The 1,4-Insertion Reactions of 1,1-Bis(perhalogenomethyl)-2,2-dicyanoethylenes to Produce Ketenimines

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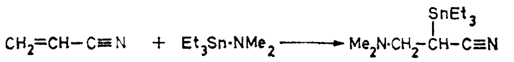
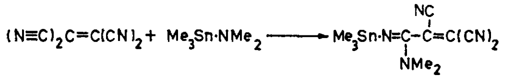
The two olefins $(CF_3)_2C{=}C(CN)_2$ and $(CF_3)(CF_2Cl)C{=}C(CN)_2$ undergo reaction with a wide variety of organometallic compounds by a 1,4-addition. The products are ketenimines, and in this way a good range of ketenimino-derivatives of silicon, germanium, tin, and boron have been synthesised. The spectral properties and chemical reactions of these metal and metalloid ketenimines are reported.

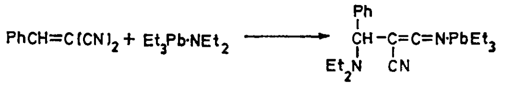
THE study of the addition reactions of cyano-olefins to organometallic compounds is of particular interest because of the variety of reactions reported. Thus cyanoethylene undergoes addition[1] simply across the olefin double-bond as illustrated in equation (1); and in contrast tetracyanoethylene is reported[1] in certain cases to add simply across the cyano-group, as illustrated in equation (2). In the case of 1-phenyl-2,2-dicyanoethylene, however, both the olefin and the cyanide are utilised[2] to bring about a 1,4-addition as illustrated in equation (3).



$$CH_2{=}CH{-}C{\equiv}N + Et_3Sn{\cdot}NMe_2 \longrightarrow Me_2N{\cdot}CH_2{-}\overset{SnEt_3}{CH}{-}C{\equiv}N \qquad (1)$$

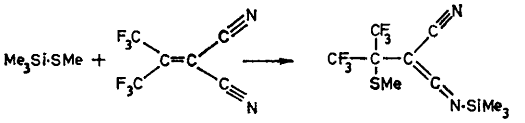


$$(N{\equiv}C)_2C{=}C(CN)_2 + Me_3Sn{\cdot}NMe_2 \longrightarrow Me_3Sn{\cdot}N{=}\underset{NMe_2}{C}{-}\overset{NC}{C}{=}C(CN)_2 \qquad (2)$$



$$PhCH{=}C(CN)_2 + Et_3Pb{\cdot}NEt_2 \longrightarrow \underset{Et_2N}{\overset{Ph}{CH}}{-}\underset{CN}{C}{=}C{=}N{\cdot}PbEt_3 \qquad (3)$$

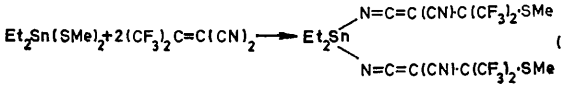
We have found the two perhalogenocyano-olefins 1,1-bis(trifluoromethyl)-2,2-dicyanoethylene[3] and 1-trifluoromethyl-1-chlorodifluoromethyl-2,2-dicyanoethylene to be exceedingly reactive with an extensive range of organometallic compounds, especially organometallic bases. A typical reaction occurs with methylthiotrimethylsilane.



(4)

Evidence for the 1,4-addition and ketenimino-structure of the product is solely spectroscopic. The i.r. spectrum of the addition compound contains a strong band at 2210 cm^{-1} which is characteristic[4] of a conjugated nitrile, such a band would be absent if the addition had taken place 1,2 across the olefin. An even stronger band in the i.r. spectrum at 2140 cm^{-1} is characteristic[5] of alkyl and metal substituted ketenimines. The u.v. spectrum contains an absorption at 229 nm ($\varepsilon = 7 \times 10^3$), which is believed characteristic[6] of the C=C=N chromophore. The n.m.r. spectrum of the MeS group shows the protons as a septet ($J_{F\text{-}H} = 1{\cdot}5$ Hz) confirming the presence of the $(CF_3)_2(MeS)C$ group in the product. Similar spectroscopic properties were noted for all the products reported in Table 1. In addition to these reactions 1,1-bis(trifluoromethyl)-2,2-dicyanoethylene underwent analogous reactions with dimethylaminotrimethylsilane, dimethylarsinotrimethylsilane, tris(methylthio)borane, and tris(dimethylamino)borane, but in each case the reaction was so violent that pure products could not be isolated. From the spectra of the impure materials, however, it would appear the 1,4-addition reactions occurred in these compounds also.

