desired base was added by syringe in 5–10 molar excess. Commercial solutions of *n*-butyllithium in hexane and methyllithium in diethyl ether were used. Dimsylsodium was prepared by the reaction of sodium hydride with dry Me_2SO and dimsyllithium by addition of commercial methyllithium in ether to Me_2SO. It was discovered that a dimsylsodium Me_2SO solution exposed to air for only a few minutes remained sufficiently basic to form Ph_3C^- from Ph_3CH but would no longer react with 1 to form 2, possibly the result of sodium trimesitylhydroxyborate formation.

Deuterium Oxide Quenching of Anion 2. Deuterium oxide in large excess was added to THF solutions of 2, followed by adjustment of pH to 7 with dilute hydrochloric acid. The solid residue from dried ether extracts of the quenched reaction was chromatographed on silica gel, and the fraction containing 1 was recrystallized from ethanol. GC–mass spectrometry indicated a purity of recovered 1 better than 97%.

Deuterium Oxide Quenching of Radical Anion 4. Quenching of 4 by D_2O followed the procedure outlined for 2. Starting material 3 was recovered in 80% yield based on mass balance. The remaining 20% of material was gas chromatographed on a 3-ft SP 2100 column, temperature programmed between 150 and 300 °C, to yield one major and at least four minor components. The mass spectrum of the major component exhibited a parent ion peak at mass 384 (base peak, mass 221) and other peaks at 327, 325, 278, and 276 mass numbers, consistent with structure 5.

Spectroscopic Measurements. Visible spectra were determined on a Cary 15 UV–visible spectrophotometer.

Electron impact mass spectra was obtained with a Du Pont Model 21-491B GC–MS system operated at 70 eV. Field-ionization mass spectra were obtained with a modified Hitachi RMU-7 mass spectrometer equipped with a field-ionization/field-desorption source at the Oregon Graduate Center, Beaverton, OR.

Nuclear magnetic resonance spectra (^2H, ^{13}C, and ^{11}B) were carried out on a Varian XL-100 spectrometer at the University of Oregon, Eugene, OR. The ^{11}B spectra were run by utilizing the ^{13}C probe and running the spectra without field lock and are, therefore, accurate to only a few parts per million.

Electron spin resonance spectra of the radical anions of trimesitylborane and tris-*m*-xylylborane in THF were obtained on a Varian E-12 spectrometer at San Francisco State University. The ESR spectrum of the radical anion of 1 is well-known[7] and that of 4 is a similar quarter but with little of the fine structure characteristic of the radical anion of 1. A boron hyperfine splitting constant of 9.2 G was obtained for 4.


A New Synthesis of Cyanohydrin Esters

James M. Photis

Stauffer Chemical Company, Dobbs Ferry, New York 10522

Cyanohydrins are commonly obtained by reaction of aldehydes and ketones with hydrogen cyanide.[1] Cyanohydrin esters are obtained by acylation of cyanohydrins which are often generated in situ[2] or by reaction of carbonyl compounds with specialized cyanation reagents.[3] We have investigated the possibility of reduction of the carbonyl group of acyl cyanides[4] (reaction 1) as an alter-
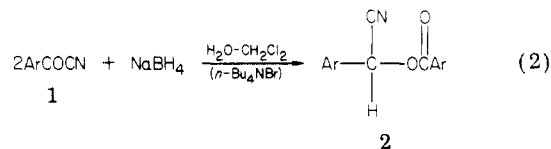
$$R-\underset{\underset{O}{\|}}{C}-CN\ +\ 2[H]\ \longrightarrow\ R-\underset{\underset{OH}{|}}{CH}-CN \qquad (1)$$
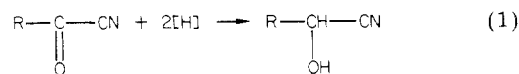
native route to aldehyde-derived cyanohydrin intermediates. The starting material for this sequence is the corresponding carboxylic acid since acyl cyanides can be obtained from acid chlorides[5] or anhydrides.[6] Thus, this would be a more versatile synthetic route since an aromatic carboxylic acid is often more readily available than the corresponding aldehyde. Cyanohydrin esters are used commercially as potent insecticides.[7]

