tion of di-(1,1-dimethylbutyl) oxalate was dissolved in 2.5 ml. of ethyl acetate and placed in a 50-ml. erlenmeyer flask with 0.05 g. of hydrogenation catalyst (10% Pd on charcoal). The flask was attached to a low pressure hydrogenation apparatus and the mixture was stirred magnetically overnight at room temperature under 1 atm. of hydrogen pressure. After filtering, the solution was submitted to gas chromatographic analysis. In addition to the solvent peak only one more peak was obtained which had identical retention time with that of authentic 2-methylpentane.

Gas chromatographic analyses were obtained from a Perkin-Elmer Model 154, an F and M Model 500, and a Beckman GC-2. All n.m.r. spectra were taken on an Varian A-60 n.m.r. spectrometer.

**Acknowledgment.**—One of us, J. M. Corbett, thanks the Dow Chemical Company, Midland, Michigan, for a leave of absence and generous support during the summer of 1962.

# Organometallic Isocyanates and Isocyanurates of Groups IV and V[1]

WALTER STAMM

*Stauffer Chemical Company, Chauncey Research Center, Chauncey, New York*

*Received September 24, 1964*

New synthetic methods are described for organotin, -antimony, and -arsenic isocyanates. They consist of fusing organometallic oxides with urea at 130°. Identical isocyanates were obtained by fusion of organometallic oxides with biuret at 170° and with isocyanic acid solutions at 70° and by metathetical reactions of organometallic halides with sodium cyanate. Organotin isocyanurates, a new class of compounds, were prepared by fusion of organotin oxides with cyanuric acid. They are remarkably thermostable.

Little is known about the synthesis and properties of organometallic isocyanates. The only organotin isocyanate described is triethyltin isocyanate,[2] prepared from triethyltin chloride and silver cyanate in alcohol. E. Krause[3] mentioned the preparation of triphenylantimony diisocyanate from triphenylantimony dichloride and silver cyanate. This paper is primarily concerned with new preparative methods for organometallic isocyanates of tin, antimony, and arsenic.

**Urea Fusion.**—In the course of an investigation into the preparation of N-organotin- and N-organoantimonyureas, the following discovery was made. When organotin oxides were fused with urea at 130°, ammonia was evolved and organotin isocyanates were obtained by the reactions shown below. Yields of 85–95% were

$$R_3SnOH + (H_2N)_2CO \longrightarrow R_3Sn(NCO) + NH_3 + H_2O$$

$$(R_3Sn)_2O + 2(H_2N)_2CO \longrightarrow 2R_3Sn(NCO) + 2NH_3 + H_2O$$

$$\begin{array}{l} \text{I, } R = n\text{-}C_4H_9 \\ \text{II, } R = i\text{-}C_4H_9 \\ \text{III, } R = C_2H_5 \end{array}$$

achieved if dry nitrogen was bubbled through the melt at 130–140°, thereby removing ammonia and water from the reaction mixture.

In analogous reactions trialkylantimony diisocyanates were obtained by fusion of trialkylantimony oxides (or bishydroxides) with urea. The reaction mixtures were quite viscous, and it became difficult to isolate trialkylantimony diisocyanates by distillation unless reduced pressure was applied during the fusion reaction for the removal of ammonia and water. Also triphenylarsenic diisocyanate was prepared by fusing triphenylarsenic oxide with urea.

$$R_3MO + 2(H_2N)_2CO \longrightarrow R_3M(NCO)_2 + 2NH_3 + H_2O$$

$$\begin{array}{l} \text{V, } R = i\text{-}C_4H_9;\ M = Sb \\ \text{VI, } R = n\text{-}C_4H_9;\ M = Sb \\ \text{VII, } R = C_6H_5;\ M = As \end{array}$$

Fusion of polymeric dibutyltin oxide with urea resulted in evolution of ammonia and water, after which a clear melt was formed at 170–180°, which soon solidified at this temperature. Analyses of the wax-like reaction product (melting range 195–215°) indicated a conversion of the oxide to a polymeric isocyanate corresponding to the following complex structure.

$$[(C_4H_9)_2SnOSn(C_4H_9)_2(NCO)_2]_n$$

X

Fused urea also reacted with organotin and organoantimony chlorides. However, yields of isocyanates were only in the order of 20–30%, and the separation of the isocyanates from unreacted chlorides by fractional distillation was difficult.

The identity of isocyanates obtained by fusion with urea was confirmed by syntheses from organometallic chlorides and excess sodium cyanate. Excellent yields were obtained by refluxing the components in acetonitrile. Under these conditions, the sodium cyanate method appeared to be particularly suitable for organometallic diisocyanates.