In the case of organometallic bases with more than one reactive bond, it is possible to add the reactive olefins to each of these bonds as illustrated in equations (5) and (6). Nevertheless, it is possible to utilise only one of the available reactive bonds, by using exactly stoicheiometric quantities of reagents as illustrated in equation (7). Here the two different methylthio-groups are clearly differentiated in the n.m.r. spectrum.



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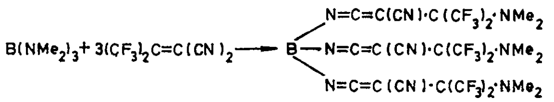

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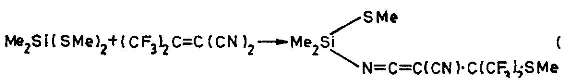

(7)

Although allyl- and methallyl-trimethyltins gave the expected 1,4-linear insertion product analogous to those reported above, cyclopentadienyltrimethylsilane gave a 1 : 1 compound with 1,1-bis(trifluoromethyl)-2,2-dicyanoethylene which had none of the characteristics of a ketenimine. From the ^{19}F n.m.r. spectrum it is apparent that the olefin has undergone a Diels–Alder type of addition to the cyclopentadienyl ring, and a mixture of isomers results. The problem of these isomers is especially complex, as in addition to the usual *syn* and *anti* possibilities, a number of other isomers are formed

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[1] T. A. George and M. F. Lappert, *J. Organometallic Chem.*, 1968, **14**, 328.

[2] W. P. Neumann and K. Kuhlein, *Tetrahedron Letters*, 1966, 3423.

[3] W. J. Middleton, *J. Org. Chem.*, 1965, **30**, 1402.

[4] L. J. Bellamy, 'The Infrared Spectra of Complex Molecules,' Methuen, London, 2nd edn., p. 264.

[5] W. Beck, H. S. Smedal, and H. Kohler, *Z. anorg. Chem.*, 1967, **354**, 69.

[6] R. Dijkstra and H. J. Backer, *Rec. Trav. chim.*, 1954, **73**, 575.

due to the prototropic isomerisations in trimethylsilylcyclopentadiene itself, resulting in 1,2- and 5-substituted isomers of this compound.[7,8]

The ketenimino-metalloid derivatives listed in Table 1 are either involatile, colourless viscous liquids or white solids. All were sufficiently soluble in deuteriochloroform to allow n.m.r. measurements, which were all in accord with the proposed structures for these products and are reported in Table 2.

TABLE 1

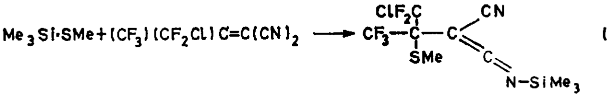
Interaction of organometallic compounds with $(CF_3)_2C{:}C(CN)_2$ and $(CF_3)(CF_2Cl)C{:}C(CN)_2$ to form organometallic ketenimides