Catalytic hydrogenation of benzoyl cyanide[8] proceeds with reduction of the nitrile functionality. The reaction of lithium aluminum hydride with benzoyl cyanide is reported[9] to give complete reduction to 2-amino-1-phenylethanol. The sodium borohydride reduction of acyl cyanides is not known; however, it is known that borohydride does not react with the cyano functionality of ordinary nitriles[10] unless the reagent is chemically modified.[11] The use of alcoholic solvents was avoided because aroyl cyanides decompose in such solvents to give benzoates.[12] Phase-transfer-catalyzed (PTC) borohydride reactions of carbonyl compounds in $H_2O–ClCH_2CH_2Cl$ have been reported,[13] and this method appears to be reasonable because acyl cyanides have been shown to be stable to PTC conditions.[14]

An acyl cyanide (1) in CH_2Cl_2 was treated with a solution of $NaBH_4$ in water in the presence of tetra-*n*-butylammonium bromide catalyst (reaction 2). An exothermic

$$2ArCOCN\ +\ NaBH_4\ \xrightarrow[\ (n\text{-}Bu_4NBr)\ ]{H_2O\text{-}CH_2Cl_2}\ \underset{\underset{H}{|}}{Ar-\overset{\overset{CN}{|}}{C}}-\overset{\overset{O}{\|}}{O}CAr \qquad (2)$$

$$\underset{\mathbf{1}}{} \qquad\qquad\qquad \underset{\mathbf{2}}{}$$

a, Ar = C_6H_5; **b**, Ar = *m*-$C_6H_4CH_3$; **c**, Ar = *p*-$C_6H_4CH_3$

reaction occurred and the acyl cyanide was completely consumed in just a few minutes. Removal and concentration of the CH_2Cl_2 layer produced an orange oil. The spectral data were identical with those reported[15] for a cyanohydrin ester structure, 2, rather than a cyanohydrin. The yield was quantitative. Conversion of an acyl cyanide to a cyanohydrin ester is not without precedent. The low-temperature reaction of benzoyl cyanide with Grignard

(1) R. F. B. Cox and R. T. Stormont, "Organic Syntheses", Collect. Vol. 2, Wiley, New York, 1943, p 7; E. C. Wagner and M. Baizer, *Ibid.*, Collect. Vol. 3, 1955, p 324.

(2) N. Itaya and T. Nishioka, Japan. Kokai 77 142 046 (1977).

(3) P. G. Gassman and J. J. Talley, *Tetrahedron Lett.*, 3773 (1978).

(4) D. Nasipuri and C. K. Ghosh, *J. Indian Chem. Soc.*, 44, 556 (1967).

(5) T. S. Oakwood and C. A. Weisgerber, "Organic Syntheses", Collect. Vol. 3, Wiley, New York, 1955, p 112; K. Findeisen, W. Draber and H. Schwarz, U.S. Patent 4 069 252 (1978); H. Klenk et al., U.S. Patents 4 113 773 (1979) and 4 144 269 (1979).

(6) K. Findeisen, Ger. Offen 2 614 240 (1977); K. Findeisen and H. Schwartz, Ger. Offen 2 614 241 (1977).

(7) Several books are available on the subject. See for example M. Elliot in "The Future for Insecticides; Needs and Prospects", Vol. 6, R. L. Metcalf and J. J. McKelvey, Eds., Wiley and Sons, New York, 1976, pp 163–190.

(8) R. Escourrou, *Bull. Soc. Chim. Fr.*, 45, 735 (1929).

(9) A Burger and E. D. Hornbaker, *J. Am. Chem. Soc.*, 74, 5514 (1952).

