## 1,4 Insertion Reactions of 1,1-Bis(trihalogenomethyl)-2,2-dicyanoethylenes

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Sumn ary Insertion reactions of the title compounds give adducts and ketenimines under mild conditions.

OUR work<sup>1</sup> upon the insertion reactions of unsaturated perhalogeno-compounds caused us to study the addition of two o efins, 1,1-bistrifluoromethyl-2,2-dicyanoethylene<sup>2</sup> and 1-trifluoromethyl-1-chlorodifluoromethyl-2,2-dicyanoethylene, to certain organometallic bases and other compounds. Metal and metalloid ketenimines were formed by an overall 1,4 addition, as shown for methylthiotrimethylsilane:



Table 1 contains a selection of these insertions, which illustrates the wide range of this reaction. The easy insertion into a tin-carbon bond and into the stable tinsulphur bond are notable.

All of the products reported have good analytical data, and are either crystalline solids or viscous oils. The i.r. spectrum of every compound has a strong band at about 2210 cm.<sup>-1</sup> characteristic<sup>3</sup> of the C=C-C=N group, and another at 2140 cm.<sup>-1</sup> characteristic<sup>4</sup> of the C=C=N group. The ultraviolet spectra all contain a band around 225 nm ( $\epsilon \ 8 \times 10^3$ ), believed to be due<sup>5</sup> to the C=C=N chromophore. The <sup>1</sup>H and <sup>19</sup>F n.m.r. spectra of all products are in perfect accord with the formulations.

Molecular weight measurements indicate that these materials are telomeric, and that the degree of polymerization is concentration dependent. Further, this polymerization prevents sublimation or distillation of these ketenimines, but they are nevertheless easily recrystallized.

It is probable that the polymerization of these ketenimines arises by the presence of the second cyano-group; this in turn produces the opportunity for resonance,<sup>6</sup> as shown for one of the polymeric boron products.



Some insertion reactions of the olefins  $(CF_3)_2C = C(CN)_2$  and  $(CF_3)(CF_2Cl)C = C(CN)_2$ 

Reagents Product  $\begin{array}{c} (CF_{3})_{2}C = C(CN)_{2} \\ (CF_{3})_{3}(CF_{2}CI)C = C(CN)_{2} \\ (CF_{3})_{4}C = C(CN)_{4} \end{array}$  $\begin{array}{l} (CF_{3})_{2}(MeS)C \cdot C(CN) = C = N \cdot SiMe_{3} \\ (CF_{3})(CF_{2}CI)(MeS)C \cdot C(CN) = C = N \cdot SiMe_{3} \\ (CF_{3})_{2}(PhNH)C \cdot C(CN) = C = N \cdot SiMe_{3} \\ (CF_{3})_{2}(H)C \cdot C(CN) = C = N \cdot SiMe_{3} \\ (CF_{3})_{2}(Me_{3}SINH)C \cdot C(CN) = C = N \cdot SiMe_{3}^{\dagger} \\ (CF_{3})_{2}(MeS)C \cdot C(CN) = C = N \cdot SnMe_{3} \\ (CF_{3})_{3}(MeS)C \cdot C(CN) = C = N \cdot SnMe_{3} \\ (CF_{3})_{3}(Me_{3}CC)C(CN) = C = N \cdot SnMe_{3} \\ (CF_{3})_{3}(Me_{3}CC)C(CN) = C = N \cdot SnMe_{3} \\ \end{array}$ Me<sub>3</sub>SiSMe Me<sub>3</sub>SiSMe + + + Me<sub>3</sub>SISMe Me<sub>3</sub>SINPh Me<sub>3</sub>SIH (Me<sub>3</sub>SI)<sub>2</sub>NH Me<sub>3</sub>SnSMe Me<sub>3</sub>SnSMe  $\begin{array}{l} (Cf_{3})_{2}(Me_{2}AS)C C(CN) = C = N \cdot SnMe_{3} \\ (Cf_{3})_{2}(CH_{2} = CH \cdot CH_{2})C \cdot C(CN) = C = N \cdot SnMe_{3} \\ [(Cf_{3})_{2}(Me_{3}C)C \cdot C(CN) = C = N]_{3}B \\ [(Cf_{3})_{2}(Me_{3}C)C \cdot C(CN) = C = N]_{3}B \\ \end{array}$ Me<sub>3</sub>SnAsMe  $(CF_3)_2C = C(CN)_2$  $(CF_3)_2C = C(CN)_2$  $(CF_3)_2C = C(CN)_2$  $3(CF_3)_2C = C(CN)_2$  $Me_3SnCH_2CH = CH$ , (MeS)<sub>3</sub>B +  $(Me_2N)_3B$  $3(CF_3)_2C = C(CN)_2$  $[(CF_3)_2(Me_2N)C \cdot C(CN) = C = N]_3B$ 

 $\dagger$  In this sole case, the insertion reaction appears to be easily reversed, and olefin may be recovered by low-pressure pumping at about 30°.

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With the exception of some of the organotin ketenimines, all of the products undergo rapid alcoholysis and hydrolysis; the non-metalloid product reverting to the dicyano-form: e.g.,

$$(CF_3)_2(MeS)C \cdot C(CN) = C = N \cdot SiMe_3 + MeOH \rightarrow Me_3SiOMe +$$

 $(CF_3)_2(MeS)C \cdot CH(CN)_2 \leftarrow \{(CF_3)_2(MeS)C \cdot C \cdot (CN) = C = NH\}$ 

These alcoholysis products have been characterised by analysis, mass spectra, and n.m.r. spectra; and they show a complete loss of the intense C=C=N chromophore in the u.v. spectrum. Hydrolysis of the trimethylsilane adduct produces  $(CF_3)_2HC \cdot CH(CN)_2$ , the overall reaction thus effecting a mild<sup>7</sup> and convenient hydrogenation of  $(CF_3)_2$ - $C = C(CN)_2$ .

All of the reactions proceed under mild conditions,



though more rapidly when impurities are present, e.g., a



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