Reactants	Product †	Analysis Found (%) C	Found (%) H	Required (%) C	Required (%) H
$Me_3Si{\cdot}SMe + (CF_3)_2C{=}C(CN)_2$	$Me_3SiNCC(CN)C(CF_3)_2SMe$	35·6	3·5	35·9	3·6
$Me_3Si{\cdot}SMe + (CF_3)(CF_2Cl)C{=}C(CN)_2$	$Me_3SiNCC(CN)C(CF_3)(CF_2Cl)SMe$	34·0	3·3	34·2	3·4
$Me_3Si{\cdot}SPh + (CF_3)_2C{=}C(CN)_2$	$Me_3SiNCC(CN)C(CF_3)_2SPh$	45·6	3·5	45·5	3·5
$Me_2Si(SMe)_2 + (CF_3)_2C{=}C(CN)_2$	$Me_2Si(SMe)NCC(CN)C(CF_3)_2SMe$	32·8	3·1	32·8	3·3
$Me_3Si{\cdot}NHPh + (CF_3)_2C{=}C(CN)_2$	$Me_3SiNCC(CN)C(CF_3)_2NHPh$	47·5	4·2	47·5	4·0
$Me_3SiH + (CF_3)_2C{=}C(CN)_2$	$Me_3SiNCC(CN)C(CF_3)_2H$ ‡				
$Me_3SiH + (CF_3)(CF_2Cl)C{=}C(CN)_2$	$Me_3SiNCC(CN)C(CF_3)(CF_2Cl)H$	34·9	3·0	35·4	3·3
$Me_3Sn{\cdot}SMe + (CF_3)_2C{=}C(CN)_2$	$Me_3SnNCC(CN)C(CF_3)_2SMe$ [a]	28·3	3·1	28·3	2·8
$Me_3Sn{\cdot}SMe + (CF_3)(CF_2Cl)C{=}C(CN)_2$	$Me_3SnNCC(CN)C(CF_3)(CF_2Cl)SMe$ [b]	27·0	2·8	27·2	2·7
$Et_2Sn(SMe)_2 + 2(CF_3)_2C{=}C(CN)_2$	$Et_2Sn[NCC(CN)C(CF_3)_2SMe]_2$ [c]	31·1	2·0	30·9	2·3
$Me_3Sn{\cdot}AsMe_2 + (CF_3)_2C{=}C(CN)_2$	$Me_3SnNCC(CN)C(CF_3)_2AsMe_2$ [d]	26·6	3·2	27·4	3·1
$Me_3SnC_3H_5 + (CF_3)_2C{=}C(CN)_2$	$Me_3SnNCC(CN)C(CF_3)_2C_3H_5$	34·3	3·3	34·4	3·3
$Me_3Sn{\cdot}C_4H_7 + (CF_3)_2C{=}C(CN)_2$	$Me_3SnNCC(CN)C(CF_3)_2C_4H_7$ [e]	36·0	3·8	36·3	3·7
$Bu^n{}_3Ge{\cdot}NMe_2 + (CF_3)_2C{=}C(CN)_2$	$Bu^n{}_3GeNCC(CN)C(CF_3)_2NMe_2$	48·4	7·1	48·0	6·6
$B(NMe_2)_3 + 3(CF_3)_2C{=}C(CN)_2$	$B[NCC(CN)C(CF_3)_2NMe_2]_3$	36·9	2·5	36·7	2·3
$Ph_2BCl + (CF_3)_2C{=}C(CN)_2$	$Ph_2BNCC(CN)C(CF_3)_2Cl$	52·3	3·0	52·2	2·4
$Me_3Si(\pi\text{-}C_5H_5) + (CF_3)_2C{=}C(CN)_2$	$Me_3Si(\pi\text{-}C_5H_5)(CF_3)_2C{=}C(CN)_2$ §	47·4	4·4	47·7	4·0
$(Me_3Si)_2S + (CF_3)_2C{=}C(CN)_2$	$(Me_3Si)_2S(CF_3)_2C{=}C(CN)_2$ *	36·6	3·4	36·7	4·1

[a] M.p. 145—147°. [b] M.p. 127—128°. [c] M.p. 143°. [d] M.p. 120°. [e] M.p. 91°.

* Not ketenimide, possibly a charge-transfer complex. † All yields were virtually quantitative. ‡ Spectroscopic characterisation only. § Diels–Alder adduct, not ketenimide.

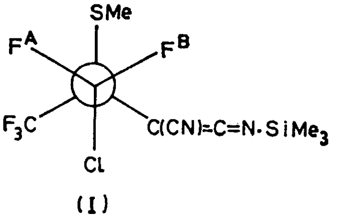
Of particular interest are the ^{19}F n.m.r. spectra of the addition products from 1-trifluoromethyl-1-chlorodifluoromethyl-2,2-dicyanoethylene. As illustrated in



(8)

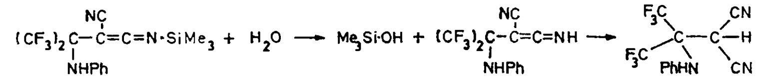
equation (8) addition of this olefin invariably results in the generation of an asymmetric carbon atom. In turn this renders the two fluorine atoms of the chlorodifluoromethyl group non-equivalent as illustrated in (I). Thus the ^{19}F spectra of these compounds have a complex ABX_3 pattern for the fluorine atoms of the CF_2Cl group. The values of J_{AB} and δ_{AB} for these non-equivalent fluorines have been calculated from the ABX_3 spectra by a previously reported method,[9] and are noted in Tables 2 and 3.