(10) V. N. Rusinova et al., *Khim. Geterotsikl. Soedin.*, 211 (1974); Y. Kikugawa, M. Kuramoto, I. Saito, and S. Yamada, *Chem. Pharm. Bull.*, 1927 (1973).

(11) N. Umino, T. Iwakuma, and N. Itoh, *Tetrahedron Lett.*, 2875 (1976).

(12) J. M. Photis, *Tetrahedron Lett.*, in press.

(13) R. Kinishi, Y. Nakajima, J. Oda and Y. Inouye, *Agric. Biol. Chem.*, 42, 869 (1978); T. Sugimoto, Y. Matsumura, S. Tanimoto, and M. Okano, *J. Chem. Soc., Chem. Commun.*, 926 (1978).

(14) K. E. Koenig and W. P. Weber, *Tetrahedron Lett.*, 2275 (1974).

(15) J. P. Coic, P. Rollin, and R. Setton, *C. R. Hebd. Seances Acad. Sci.*, 1554 (1971).

reagents gave the anticipated alkanophenone, but acetyl cyanide and β-hydrogen-containing Grignard reagents led to acetaldehyde cyanohydrin acetate.[16]

Acyl cyanides themselves can be synthesized by a PTC reaction between an acid chloride and aqueous sodium cyanide.[14] The possibility was investigated of performing both the cyanation and reduction processes in one step. p-Methylbenzoyl chloride in CH_2Cl_2 was treated with an aqueous mixture of NaCN and $NaBH_4$ in the presence of n-Bu_4NBr catalyst. Infrared analysis of the product revealed a single carbonyl absorption band at 1740 cm^{-1} and the structure **2c** was tentatively assigned. The yield was 92%. Compound **2c** was independently synthesized from p-tolualdehyde by standard techniques. This ester was found to be identical in spectral properties with the cyanation–reduction product. Koenig and Weber[14] found that considerable amounts of acyl cyanide "dimers"[17] (**3**) re-

3
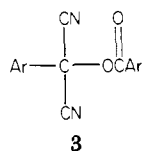
sulted from the PTC reaction between ArCOCl and aqueous NaCN. None of these "dimers" have been detected in our work with sodium borohydride. Subjection of authentic acyl cyanide "dimer" to the reaction conditions did not lead to a cyanohydrin ester, and therefore it can be concluded that **3** is not an intermediate to **2**.

The amount and concentration of both NaCN and $NaBH_4$ proved to be important. With a large excess of borohydride or under dilute conditions the product was a benzyl alcohol instead of **2**. The best yield of cyanohydrin ester from acid chlorides was realized with 1.1 mol of NaCN and 0.33 mol of $NaBH_4$ per mol of ArCOCl with a total volume of water of 300–500 mL. At least a full equivalent of NaCN was necessary for complete reaction even though the overall stoichiometry requires only 0.5 equiv.

Cyanohydrin esters of commercial interest as potent insecticides[7] are derived from two different acid moieties. The cyanation–reduction reaction of a mixture of acid chlorides **4** and **5** did lead to the formation of the "mixed" cyanohydrin ester **6** (known as NRDC 149), as well as other cyanohydrin esters (reaction 3). The presence of **6** was
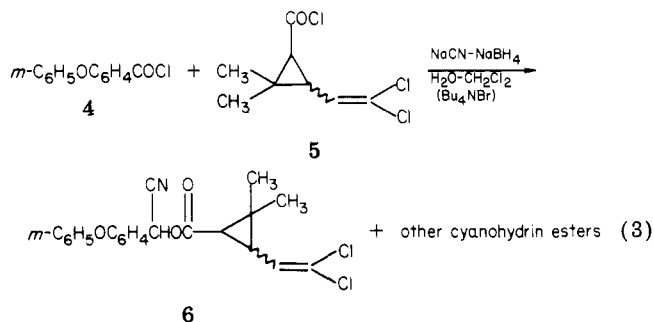

