addition of 40 ml of diethyl ether, the mixture was washed with 30 ml of 10% NaOH, dried over $MgSO_4$, and distilled to provide the title compound quantitatively: bp 51 °C (2 mm); $n^{23}D$ 1.4559; ^1H NMR (CCl_4) δ 1.2–1.76 (m, 6 H), 1.87 (t, J = 2 Hz, 1 H), 2.40 (td, J = 7 and 2 Hz, 2 H), 4.06 (m, 4 H), and 4.60 ppm (s, 1 H); ir (neat) 3235 (s), 2910 (s), 2840 (s), 2110 cm^{-1} (w).

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work and the National Science Foundation for an instrument grant (MPS75-06106). We also thank Mr. Albert A. Kruger, who partially carried out anexperiment in Table I (entry 3).

Registry No.—5-Decyne, 627-19-0; 4-*tert*-butoxy-1-butyne, 59574-66-2; 5-*tert*-butoxy-2-pentyne, 59574-67-3; 4-tetrahydropyranyloxy-1-butyne, 40365-61-5; dihydropyran, 110-87-2; 3-butyn-1-ol, 927-74-2; 2,2-dimethyl-3-octyne, 19482-57-6; cyclohexylethyne, 931-48-6.

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(7) Other dialkylboranes may be used. However, we have found that dicyclohexylborane is generally more satisfactory than bis(3-methyl-2-butyl)borane (disiamylborane).

(8) Vigorous stirring is essential to observe satisfactory results.

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Preparation of Cyanoformates. Crown Ether Phase Transfer Catalysis

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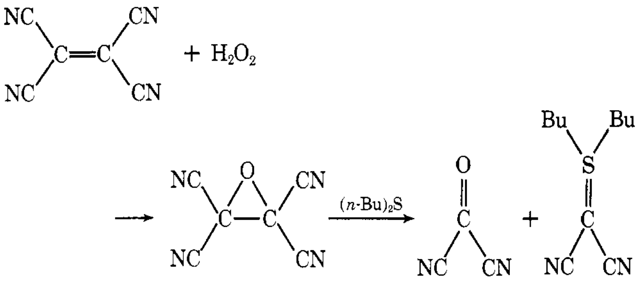
Received May 10, 1976

While the chemistry of chloroformates is extensive, that of cyanoformates is not. Thermal decomposition of primary alkyl chloroformates leads to alkyl chlorides and carbon dioxide at reasonable temperatures (150–200 °C).[1-3] By comparison, benzyl cyanoformate decomposes smoothly at 700 °C in the gas phase to yield benzyl nitrile and carbon dioxide.[4] The cyano group of cyanoformates can function as a dienophile in Diels–Alder reactions. For example, reaction of tetraphenylcyclopentadienone with phenyl cyanoformate yields 3,4,5,6-tetraphenylpyridine-2-carboxylic acid after hydrolysis.[5] Photolysis of ethyl cyanoformate in the presence of alkenes yields oxetanes. For example, photolysis of ethyl cyanoformate in 1,1-diphenylethylene yields 2-cyano-2-ethoxy-3,3-diphenyloxetane.[6] Photolysis of ethyl cyanoformate in cyclohexane yields products which may be rationalized as arising from primary cyano and ethoxycarbonyl radicals: cyclohexyl cyanide and ethyl cyclohexanecarboxylate respectively.[7,8] Finally, *tert*-butyl cyanoformate reacts with amino acids to yield *N*-*tert*-butyloxycarbonyl derivatives which are useful in peptide synthesis[9,10].

Table I. Preparation of Cyanoformates by Phase Transfer Catalysis

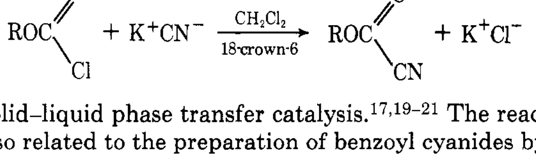
R	Yield, %	Bp, °C (mm)	Lit. bp, °C (mm)	Ref
Methyl	76	95–96 (760)	99 (760)	4
Ethyl	72	115–116 (760)	117 (760)	4
n-Butyl	90	55–56 (25)		
Isobutyl	94	52–53 (20)		
2,2,2-Trichloroethyl	88	100 (25)		
Isopropyl	62	36–37 (25)	35 (20)	11
2-Octyl	88	113–114 (25)		
Cyclohexyl	90	96–97 (20)	43 (1)	11
Benzyl	65	66–67 (0.6)	80 (2.5)	4
Phenyl	82	52–53 (mp)	51.6–53 (mp)	4, 11

The apparent lack of interest in this class of compounds may be due to difficulty in their synthesis. Benzyl, methyl, and ethyl cyanoformates have been prepared (~30% yield) by reaction of the corresponding alkyl chloroformates with powdered sodium cyanide.[4] Far better yields (70–90%) have been reported for the reaction of carbonyl cyanide with a wide variety of alcohols.[11] Unfortunately, carbonyl cyanide is not a commercially available reagent. It can be prepared (~60% yield) in two steps starting from tetracyanoethylene.[12,13] However, the price of tetracyanoethylene makes this a costly procedure.