The reported ketenimines of boron and silicon are readily attacked by both water and alcohol at the nitrogen-metalloid bond. The ketenimines formed in



(I)

such reactions undergo instant rearrangement to the isomeric dinitriles as illustrated in equations (9) and (10).



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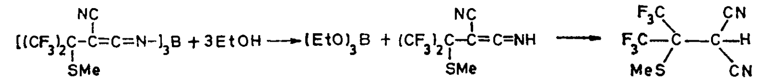

(10)

A number of the dicyanoalkanes prepared by such hydrolyses and alcoholyses are characterised in Table 3. The use of heavy water or a deuterio-alcohol allows placement of a deuterium atom upon the dicyano-carbon atom of the alkane.

If the original addition to the olefin is carried out with trimethylsilane, hydrolysis of the addition product gives the alkane, which overall represents a convenient

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[7] C. S. Kraihanzel and M. L. Losee, *J. Amer. Chem. Soc.*, 1968, **90**, 4701.

[8] A. J. Ashe III, *J. Amer. Chem. Soc.*, 1970, **92**, 1233.

[9] E. W. Abel, M. A. Cooper, R. J. Goodfellow, and A. J. Rest, *Trans. Faraday Soc.*, 1969, 1967.

TABLE 2

N.m.r. spectra of organometallic ketenimides formed by 1 : 4-cyano-olefin insertions