inferred from insecticidal activity test data.[7] The product displayed LD_{50} 0.28 $\mu g/25$ female houseflies when evaluated in a standard housefly residue contact bioassay. Independent preparations of the other three possible products were performed and these substances proved to be inert when tested for insecticidal activity.
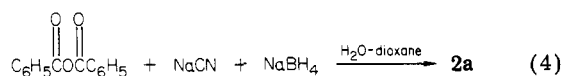
(16) R. B. Borch, S. R. Levitan, and F. A. VanCatledge, *J. Org. Chem.*, **37**, 726 (1972).
(17) See also R. K. Smalley and H. Suschitzky, *J. Chem. Soc.*, 755 (1964); D. Westwood and R. K. Smalley, *Chem. Ind. (London)*, 1408 (1970).

Scheme I
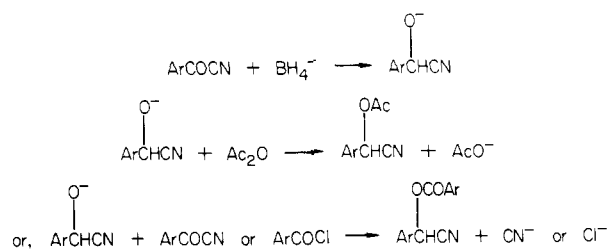
Cyanohydrin ester formation was also observed to take place in aqueous dioxane medium without a phase-transfer catalyst (reaction 4). Under these conditions the reaction

with acid chlorides did not proceed without appreciable hydrolysis. It was found, however, that acid anhydrides were transformed rapidly and cleanly to **2**. Thus, benzoic anhydride was converted to benzaldehyde cyanohydrin benzoate (**2a**). The maximum yield of **2a** which could be obtained experimentally from 1 mol of benzoic anhydride was 0.5 mol. It is likely that the reaction involves the formation of benzoyl cyanide which is reduced by sodium borohydride and acylated by benzoic anhydride or benzoyl cyanide. Thus, half of the anhydride is lost as benzoate.

The borohydride reduction of acyl cyanides in acetic anhydride medium proceeded slowly and incompletely to give only cyanohydrin acetates. Sodium borohydride reduction of m-methylbenzoyl cyanide in acetic anhydride solution (reaction 5) led to cyanohydrin acetate **7** in 66%
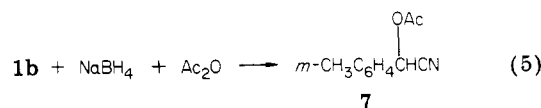
yield. Thus, it is possible to prevent interaction of two acyl cyanide molecules by swamping the reaction with another acylating agent.

Marvel and others[18] have reported an addition reaction between benzoyl cyanide and aromatic aldehydes giving cyanohydrin esters, while Ulich and Adams[19] have reported the addition reaction of acid halides and aldehydes giving halogenated esters. These reports lead one to suspect that the mechanism of the cyanation–borohydride reduction reaction might involve an aldehyde rather than a cyanohydrin intermediate. An aldehyde intermediate is not thought to be involved in the present cases since aldehydes would be expected to undergo rapid reduction to alcohols in the presence of sodium borohydride.

It was not possible to isolate a free cyanohydrin from the reduction of an acyl cyanide with sodium borohydride even when water was excluded in ether solvents under non-PTC conditions. In this regard a precise mechanism by which only esters are obtained remains unresolved. Superficially, the mechanism is viewed as proceeding via a cyanohydrin anion which is very quickly captured by acid anhydrides, acid chlorides, or acyl cyanides (Scheme I).