**Mechanism.**—The formation of organotin isocyanates by fusion of organotin oxides with urea could conceivably proceed in different ways. Isocyanic acid, cyanuric acid, biuret, or organotinurea derivatives are possible reactive intermediates.

Triethyltin oxide is reported[2b] not to react with free isocyanic acid to form triethyltin isocyanate. Perhaps the reaction conditions in these attempts had been too mild. It has now been found that isocyanic acid reacts rapidly and almost quantitatively with organotin oxides at 70–80°. Refluxing benzene was found to be most suitable if the water of reaction was azeotropically removed into a Dean–Stark trap. Also trialkylantimony diisocyanates could be isolated by treating trialkylantimony oxides with isocyanic acid, which,

$$(R_3Sn)_2O + 2HNCO \longrightarrow 2R_3Sn(NCO) + H_2O$$

$$\begin{array}{l} \text{I, } R = n\text{-}C_4H_9 \\ \text{III, } R = C_2H_5 \end{array}$$

---

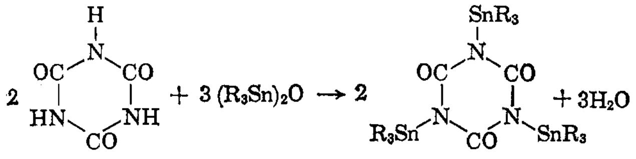
[1] After completion of this work, the synthesis of tributyltin isothiocyanate from thiourea was published by R. A. Cummins and P. Dunn [*Australian J. Chem.*, **17**, 411 (1964)]. Since their results are identical with observations in this work, reactions with thiourea have been eliminated from this paper.

[2] (a) P. Kulmiz, *J. prakt. Chem.*, **80**, 91 (1860); (b) H. H. Anderson and J. A. Vasta, *J. Org. Chem.*, **19**, 1300 (1954).

[3] E. Krause and W. v. Grosse, "Die Chemie der metall-organischen Verbindungen," Gebr. Borntraeger, Berlin, 1937, p. 631.

therefore, is a possible intermediate in the fusion reaction with urea.

The possibility of cyanuric acid as a reactive intermediate was disproved by independent preparation of remarkably stable organotin derivatives of cyanuric acid at 130°. These novel organotin triazones were



VIII, R = $n$-$C_4H_9$
IX, R = $C_6H_5$

found to possess extraordinary thermal and good hydrolytic stability.. For example, compound VIII withstood temperatures in excess of 300° without degradation. No organotin cyanurate was found in the urea fusion process.

Also the involvement of biuret in the urea reaction was disproved, because trialkyltin oxides did not react with biuret (m.p. 192°) at 140°. At 160–170°, however, ammonia and water evolved with foaming and trialkyltin isocyanates were isolated in excellent yields. Since HNCO is not liberated from biuret at 160°, the formation of isocyanates might proceed through N-organotin derivatives, at least in this latter case (R′ = $CO\cdot NH_2$).

$$R_3SnOH + H_2N\cdot CO\cdot NH\cdot R' \underset{+H_2O}{\overset{-H_2O}{\rightleftarrows}} R_3SnNH\cdot CO\cdot NH\cdot R' \underset{+H_2NR'}{\overset{-H_2NR'}{\rightleftarrows}} R_3SnNCO$$

**Properties.**—Most suitable for the identification of organometallic isocyanates of groups IV and V was found to be their sharp and very strong absorption between 4.50–4.70 μ.

In the preceding discussions the term isocyanate was used because these compounds behaved principally like organic isocyanates, although at a very much reduced rate. No trimerization to VIII took place by heating tributyltin isocyanate (I) with pyridine or with trialkylphosphine. At room temperature, I was remarkably inert to water. Only boiling water slowly hydrolyzed I to tributyltin oxide. Alcohols and phenols reacted slowly with I or VI to form carbamates. I reacted rapidly with aliphatic amines to give N-tributyltin-N′-alkylureas. The reaction with ammonia was slow, but tributyltinurea was identified. Generally, the species $R_3SnNH\cdot CO\cdot NH\cdot R'$ was found to contain a highly polar Sn–N bond which was readily broken by protic reagents HA (including water), liberating ureas and $R_3SnA$.

A detailed description of various reactions with organometallic isocyanates of groups IV and V will be published at a later date.

