10] was prepared according to Dumas, b.p. 151° (atmospheric pressure), and pyridine N-oxide,[11] b.p. 120° (3 mm.), was distilled prior to use.

Phenyl(trichloromethyl)mercury as Carbene Precursor.—Phenyl(trichloromethyl)mercury[12] (17.5 g.), pyridine N-oxide (12.7 g.), and 100 ml. of anhydrous thiophene-free benzene were refluxed with stirring for 44 hr. The benzene was distilled, b.p. to 110°, and treated with a saturated solution of picric acid in benzene. The pyridine picrate (3.12 g., 23%) was recovered (melting point and mixture melting point were identical with an authentic sample).

The residue remaining after the benzene was distilled was concentrated to dryness. This second distillate was extracted with three 5-ml. portions of 10% hydrochloric acid and the combined extracts were made strongly basic with potassium hydroxide pellets while cooling. The basic solution was then extracted with ether, dried (potassium hydroxide), and distilled. Pyridine (1.41 g., 40%) was collected, b.p. 114°. Its infrared spectrum and picrate were identical with an authentic sample. Therefore, a total yield of 63% of pyridine was obtained. The yields of pyridine in all the other experiments mentioned were determined as shown in the following procedure.

Methyltrichloroacetate as Carbene Precursor.—Sodium methoxide (17.6 g.) was added slowly from an enclosed erlenmeyer flask through a flexible tubing to a cold (10–15°) solution of methyl trichloroacetate (18.5 g.) and pyridine N-oxide (49.5 g.) in 250 ml. of anhydrous, thiophene-free benzene. The mixture was stirred at ice–water bath temperature for 1 hr. after completion of the base addition. The mixture was transferred to a rotary evaporator and evaporated to dryness at water aspirator pressure and a temperature not exceeding 65°. The distillate was collected in two Dry Ice–acetone traps. An aliquot (3.0025 g.) of the benzene distillate (166.1 g. recovered) was treated with a saturated solution of picric acid in benzene. The resulting dried pyridine picrate (melting point and mixture melting point checked with an authentic sample) weighed 0.229 g. and represented 1.96% by weight of the aliquot. Therefore, the pyridine obtained was calculated to be 3.25 g. (40% yield). A similar solution of the pyridine N-oxide used was treated in the same manner employed for the work-up described previously and the benzene concentrate was shown to give no picrate of either pyridine or pyridine N-oxide.

Chloroform as the Carbene Precursor.—Sodium methoxide (17.6 g.), chloroform (12.3 g.), and pyridine N-oxide (49.5 g.) were allowed to react in benzene (250 ml.) solution as described previously. The work-up procedure was identical with that used in the preceding experiment and the calculated yield of pyridine was 17%. The gas chromatogram of the benzene concentrate showed a peak for dimethyl carbonate; peak enhancement also was observed when an authentic sample of carbonate was introduced with the benzene concentrate. The infrared spectrum of the benzene layer contained all the characteristic carbonate peaks of particular interest are the peaks at 790 cm.$^{-1}$ and 1265 cm.$^{-1}$, which are not found in the spectrum of methyl orthoformate, indicating that the carbonate was obtained.

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[7] The ratio of sodium methoxide to methyl trichloroacetate was always 3:1 in order to absorb the phosgene proposed as an intermediate in the reaction.

[8] The Matheson Co., Inc., East Rutherford, N. J.

[9] MSA Research Corp., Callery, Pa.

[10] J. Dumas, *Ann. Chem.*, **32**, 111 (1839).

[11] Reilly Tar and Chemical Corp., Indianapolis 4, Ind.

[12] Prepared according to E. E. Schwiezer and G. J. O'Neill, *J. Org. Chem.*, **28**, 851 (1963).