Experimental Section

General Procedures. (A) Cyanohydrin Esters from Acid Chlorides. p-Tolualdehyde Cyanohydrin p-Toluate (2c). To a magnetically stirred solution of 10.0 g (0.204 mol) of sodium cyanide, 0.56 g (0.0171 mol) of sodium borohydride, and 0.15 g

(18) C. S. Marvel, N. O. Brace, F. A. Miller, and A. R. Johnson, *J. Am. Chem. Soc.*, **71**, 34 (1949).
(19) L. H. Ulich and R. Adams, *J. Am. Chem. Soc.*, **43**, 660 (1921).

of tetra-*n*-butyl ammonium bromide in 40 mL of water was added a solution of 15.5 g (0.10 mol) of *p*-methylbenzoyl chloride in 150 mL of methylene chloride all at once. In about 10 min the reaction temperature had risen to 32 °C. After 50 min, infrared analysis revealed the presence of cyanohydrin ester (1730 cm^{-1}) and acyl cyanide (1680 cm^{-1}). An additional quantity of 0.10 g (0.0026 mol) of sodium borohydride in 5 mL of water was added. After an additional 70 min the organic layer was removed, dried over anhydrous magnesium sulfate, filtered, and concentrated in vacuo at 30 °C. Crude yield was 12.2 g (92.2%) of cyanohydrin ester **2c** as an orange liquid, identical in all respects with a sample of **2c** prepared from *p*-tolualdehyde cyanohydrin, *p*-methylbenzoyl chloride, and triethylamine.

(B) Cyanohydrin Acetates from Acyl Cyanides. *m*-**Tolualdehyde Cyanohydrin Acetate (7).** A magnetically stirred solution of 3.0 g (0.0206 mol) of *m*-methylbenzoyl cyanide[14] in 37 mL of acetic anhydride was treated with 0.60 g (0.0158 mol) of finely ground sodium borohydride in 0.10-g portions over a 1-h period. Thirty minutes after the final addition volatiles were removed under reduced pressure. The residue was treated with water and methylene chloride. The organic layer was stirred with 5% aqueous sodium hydroxide to remove unreacted acyl cyanide, washed with water, dried over anhydrous magnesium sulfate, filtered, and concentrated in vacuo at 30 °C. Crude yield was 2.6 g (66.5%) of **7**, IR ν_{max} (neat) 1755 cm^{-1}, identical in all respects with a sample prepared from *m*-tolualdehyde cyanohydrin, acetyl chloride, and triethylamine.

Acknowledgment. I am grateful to Dr. Ashe Freiberg and Mr. Peter Letchworth for performing the insecticidal activity measurements.

Synthesis of 4,4'-(Ethanediylidene)bis(4*H*-pyran) and -(thiopyran) Derivatives

George A. Reynolds* and Chin H. Chen

*Research Laboratories, Eastman Kodak Company, Rochester, New York 14650*

The 2,2',6,6'-tetraaryl-$\Delta^{4,4'}$-bis(4*H*-pyrans) and their sulfur analogues are of interest as electron-donating materials that form conducting charge-transfer salts with suitable acceptors such as tetracyanoquinodimethane.[1,2] We have investigated the related ethanediylidene bispyran derivatives **1** and found that they also form conducting salts. We had shown previously that **1** can be prepared by heating a pyridine solution of certain pyrylium and thiopyrylium salts as illustrated in eq 1.[3] This method

$$\text{(1)}$$

1

X = O, S
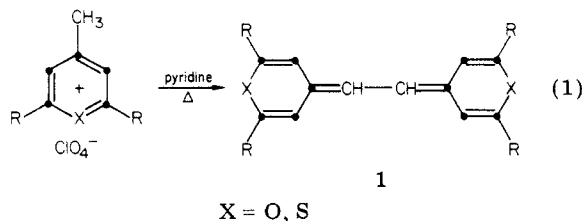
is not general, since **1** (X = O; R = phenyl) could not be prepared, and the method cannot be used to prepare *un-*