Compound	^{19}F (Upfield from CFCl$_3$)		^{1}H (τ)
$Me_3SiNCC(CN)C(CF_3)_2SMe$	CF_3 67·9		$Si(CH_3)_3$ 9·55 (singlet) SCH_3 7·61 heptet J_{F-H} = 1·5 Hz
$Me_3SiNCC(CN)C(CF_3)(CF_2Cl)SMe$	† CF_3 65·2 J_{AB} = 164 Hz	CF_2 52·1 S_{AB} = 1·64 p.p.m.	$Si(CH_3)_3$ 9·57 (singlet) SCH_3 7·52 hextet J_{F-H} = 1·4 Hz
$Me_3SiNCC(CN)C(CF_3)_2SPh$	CF_3 67·0		$Si(CH_3)_3$ 9·66 (singlet); SPh 2·1—2·8 multiplet
$Me_3SiNCC(CN)C(CF_3)(CF_2Cl)SPh$	† CF_3 64·2 J_{AB} = 134 Hz	CF_2 51·2 S_{AB} = 0·41 p.p.m.	$Si(CH_3)_3$ 9·62 (singlet); SPh 2·1—2·6 (multiplet)
$Me_3SiNCC(CN)C(CF_3)_2NMe_2$	CF_3 66·9		$Si(CH_3)_3$ 9·57 (singlet); $N(CH_3)_2$ 7·39 (broad)
$Me_3SiNCC(CN)C(CF_3)_2NHPh$	CF_3 72·0		$Si(CH_3)_3$ 9·78 (singlet); NH 5·6 (broad) NPh 2·3—3·5 (broad)
$Me_3SiNCC(CN)C(CF_3)_2AsMe_2$			$Si(CH_3)_3$ 9·50; $As(CH_3)_2$ 8·50
$Me_3SiNCC(CN)C(CF_3)_2H$	CF_3 68·4 Doublet J_{FH} = 7 Hz		$Si(CH_3)_3$ 9·8 CH 6·7 (heptet) J_{F-H} = 7 Hz
$Me_3SiNCC(CN)C(CF_3)(CF_2Cl)H$	† CF_3 66·8	CF_2 54·5 J_{F-H} = 8 Hz J_{AB} = 172 Hz S_{AB} = 3·16 p.p.m.	$Si(CH_3)_3$ 9·56; CH 5·9—6·65 multiplet
$Me_2Si(SMe)NCC(CN)C(CF_3)_2SMe$	CF_3 67·9		$Si(CH_3)_2$ 9·32; $Si-SCH_3$ 7·57 $(CF_3)_2CSCH_3$ 7·32 (heptet); J_{F-H} = 1 Hz
$Me_2Si[NCC(CN)C(CF_3)_2SMe]_2$	CF_3 67·8		$Si(CH_3)_2$ 9·17; SCH_3 7·56; J_{F-H} = 1 Hz
$Me_3SnNCC(CN)C(CF_3)_2SMe$	CF_3 68·3		$Sn(CH_3)_3$ 9·39; J_{Sn} 117_{-C-H} 68·5 Hz J_{Sn} 119_{-C-H} 71·5 Hz; SCH_3 7·69 (multiplet)
$Me_3SnNCC(CN)C(CF_3)(CF_2Cl)SMe$	CF_3 65·4	CF_2 52·0	$Sn(CH_3)_3$ 9·37; J_{Sn} 117_{-C-H} 72 Hz; J_{Sn} 119_{-C-H} 74 Hz; SCH_3 7·64 (multiplet)
$Et_2Sn[NCC(CN)C(CF_3)_2SMe]_2$	CF_3 67·2		
$Bu^n{}_3GeNCC(CN)C(CF_3)_2NMe_2$	CF_3 66·8		NMe_2 7·36 (heptet); J_{F-H} = 1·5 Hz Bu^n 8·53—9·16 (multiplet)
$Me_3SnNCC(CN)C(CF_3)_2AsMe_2$	CF_3 62·6		$Sn(CH_3)_3$ 9·45; J_{Sn} 1117_{-C-H} 68·5; J_{Sn} 119_{-C-H} 71·5 Hz $As(CH_3)_2$ 8·68
$Me_3SnNCC(CN)C(CF_3)_2C_3H_5$	CF_3 70·0		$Sn(CH_3)_3$ 9·4; J_{Sn} 117_{-C-H} 72·5 Hz; J_{Sn} 119_{-C-H} 74·5 Hz $SnCH_2$ 7·45 (doublet); $-CH=CH_2$ 3·8—5·2 (multiplet)
$Me_3SnNCC(CN)C(CF_3)_2CH_2C(CH_3)=CH_2$	CF_3 69·9		$Sn(CH_3)_3$ 9·4; $C-CH_3$ 8·09; $SnCH_2$ 7·5; $C=CH_2$ 5·02
$(Me_3Si)_2S\cdot(CF_3)_2C=C(CN)_2$			$Si(CH_3)_3$ 9·6
$PhB[NCC(CN)C(CF_3)_2SMe]_2$	CF_3 68·3		$S(CH_3)$ 7·75; Ph 2·64
$Ph_2BNCC(CN)C(CF_3)_2SMe$	CF_3 68·2		$S(CH_3)$ 7·92; Ph 2·72
$Ph_2BNCC(CN)C(CF_3)_2Cl$	CF_3 73·4		Ph 2·0—2·8
$Me_3Si(\pi-C_5H_5)\cdot(CF_3)_2C=C(CN)_2$ *	CF_3 57·5 Broad quartet		$Si(CH_3)_3$ 10·3 (+ small peak at 9·75)
	CF_3 62·5 Sharp quartet		Ring protons 3·62, 6·04, 6·47

* Diels–Alder product, not a ketenimide. † F_A and F_B are the non-equivalent fluorine atoms.

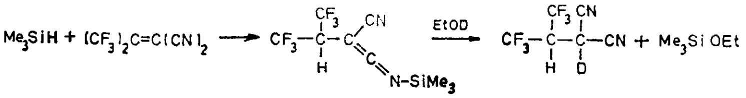
TABLE 3

Substituted ethanes formed by hydrolysis and subsequent rearrangement of organometallic ketenimides