The Formation of Substituted Pyridines from the Reaction of the Sodium Salt of Malononitrile with Haloforms in the Alcohol–Alkoxide System

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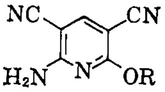
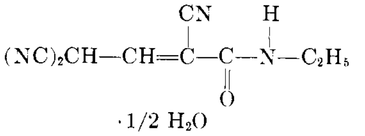
In continuation of a study of the reaction of carbanions with haloforms in the alcohol–alkoxide system,[2] we have investigated the reaction of the sodium salt of malononitrile and wish to report a convenient one-step synthesis of pyridines of type I.

The reaction of the sodium salt of malononitrile with chloroform and sodium ethoxide in ethanol has been reported by Kötz and Zörnig[3] as yielding a product formulated as either II or III. The questionable structural assignment rested solely on an elemental analysis, and a degradation attempt was reported as being unsuccessful. A reexamination has shown that the structure of the product is I (R = C_2H_5) rather than II or III. This was readily established by an infrared comparison and by a mixture melting point determination with the pyridine prepared according to the procedure reported by Little, *et al.*[4]

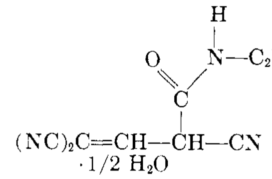


I



$$(NC)_2CH{-}CH{=}C(CN){-}C({=}O){-}N(H){-}C_2H_5 \cdot 1/2\ H_2O$$

II



III

To test the general applicability of this method for the synthesis of 2-amino-3,5-dicyano-6-alkoxypyridines, several alcohols and alkoxide ions were utilized. The results of this study are recorded in Table I.

It can be seen from Table I that fairly good yields of the pyridines were obtained in all cases except with potassium *t*-butoxide in *t*-butyl alcohol where no pyridine could be isolated from the reaction mixture.

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[1] National Defense Education Act Fellow.

[2] A. P. Krapcho, P. S. Huyffer, and I. Starer, *J. Org. Chem.*, **27**, 3096 (1962).

[3] A. Kötz and W. Zörnig, *J. prakt. Chem.*, **182**, 425 (1906).

[4] E. L. Little, Jr., W. J. Middleton, D. D. Coffman, V. A. Engelhardt and G. N. Sausen, *J. Am. Chem. Soc.*, **80**, 2832 (1958).

TABLE I

PREPARATION AND PROPERTIES OF 2-AMINO-3,5-DICYANO-6-ALKOXYPYRIDINES

Pyridine I[a] R	Reaction[b] time	Crude[c] yield, %	M.p.,[d] °C.
C_2H_5	25 min.	50	219–220[e]
CH_3	30 min.	50	253–254[f]
CH_3[g]	4 hr.	65	253–254
n-C_3H_7	16 hr.[h]	35	168–169[i]
i-C_3H_7	2 hr.	50	215–216[j]
t-C_4H_9[k]	17 hr.	0[l]	. . .

[a] All were prepared according to the general procedure described in the Experimental section using the alcohol and alkoxide ion corresponding to the R group. Chloroform was utilized in all runs except where noted. [b] At the boiling point of the alcohol except where noted. [c] The yields are based on malononitrile and no attempt was made to optimize reaction conditions. [d] Melting points of pure crystallized samples. [e] Lit.[4] m.p. 223–224°, m.m.p. 219–220°. [f] Lit.[5] m.p. 258–259°, m.m.p. 253–255°. [g] With bromoform. [h] Performed at room temperature under a nitrogen atmosphere. [i] *Anal.* Calcd. for $C_{10}H_{10}N_4O$: C, 59.40; H, 4.98; N, 27.78. Found: C, 59.38; H, 5.25. [j] *Anal.* Calcd. as in *i*. Found: C, 59.65; H, 5.12; N, 27.62. [k] With potassium *t*-butoxide in *t*-butyl alcohol. [l] No water-insoluble material was isolated.