## Experimental

**Tri-*n*-butyltin Isocyanate** (I).—One mole (600 g.) of bis(tri-*n*-butyltin) oxide was mixed with 2.05 moles (126 g.) of finely powdered dry urea. With a slow stream of nitrogen bubbling through this vigorously agitated slurry, the temperature was slowly raised to 125°; between 125 and 130° some foaming started indicating the evolution of ammonia. The temperature was kept at 130–140° for 1 hr., during which a moderate stream of nitrogen was led through the agitated mixture in order to remove ammonia and water. The liquid crude reaction product was purified by two vacuum distillations. Pure tri-*n*-butyltin isocyanate (I) was obtained in 82% yield (540 g.). It distilled at 112–115° (0.5 mm.), $n^{22}D$ 1.490. Strong infrared bands were at 3.4 (CH stretch) and 4.53 μ (NCO).[4]

*Anal.* Calcd. for $C_{13}H_{27}NOSn$: C, 47.05; H, 8.13; N, 4.22; Sn, 35.80. Found: C, 47.12; H, 8.05; N, 4.38; Sn, 35.44.

**I from Isocyanic Acid.**—The hot-tube reactor, in which cyanuric acid was pyrolized at 500°, was connected with a three-neck reaction flask. This reaction flask, equipped with stirrer and Dean–Stark reflux condenser, was charged with a solution of 60 g. (0.1 mole) of bis(tri-*n*-butyltin) oxide in 120 ml. of benzene. The reaction flask was deeply immersed in an ice bath, and approximately 11 g. (0.255 mole) of free isocyanic acid was distilled into the agitated benzene solution directly from the hot tube containing initially 16 g. (0.12 mole) of cyanuric acid. After completing the pyrolysis, the hot-tube reactor was disconnected, and the benzene solution was brought to reflux. At 75° a vigorous foaming indicated reaction. Within 1 hr., 1.2 ml. (0.067 mole) of water was collected in the trap. After 2-hr. reflux about 2.5 g. of cyanuric acid was removed by filtration. Benzene was flash evaporated at reduced pressure. The remaining clear oil was purified by high vacuum distillation; b.p. 104–106° (0.3 mm), $n^{22}D$ 1.489, strong infrared bands at 3.38 and 4.54 μ, yield 59.8 g. (90%).

**Tri-*i*-butyltin Isocyanate** (II).—This compound was prepared according to the preceding procedure. From 60 g. (0.1 mole) of bis(tri-*i*-butyltin) oxide and 12.12 g. (0.22 mole) of urea was obtained 53 g. (81%) of distilled II, b.p. 103° (0.3 mm), $n^{21}D$ 1.489.

*Anal.* Calcd. for $C_{13}H_{27}NOSn$: N, 4.22; Sn, 35.80. Found: N, 4.41; Sn, 35.39.

**Triethyltin Isocyanate** (III).—Bis(triethyltin) oxide (42.8 g., 0.1 mole) was intimately contacted with fused urea (14.4 g., 0.22 mole) for a period of 1.5 hr. at 135°. Nitrogen was employed to remove evolving ammonia and water. Colorless triethyltin isocyanate (III) was distilled from the reactor through a short Vigreux column; b.p. 70° (0.4 mm). Pure III crystallized in the receiver; m.p. 51–53°[5], yield 46.2 g. (92%). The infrared spectrum showed strong NCO absorption at 4.53 μ.

*Anal.* Calcd. for $C_7H_{15}NOSn$: N, 5.64; Sn, 47.90. Found: N, 5.50; Sn, 47.65.

**Tri-*i*-butylantimony Diisocyanate** (V).—In 200 ml. of acetonitrile was dissolved 36.4 g. (0.1 mole) of triisobutylantimony dichloride. To this was added 26 g. (0.4 mole) of powdered sodium cyanate. The agitated mixture was refluxed for 3 hr. The warm solution was quickly filtered, and the solids were washed with fresh acetonitrile. After flash evaporation at 0.2 mm., 38 g. (100%) of a clear, oily liquid was recovered. This could be purified by two quick high-vacuum distillations, during which the bath temperature was kept below 170°. Twenty-five grams (75%) of colorless V was recovered; b.p. 122–124° (0.15 mm), $n^{20}D$ 1.5128, strong infrared band at 4.6 μ (NCO).

*Anal.* Calcd. for $C_{14}H_{27}N_2O_2Sb$: C, 44.55; H, 7.16; N, 7.43; Sb, 32.3. Found: C, 43.95; H, 7.08; N, 7.23; Sb, 32.3.