	Analysis					
	Found (%)		Calc. (%)			
Product	C	H	C	H	^{19}F (Upfield from CFCl$_3$)	^{1}H (τ)
$(CF_3)_2CHCH(CN)_2$	33·5	1·6	33·3	0·9	CF_3 65·5 Doublet J_{F-H} = 7 Hz	$(CN)_2CH$ 5·29 (doublet); J_{H-H} = 3 Hz
$(CF_3)(CF_2Cl)CHCH(CN)_2$	31·3	2·3	31·0	0·9	CF_3 64·1 CF_2 52·1	$(CN)_2CH$ 4·92 (doublet); J_{H-H} = 4 Hz $(CF_3)(CF_2Cl)CH$ 5·35—5·95 (multiplet)
$(CF_3)_2C(SMe)CH(CN)_2$ [a]	31·9	1·6	32·1	1·5	CF_3 67·6	$S(CH_3)$ 7·48 (heptet); J_{F-H} = 1·5 Hz CH 5·52
$(CF_3)(CF_2Cl)C(SMe)CH(CN)_2$ [b]	30·0	1·4	30·2	1·4	CF_3 63·4 J_{AB} 184 Hz CF_2 50·8	$S(CH_3)$ 7·45 (hextet); J_{F-H} = 1·4 Hz CH 5·21
$(CF_3)_2C(SPh)CH(CN)_2$	44·1	1·9	44·3	1·9	CF_3 64·2	SPh 2·15—2·55; CH 5·64
$(CF_3)(CF_2Cl)C(SPh)CH(CN)_2$	42·5	1·8	42·3	1·8	CF_3 62·2 CF_2 49·1	SPh 2·1—2·5; CH 5·58
$(CF_3)_2C(NHPh)CH(CN)_2$ [c]	46·6	2·6	46·9	2·3	CF_3 65·0	CH 5·0 (broad); N–Ph 2·6—3·6
$(CF_3)(CF_2Cl)C=C(CN)_2$ [d]	31·2		31·2		CF_3 61·1 CF_2 53·3 J_{F-F} = 10 Hz	

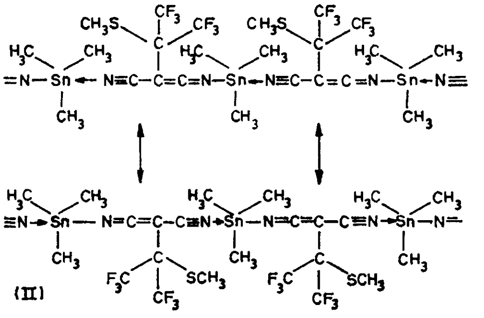
[a] M.p. 29—31°. [b] B.p. 68/0·15 mm. [c] M.p. 104—106°. [d] B.p. 133—135° (this new olefin is characterised for convenience here).

hydrogenation of the original dicyano-alkene. The use of heavy water or a deuterio-alcohol brings about in effect the overall stereospecific addition of HD to the original olefin, as illustrated in equation (11).


(11)

The involatile nature of the ketenimines reported herein is very likely due to the association of the second nitrile group with the metal or metalloid atom of another molecule, giving rise to chains as illustrated in (II).

Such chains appear to break down in solution, and the molecular weight of certain of the ketenimines are dependent upon solution concentration. The interesting possibility of resonance in such chains is illustrated in (II).


(II)

In contrast to the addition compounds of silicon and boron, which are easily hydrolysed as mentioned above, all the tin ketenimines are stable to water. This is analogous to the hydrolytic stability already reported for nitrogen co-ordinated, polymeric five-co-ordinate tin compounds.[10]

EXPERIMENTAL

All reactions, as a matter of course, were conducted under dry nitrogen, and solvents were dried before use. The n.m.r. spectra were run on Perkin-Elmer R10 and Varian HA100 spectrometers, either as neat liquids or as deuteriochloroform solutions. U.v. spectra were obtained on a Unican SP 800 spectrometer. 1,1-Bis(trifluoromethyl)-2,2-dicyanoethylene was prepared by the method of Middleton,[3] and the new olefin 1-trifluoromethyl-1-difluoromethyl-2,2-dicyanoethylene was prepared by an analogous method described below. All other reagents were prepared by literature methods.

Preparation of 1-*Trifluoromethyl*-1-*difluorochloromethyl*-2,2-*dicyanoethylene*.—Malononitrile (20 g), monochloropentafluoroacetone (58 g), and zinc chloride (5 g) were sealed in a heavy-walled glass tube and heated at 80° for 50 h. Phosphorus pentoxide (10 g) was added to the resulting solution, and after being set aside (5 h) volatiles were pumped into a cold trap (−180°). Subsequent distillation of the condensate yielded the required olefin (35%) as characterised in Table 3.

Reactions of Polyhalogenocyano-olefins to Produce Ketenimides (*Table* 1).—The polyhalogenocyano-olefin was added dropwise to the other reactant in the exact stoicheiometric quantity required. Where the reaction was particularly violent, cyclohexane was used as a solvent. After removal of volatiles (25°/0·001 mm), the product was either a viscous non-volatile oil or a white solid. Yields were virtually quantitative.

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[1/1058 *Received*, 25*th June*, 1971]

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