According to the results of previous investigations the pyridine system (I) undoubtedly arises from the basic cyclization of the salt of 1,1,3,3-tetracyanopropene (IV). It has been reported that, if the potassium salt

$$(NC)_2C{=}CH{-}C(CN)_2^- \ M^+$$

IV

of IV is refluxed with a solution of aqueous methanolic potassium hydroxide, I ($R = CH_3$) is formed; but under similar conditions with aqueous ethanol as solvent, 2-amino-5-cyano-6-ethoxy-3-pyridinecarboxamide results.[5] The synthesis of I ($R = C_2H_5$) has been reported from the reaction of the salts of IV in ethanol with sulfuric acid and also from the reaction of the sodium salt of malononitrile with ethoxymethylenemalononitrile.[4] In the latter reaction, control of the temperature is important in determining the nature of the product. If the reaction is allowed to proceed without cooling, the pyridine I ($R = C_2H_5$) is obtained in ethanol medium, but, if the reaction is run at 0°, the sodium salt of IV is formed.

We have investigated the cyclization of the potassium salt of IV under the reaction conditions utilized for the haloform–malononitrile reaction and in several cases have found that high yields of the corresponding alkoxypyridine (I) can be obtained. The results of these experiments are recorded in Table II.

TABLE II

Pyridine I[a] R	Alkoxide	Crude yield, %	Reflux period, hr.
CH_3	Sodium methoxide	70	1
C_2H_5	Sodium ethoxide	70	1
i-C_3H_7	Sodium isopropoxide	66	1
t-C_4H_9	Potassium *t*-butoxide	20	17

[a] All were prepared according to the general procedure described in the Experimental section.

It is apparent from Table II that the pyridine system (I) is produced in very good yields with short reaction periods except in the potassium *t*-butoxide run. The low yield in this case is significant and represents a slow cyclization rate, since the material not converted into the pyridine was identified as unchanged starting material.

Mechanism of Pyridine Formation.—From the aforementioned results it may be concluded that the intermediate precursor of I is the salt IV. In one run utilizing sodium isopropoxide, isopropyl alcohol, malononitrile, and chloroform, when the reflux period was shortened, it was possible to isolate the sodium salt of IV in a 27% yield. Similarly, the reaction using potassium *t*-butoxide yielded 20% of the potassium salt of IV.

In a previous paper we have proposed that the sodium salt of tetraethylpropene-1,1,3,3-tetracarboxylate, formed by treating the sodium salt of diethyl malonate with chloroform in the presence of ethanolic sodium ethoxide, is probably produced by an initial carbanion attack on dichlorocarbene.[2] The salt IV probably arises by the same mechanistic route.

In order to obtain evidence for the possible intermediacy of dichlorocarbene, a few experiments were performed using sodium trichloroacetate.[6] The thermal decomposition of sodium trichloroacetate in the presence of the sodium salt of malononitrile using 1,2-dimethoxyethane as solvent yielded none of the sodium salt of IV. However, the use of tetrahydrofuran as solvent yielded small amounts of IV (about 1% as ascertained by ultraviolet spectroscopy).

The results of the sodium trichloroacetate experiments can probably be attributed to the insolubility of the sodium salt of malononitrile in the aprotic solvents with added sodium trichloroacetate. This was ascertained by performing the reaction in tetrahydrofuran using a short reflux period. The sodium salt of malononitrile precipitated in a 90% yield.

The failure to obtain any *t*-butoxypyridine in the potassium *t*-butoxide–*t*-butyl alcohol–chloroform system might be due, to a great extent, to the reaction of the *t*-butoxide ion with the initially formed dichlorocarbene, with the consequent destruction of this ion making it unavailable for the cyclization step. This also is given some support by the fact that the reactions of dihalocarbenes with alkoxide ions to produce carbonium ion intermediates fall in the following order: tertiary > secondary > primary.[7]

Experimental[8]

A. General Procedure from the Haloforms.—To a sodium alkoxide solution prepared by treating sodium (0.2 g.-atom) with about 150 ml. of the dry alcohol, Eastman practical-grade malononitrile (0.1 mole), dissolved in about 30 ml. of the alcohol, was added. After the haloform (0.05 mole) was added, the mixture was heated gently with magnetic stirring, and in a few minutes a vigorous exothermic reaction occurred with precipitation of the sodium halide. The mixture was then refluxed for the desired period, filtered, and the residue washed with hot alcohol. The filtrate was concentrated on a Rinco evaporator, and the mixture was poured into ice–water. The precipitated solid was recrystallized from the corresponding alcohol. The infrared spectra of the crude and crystallized material were identical.