Table I. Bispyran Derivatives[a]
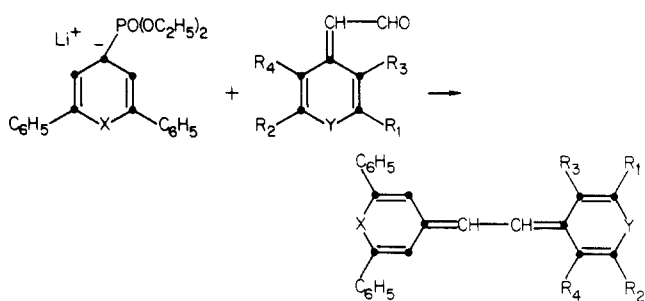
compd	R	X	Y	mp, °C	% yield
4	$R_1 = R_2 = C_6H_5$; $R_3 = R_4 = H$	O	O	297–298	76
5	$R_1 = R_2 = C_6H_5$; $R_3 = R_4 = H$	S	S	301–302	29
6	$R_1 = R_2 = C_6H_5$; $R_3 = R_4 = H$	O	S	257–258	6.2
6	$R_1 = R_2 = C_6H_5$; $R_3 = R_4 = H$	S	O	257–258	3.7
7	R_1R_3 = benzo; R_2R_4 = benzo	O	S	304–305	62
8	R_1R_3 = 1,2-naphtho; R_2R_4 = 1,2-naphtho	O	O	273–274	40
9	$R_1 = C_6H_5$; $R_3 = H$; R_2R_4 = benzo	O	S	184–185	61

[a] Satisfactory analytical data were reported for all compounds in this table.

symmetrical derivatives with differently substituted pyran or thiopyran rings. We now describe a general method for synthesizing a variety of symmetrical and unsymmetrical 4,4'-(ethanediylidene)bis(4*H*-pyrans) and -(thiopyrans).

The general method is based on the reaction of a phosphonate anion **2** with aldehydes **3** to yield **1**. Since a variety of anions **2** are available,[4,5] and the aldehydes are readily prepared from methyl-substituted pyrylium salts,[6] the method can be used to prepare many bispyrans.
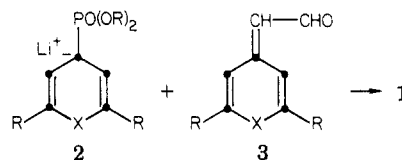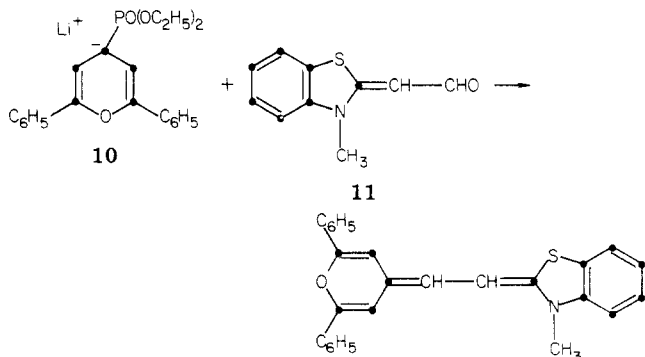

Table I lists the derivatives of **1** that were prepared by this procedure.

The method also was used to prepare **12**, which has different heterocyclic rings.

(1) Fabre, C.; Fugmitto, R.; Strzelecka, H.; Normant, H. *C. R. Hebd. Seances Acad. Sci., Ser. C.* **1976**, *19*, 175.
(2) Perlstein, J. H. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 519.
(3) Van Allan, J. A.; Reynolds, G. A. *Tetrahedron Lett.* **1969**, 2047.

(4) Chen, C. H.; Reynolds, G. A., submitted to *J. Org. Chem.*
(5) Chen, C. H.; Reynolds, G. A., submitted to *J. Org. Chem.*
(6) Reynolds, G. A.; Van Allan, J. A. *J. Org. Chem.* **1969**, *34*, 2736.