**Tri-*n*-butylantimony Diisocyanate** (VI).—Tri-*n*-butylantimony oxide (15.5 g., 0.05 mole) was thoroughly mixed with powdered urea (6.6 g., 0.11 mole). This mixture was heated to 130° with stirring while the pressure in the reactor was reduced to about 30 mm. Foaming had to be carefully controlled. The reaction was completed within 1 hr. at 140°. Water and ammonia were collected in adjoining Dry Ice traps. The crude liquid VI was purified by a quick flash distillation at reduced pressure. However, by increasing the bath temperature to 180° about one-half of the crude product became very viscous and undistillable. Thermal decomposition started at 190°. There was strong NCO absorption at 4.6 μ.

*Anal.* Calcd. for $C_{14}H_{27}N_2O_2Sb$: N, 7.43. Found: N, 7.3.

**Triphenylarsenic Diisocyanate** (VII).—Triphenylarsenic oxide (32.2 g., 0.1 mole) was mixed with powdered urea (12 g., 0.2 mole) and heated to fusion at 135°. After 0.5 hr. at 140–150°, reduced pressure was applied in order to remove all water and ammonia from the reactor. Upon cooling to room temperature, the reaction product VII (37.5 g., 96%) solidified to an

---

(4) A Perkin-Elmer 21 spectrometer was used with a potassium bromide disk.

(5) A Kofler hot stage was used; uncorrected.

amorphous, glassy mass, m.p. about 40°. The product showed a strong NCO absorption at 4.68 μ.

*Anal.* Calcd. for $C_{20}H_{15}AsN_2O_2$: As, 19.22; N, 7.19. Found: As, 19.06; N, 7.20.

**1,3,5-Tri-*n*-butyltin-*s*-triazine-2,4,6-trione (VIII).**—In a flask deeply immersed in an oil bath and equipped with a Dean–Stark receiver, a stirred mixture of 180 g. (0.3 mole) of bis(tri-*n*-butyltin) oxide and 25.8 g. (0.2 mole) of powdered cyanuric acid was heated to 100°, at which point water was evolved. The temperature was slowly raised to 160°, and finally reduced pressure was applied in order to remove quantitatively the water of reaction from the liquid reaction product. After 1 hr., 5.4 ml. (0.3 mole) of water was collected in the cooled receiver. A small amount of unreacted cyanuric acid (0.6 g.) was removed by filtration. Traces of unreacted bis(tri-*n*-butyltin) oxide were removed by heating the reaction product to 200° at 0.2 mm. Colorless liquid compound VIII was obtained in almost quantitative yield (200 g.), $n^{22}_{D}$ 1.5099, infrared absorptions at 5.98 and 6.2 μ. Attempts to crystallize or to distil VIII failed. No solidification occurred at −30°, and no distillation took place at 240° (0.03 mm.). From these experiments (bath temperature 280°) VIII was recovered unchanged.

*Anal.* Calcd. for $C_{39}H_{81}N_3O_3Sn_3$: C, 47.02; H, 8.14; N, 4.22; Sn, 35.78. Found: C, 46.94; H, 7.95; N, 4.28; Sn, 35.33.

**1,3,5-Triphenyltin-*s*-triazine-2,4,6-trione (IX).**—Triphenyltin hydroxide (11 g., 0.03 mole, m.p. 93°) was thoroughly mixed with cyanuric acid (1.3 g., 0.01 mole). Upon heating to 150° complete fusion occurred, which was followed by solidification after 15 min. Approximately 0.5 ml. (about 0.03 mole) of water was collected in a trap. Colorless reaction product IX did not melt or decompose at 340°.

*Anal.* Calcd. for $C_{57}H_{45}N_3O_3Sn_3$: N, 3.58; Sn, 30.4. Found: N, 3.61; Sn, 30.1.

**$[(C_4H_9)_4Sn_2(NCO)_2O]_n$ (X).**—The finely powdered mixture of 248.7 g. (1 mole) of dibutyltin oxide and 60.1 g. (1 mole) of urea was slowly heated to 175° with agitation. Ammonia (1 mole) and water (0.5 mole) were evolved, and the mixture melted to a clear, viscous oil. It was kept at 195° for 2 hr. The colorless product solidified on cooling to a wax-like material. It had a melting range from 195–215°, good solubility in warm alcohols and acetone, and strong NCO absorption at 4.6 μ.

*Anal.* Calcd. for $C_{18}H_{36}N_2O_3Sn_2$: N, 4.96; Sn, 41.94. Found: N, 5.12; Sn, 41.8.