An alternative preparation of *tert*-butyl cyanoformate involves several steps.[9] Recently, trimethylsilyl cyanide has been shown to react with methyl and ethyl chloroformates to yield the corresponding cyanoformates.[14] However, a drawback to this latter procedure is the necessity to prepare trimethylsilyl cyanide.[15-17]

We should like to report that cyanoformates can be prepared in good to excellent yields by the 18-crown-6[18] catalyzed reaction of potassium cyanide with the corresponding chloroformates in dichloromethane solvent. This is an example of solid–liquid phase transfer catalysis.[17,19-21] The reaction is also related to the preparation of benzoyl cyanides by reaction of benzoyl chlorides with cyanide ion under PTC conditions.[22] The preparation of cyanoformates is a cleaner reaction, since no formation of dimers which was a major side reaction in the preparation of benzoyl cyanides under PTC conditions was observed to occur. The reaction is quite general and is successful for primary, secondary, benzyl, and phenyl cyanoformates (see Table I). Isolated yields of distilled cyanoformates are reported. The reaction, however, fails for the case of *tert*-butyl cyanoformate. This may be due to the well-known instability of *tert*-butyl chloroformate.[23] Also attempts to prepare carbonyl cyanide directly by the PTC reaction of potassium cyanide with phosgene failed under a wide variety of experimental conditions.


$$\mathrm{ROC}(=\mathrm{O})\mathrm{Cl} + K^+CN^- \xrightarrow[\text{18-crown-6}]{CH_2Cl_2} \mathrm{ROC}(=\mathrm{O})\mathrm{CN} + K^+Cl^-$$

We hope that this new synthetic procedure will stimulate interest in cyanoformates.

Experimental Section

Many of these cyanoformates are known compounds; however, spectral properties even on those that are known are meager. For this reason, ir and NMR spectra of all compounds are reported here. The new cyanoformates, *n*-butyl, isobutyl, 2,2,2-trichloroethyl, and 2-octyl, have been analyzed. Infrared spectra were obtained on a Perkin-Elmer 337 spectrometer and were calibrated against known bands in a polystyrene film. NMR spectra were recorded on a Varian T-60 spectrometer. Ten percent solutions in carbon tetrachloride with tetramethylsilane as internal standard were used. Vapor phase chromatography was carried out on a Hewlett-Packard F & M 700 using a 20% polyphenyl ether on Chromosorb P 4 ft × 0.25 in. column. Microanalysis was performed by Elek Microanalytical Laboratories, Torrance, Calif. Boiling points and melting points were not corrected.

Preparation of Isobutyl Cyanoformate. In a 50-ml round-bottom flask equipped with a reflux condenser, nitrogen inlet, and a Teflon-covered magnetic stirring bar was placed 30 ml of methylene chloride, 3.5 g (0.054 mol) of potassium cyanide, 6.8 g (0.05 mol) of isobutyl chloroformate (Eastman), and approximately 50 mg (0.02 mmol) of 18-crown-6.[18] The mixture was stirred at room temperature. The reaction could be followed by ir (the disappearance of the band at 1790 cm^{-1} due to the C=O of the starting chloroformate and the appearance of bands at 2250 cm^{-1} due to the C≡N and at 1750 cm^{-1} due to the C=O of the product cyanoformate) or by GLC (the starting material had a shorter retention time than the product cyanoformate in all cases which were examined). When the starting material had disappeared (~4 h), the solution was filtered. The solution was distilled through a 15-cm Vigreux column. Solvent was removed at atmospheric pressure. A fraction consisting of pure isobutyl cyanoformate by GLC, 6.0 g (0.047 mol), 94% yield, distilled at 52–53 °C (20 mm): NMR d (2 H) δ 4.1, $J = 7$ Hz, m (1 H) 2.1, d (6 H) 1.0, $J = 7$ Hz; ir 2250 C≡N, and 1750 cm^{-1} C=O. Anal. Calcd for $C_6H_9O_2N$: C, 56.68; H, 7.14. Found: C, 56.70; H, 7.03.

All other cyanoformates reported were prepared in analogous fashion.

Methyl cyanoformate from methyl chloroformate (Aldrich): NMR s (3 H) δ 4.0; ir 2250 C≡N, 1750 cm^{-1} C=O.

Ethyl cyanoformate from ethyl chloroformate (Aldrich): NMR q (2 H) δ 4.4, $J = 7$ Hz, t (3 H) 1.4, $J = 7$ Hz; ir 2250 C≡N, and 1750 cm^{-1} C=O.