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(5) S. G. Cottis and H. Tieckelmann, *J. Org. Chem.*, **26**, 79 (1961).

(6) W. M. Wagner, *Proc. Chem. Soc.*, 229 (1959).

(7) P. S. Skell and I. Starer, *J. Am. Chem. Soc.*, **81**, 4117 (1959).

(8) All melting points were determined on a Fisher-Johns melting point block and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 21 recording spectrometer. Ultraviolet analyses were performed on a Beckman DK recording spectrometer. The analyses were performed by the Schwarzkopf Microanalytical Laboratory and the Galbraith Laboratory.

The pyridines had identical ultraviolet spectra in acetonitrile exhibiting absorption maxima at 271 mμ (log ε 4.2) and 315 mμ (log ε 4.4).

Table I records the pertinent data for each pyridine prepared by this procedure.

B. **General Procedure from the Potassium Salt of 1,1,3,3-Tetracyanopropene.**—To a solution of the sodium alkoxide prepared by treating sodium metal (0.002 g.-atom) in about 20 ml. of the dry alcohol, the potassium salt of IV[9] (0.0055 mole) was added. The solution was refluxed for the desired period and the solvent was then removed with a Rinco evaporator. Water was added, and the solid which separated was removed by filtration. The infrared spectra of these solids were identical to those of the pyridines previously prepared. The pertinent data for each run is presented in Table II.

In the case of the *t*-butoxypyridine the same procedure was followed except that potassium metal was substituted for sodium. The infrared spectra of this product was similar to those of the pyridine systems previously prepared; the ultraviolet spectra in acetonitrile were identical. The compound commenced to change color at about 215° and melted at about 320°.

C. **Isolation of the Salt of IV. (a) From Malononitrile–Chloroform–Sodium Isopropoxide.**—After the reaction components were combined as in procedure A, the mixture was stirred for 2 hr. at room temperature and then refluxed for 15 min. The precipitated solid was filtered from the hot solution. The filtrate was evaporated to dryness with a Rinco evaporator and yielded a solid whose infrared spectrum indicated the presence of the salt of IV along with the sodium salt of malononitrile. The ultraviolet spectrum exhibited a molar extinction coefficient of 14,000, which corresponds to 30% of the salt of IV (molar extinction coefficient of the potassium salt of IV in methanol is 35,000).

The crude sample was dissolved in 150 ml. of methanol, and 150 ml. of ether was added to this solution. The solid which separated was filtered off and the filtrate was concentrated to 25 ml. and placed in the freezer. On standing a solid separated. The infrared spectrum of this sample was identical to the spectrum of the pure potassium salt of IV, except for a weak band at 6.2 μ. An additional amount of solid which had the same infrared spectrum as the initial product was collected from the filtrate on standing. The combined weights of these solids represent a 27% yield.

(b) From Malononitrile–Chloroform–Potassium *t*-Butoxide.—The components were combined according to procedure A using potassium (0.063 g.-atom) and the corresponding amount of the other reactants. The mixture was stirred at room temperature overnight and then refluxed for 1 hr. The precipitated solid was removed by filtration, and a solid separated from the filtrate on standing. This solid was taken up in acetone and some insoluble material was removed by filtration. The filtrate was concentrated, and an oil separated. On addition of ether a solid formed. The ultraviolet spectrum indicated this to consist of 66% of the salt of IV (20% over-all yield).