---

# Studies on Geometric Isomerism by Nuclear Magnetic Resonance. I. Stereochemistry of α-Cyano-β-alkoxy-β-alkylacrylic Esters[1]

TOSHIO HAYASHI, ISABURO HORI, HIDEO BABA, AND HIROSHI MIDORIKAWA

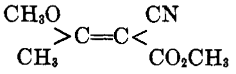
*The Institute of Physical and Chemical Research, Komagome, Bunkyo-ku, Tokyo, Japan*

*Received August 18, 1964*

The n.m.r. technique has been applied to the determination of the geometric configurations of a series of α-cyano-β-alkoxy-β-alkylacrylic esters and the spectra have been discussed on the basis of the assumption that the resonance peak of the β-methyl protons is more deshielded in the *cis* configuration than in the *trans*. It is found that these esters are more stable in the *cis* configuration, except for methyl α-cyano-β-methoxy-β-*t*-butylacrylate.

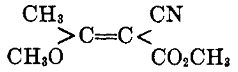
In connection with other work, a series of α-cyano-β-alkoxy-β-alkylacrylic esters have been prepared by alkylation of acylcyanoacetic esters. These esters, which possess an ethylenic bond substituted by four different groups, occur in two isomeric forms.[2] Some of them have been isolated pure, but their geometric configurations are still open to question.[3] In the case of these esters there are no infrared bands which can be reliably correlated with configurations, and ultraviolet spectra as well as dipole moment cannot be used to make a definite assignment of configuration.

Jackman[4,5] and other several authors[6-8] demonstrated that, provided both isomers of a pair are available, n.m.r. spectroscopy can be used to establish the geometric configurations of some α,β-unsaturated esters. This method is based on the fact that the protons of a *cis*-β-methyl group are more deshielded than those of a *trans*-β-methyl group. However, in the type of compound shown below, it is difficult to decide which of the protons of the two β-methyl groups is more deshielded, since these protons might experience a long-range



$$\begin{matrix}CH_3O & & CN\\ & >C{=}C< & \\ CH_3 & & CO_2CH_3\end{matrix}$$

*cis* ester



$$\begin{matrix}CH_3 & & CN\\ & >C{=}C< & \\ CH_3O & & CO_2CH_3\end{matrix}$$

*trans* ester

shielding effect of the cyano group, in addition to the effect of the methoxycarbonyl group. The present paper, therefore, discusses the geometric configurations of α-cyano-β-alkoxy-β-alkylacrylic esters on the basis of some assumption.

## Results and Discussion

The esters studied in this work are listed in Table I, together with the chemical shifts (p.p.m. downfield from internal tetramethylsilane). With samples obtained only in a stereoisomeric mixture, the percentage of the isomeric composition, determined from the relative peak areas, has also been given in Table I. Representative n.m.r. spectra of the esters are shown in Figures 1 and 2.

The resonance signals at 3.78 p.p.m. in Figure 1A and at 3.75 p.p.m. in Figure 1B were assigned to the methoxycarbonyl protons, since the spectrum of the corresponding ethyl ester (IIa) lacks a signal in this region; the signals at 4.01 p.p.m. in Figure 1A and at 4.04 p.p.m. in Figure 1B were assigned to the methoxy group by comparison with the spectrum of the corresponding ethoxy ester (IIIa). The remaining signals at 2.62 p.p.m. in

---

[1] Presented at the 3rd Symposium on N.m.r., Osaka, Japan, Nov 1963.

[2] The isomeric forms of a series of the esters are denoted as (i) *cis* (in which the alkyl and alkoxycarbonyl groups are on the same side of the C=C double bond) and (ii) *trans* (in which these groups are on opposite sides). These notations are opposite to those used by Eistert and Merkel [*Chem. Ber.*, **86**, 895 (1953)].

[3] F. Arndt, H. Scholz, and E. Frobel, *Ann.*, **521**, 95 (1935).

[4] L. M. Jackman and R. H. Wiley, *Proc. Chem. Soc.*, 196 (1958).

[5] (a) L. M. Jackman and R. H. Wiley, *J. Chem. Soc.*, 2881 (1960); (b) *ibid.*, 2886 (1960).

[6] J. W. K. Burrcel, L. M. Jackman, and B. C. L. Weedon, *Proc. Chem. Soc.*, 233 (1959).

[7] (a) R. Morris, C. A. Vernon, and R. F. M. White, *ibid.*, 304 (1958); (b) D. E. Jones, R. O. Morris, C. A. Vernon, and R. F. M. White, *J. Chem. Soc.*, 2349 (1960).

[8] S. Fujiwara, H. Shimizu, Y. Arata, and S. Akabori, *Bull. Chem. Soc. Japan*, **33**, 428 (1960).