***n*-Butyl cyanoformate** from *n*-butyl chloroformate (Aldrich): NMR t (2 H) δ 4.4, $J = 7$ Hz, multiplets (7 H) 1.7–1.0; ir 2250 C≡N, and 1750 cm^{-1} C=O. Anal. Calcd for $C_6H_9O_2N$: C, 56.68; H, 7.14. Found: C, 57.01; H, 7.10.

2,2,2-Trichloroethyl cyanoformate from 2,2,2-trichloroethyl chloroformate (Aldrich): NMR s (2 H) δ 4.75; ir 2250 C≡N, and 1760 cm^{-1} C=O. Anal. Calcd for $C_4H_2O_2NCl_3$: C, 23.73; H, 1.00. Found: C, 23.87; H, 1.32.

Isopropyl cyanoformate from isopropyl chloroformate (Research Organic/Inorganic Chemical Co.): NMR septet (1 H) δ 5.2, $J = 7$ Hz, d (6 H) 1.4, $J = 7$ Hz; ir 2250 C≡N, 1750 cm^{-1} C=O.

2-Octyl cyanoformate from 2-octyl chloroformate which had been prepared by reaction of 2-octyl alcohol with phosgene:[24] NMR m (1 H) δ 5.1, m (16 H) 1.3; ir 2250 C≡N and 1745 cm^{-1} C=O. Anal. Calcd for $C_{10}H_{17}O_2N$: C, 65.54; H, 9.35. Found: C, 65.51; H, 9.31.

Cyclohexyl cyanoformate from cyclohexyl chloroformate which had been prepared by reaction of cyclohexanol with phosgene:[24] NMR br (1 H) δ 5.0, m (10 H) centered at 1.6; ir 2245 C≡N, and 1745 cm^{-1} C=O.

Benzyl cyanoformate from benzyl chloroformate (Aldrich): NMR s (5 H) δ 7.2, s (2 H) 5.0; ir 2245 C≡N, and 1745 cm^{-1} C=O.

Phenyl cyanoformate from phenyl chloroformate (Eastman): NMR m (5 H) δ 7.3; ir 2250 C≡N, and 1760 cm^{-1} C=O.

Acknowledgments. This work was supported by a grant from the National Science Foundation, GP-40331X. M. E. Childs thanks the Stauffer Chemical Co. for a fellowship.

Registry No.—Isobutyl cyanoformate, 59873-30-2; isobutyl chloroformate, 543-27-1; methyl cyanoformate, 17640-15-2; methyl chloroformate, 79-22-1; ethyl cyanoformate, 623-49-4; ethyl chloroformate, 541-41-3; *n*-butyl cyanoformate, 5532-84-3; *n*-butyl chloroformate, 592-34-7; 2,2,2-trichloroethyl cyanoformate, 59873-31-3; 2,2,2-trichloroethyl chloroformate, 17341-93-4; isopropyl cyanoformate, 59873-32-4; isopropyl chloroformate, 108-23-6; 2-octyl cyanoformate, 59873-33-5; 2-octyl chloroformate, 15586-11-5; cyclohexyl cyanoformate, 5532-84-4; cyclohexyl chloroformate, 13248-54-9; benzyl cyanoformate, 5532-86-5; benzyl chloroformate, 501-53-1; phenyl cyanoformate, 5532-82-1; phenyl chloroformate, 1885-14-9; potassium cyanide, 151-50-8.

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An Unusual Arene Oxide Reaction. Solvent Capture during Acid-Catalyzed Solvolysis of 7,12-Dimethylbenz[*a*]anthracene 5,6-Oxide

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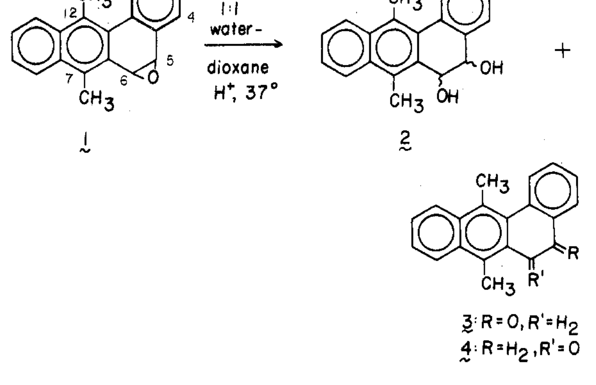
Received April 16, 1976

Recent interest in polycyclic arene oxides as mediators of polycyclic arene carcinogenesis[2] has prompted us to study the aqueous solvolysis of 7,12-dimethylbenz[*a*]anthracene 5,6-oxide (**1**), a K-region[3] metabolite[4] of the carcinogenic 7,12-



1

2

3: R = O, R' = H_2

4: R = H_2, R' = O