D. **Reaction of the Sodium Salt of Malononitrile with Sodium Trichloroacetate.**—The sodium salt of malononitrile was prepared by treating a 50% dispersion of sodium hydride in mineral oil (0.01 mole) with malononitrile (0.01 mole) in about 75 ml. of the dry solvent. An equimolar amount of sodium trichloroacetate was added and the mixture was refluxed until the evolution of carbon dioxide ceased. Then the precipitated solid was filtered and analyzed by ultraviolet and infrared spectroscopy.

In the case of 1,2-dimethoxyethane as solvent the infrared spectrum of this solid was identical to the sodium salt of malononitrile, and the ultraviolet spectrum of the sample exhibited no absorption at 344 mμ, indicating the absence of the sodium salt of IV.

In the case of tetrahydrofuran as solvent the ultraviolet absorption corresponded to about 1% of the salt of IV (ε of 420 at 344 mμ).

An additional run was performed using 20 ml. of tetrahydrofuran in the aforementioned procedure and the reflux period was shortened to 20 min. The solid which separated from the solution in a 90% yield was identified as the sodium salt of malononitrile by infrared analysis.

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The Reaction of Benzyne with Methyldiphenylphosphine. A New Route to Triphenylphosphinemethylene[1]

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The electrophilic nature of benzyne is well documented.[3] Of particular interest to this discussion is the reaction of benzyne with tertiary amines, which gave products which appear to have been obtained *via* the nitrogen ylids formed by primary coordination of the nitrogen lone pair with benzyne, followed by proton transfer to the ring from an alkyl group on the nitrogen atom.[4] More recently Franzen, *et al.*,[5] have shown that benzyne and dimethyl sulfide react to give a sulfur ylid, $C_6H_5(CH_3)\overset{\oplus}{S}—\overset{\ominus}{C}H_2$, which appears to be stabilized by the presence of an organolithium compound. The interactions of benzyne with triphenylphosphine[4] and with phosphite esters[6] have been described, but the obvious possibility of preparing a phosphinealkylidene by the reaction of benzyne with an alkyl-substituted phosphine has not yet been demonstrated.

It is the purpose of this note to show that phosphinealkylidenes in principle are accessible through a benzyne route. In practice, however, this route to triphenylphosphinemethylene itself is impractical because of complicating side reactions. Generation of benzyne by the *o*-bromofluorobenzene–magnesium reaction in tetrahydrofuran[4] in the presence of an equimolar amount of methyldiphenylphosphine at 60° gave a red solution. Addition of cyclohexanone, followed by heating of the solution at reflux for 1.5 hr., resulted in a light tan precipitate, but the red color was not discharged. Distillation of volatiles at reduced pressure and gas chromatographic analysis of the distillate showed that methylenecyclohexane had been formed in 14% yield. Presumably the following sequence accounts for this product (see p. 2464, col. 1).

The low yield of methylenecyclohexane may be the result of several complicating factors. In particular, the following were considered as possibly important: (1) deactivation of I by reaction with magnesium halide (see ref. 4); or (2) competition of triphenylphosphinemethylene, itself a potent nucleophile, for the benzyne as it was being generated after the initial stages of the

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[9] M. Strell, W. B. Braunbruck, W. F. Fühler, and O. Huber, *Ann.*, **587**, 177 (1954).

[1] Part VII of the series "Studies in Phosphinemethylene Chemistry"; Part VI, D. Seyferth, J. K. Heeren, and W. B. Hughes, *J. Am. Chem. Soc.*, **84**, 1764 (1962).

[2] (a) Alfred P. Sloan Research Fellow; (b) National Science Foundation Predoctoral Summer Fellow, 1962; Du Pont Postgraduate Teaching Assistant, 1962–1963.

[3] R. Huisgen, "Organometallic Chemistry," H. Zeiss, Ed., Reinhold Publishing Corp., New York, N. Y., 1960, pp. 36–87.

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