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THE PRINS-TYPE REACTIONS OF MONO- AND 1,1-DISUBSTITUTED ALKENES WITH TRICHLOROACETONITRILE IN THE PRESENCE OF BORON TRICHLORIDE

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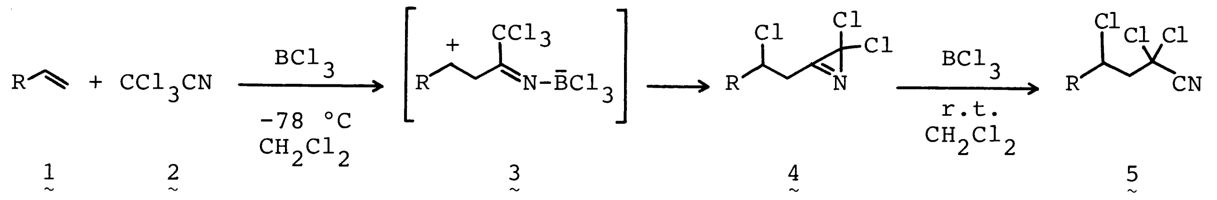
Boron trichloride was found to be a useful Lewis acid for the Prins-type reaction of alkenes with electron-deficient nitriles. In its presence, monosubstituted alkenes react with trichloroacetonitrile, giving dichloroazirine derivatives in high yields. Further exposure of the azirine derivative to boron trichloride at room temperature afforded α,α,γ-trichloroalkylnitrile. The Prins-type acylations of 1,1-disubstituted alkenes with trichloroacetonitrile are also described.

An acid-catalyzed reaction between alkenes and nitriles is usually referred to as the Ritter reaction,$^{1)}$ in which nitriles react as the nucleophile on the alkenes in the presence of an acid or mercuric salt to give acid amides. Reported here, for the first time, is the Prins-type reaction of alkenes with nitriles, in which nitriles serve as the electrophile.

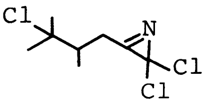
We have found that aniline and phenol undergo ortho-selective Friedel-Crafts-type substitution reactions with nitriles in the presence of boron trichloride (BCl_3)$^{2,3)}$ and the aldol-type reactions of nitriles with aldehydes proceed in the presence of dichlorodiethylaminoborane$^{4)}$ or dialkylboryl triflate.$^{5)}$ Interestingly, these reactions proceed well with these boron compounds but not with other Lewis acids, suggesting that boron-containing Lewis acids have the "nitrilephilic" property.

We applied this combination to the reaction of various alkenes and found that they react with electron-deficient nitriles in the presence of BCl_3. These reac-

Table 1. Type 1 Reaction

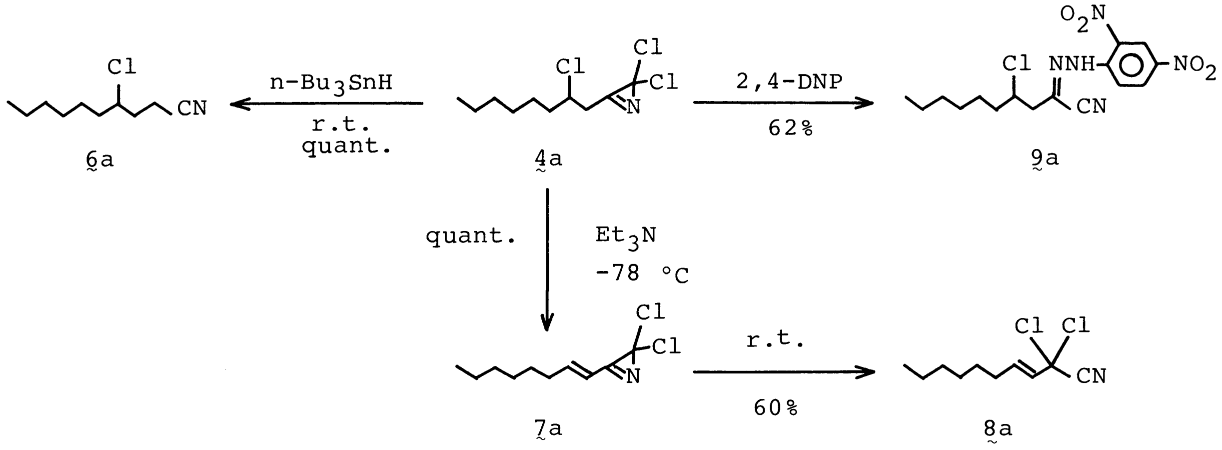


Run	R	Reaction cond. to $\underset{\sim}{4}$	Yield/% $\underset{\sim}{4}$	Reaction cond. to $\underset{\sim}{5}$	Yield/% $\underset{\sim}{5}$
1	n-C_6H_{13}-	-78 °C, 2 h	90	r.t. 16 h	60
2	n-C_4H_9-	-78 °C, 2 h	90	r.t. 16 h	66
3	$(CH_3)_2CHCH_2$-	-78 °C, 2 h	90	r.t. 20 h	77
4	$C_2H_5CH(CH_3)_2$-	-78 °C, 2 h	92	r.t. 14 h	59
5	t-C_4H_9-	-78 °C, 16 h	68[a)]	r.t. 20 h	65
6	$PhCH_2$-	r.t. 15 h[b)]	44	-	18

a)  was obtained in 22% yield. b) No reaction occurred at -78 °C.

tions can be classified into three categories according to the substitution pattern of the alkenes. In this communication, we report on the Type 1 reaction of monosubstituted alkenes with trichloroacetonitrile $\underset{\sim}{2}$ and the Type 2 reaction of 1,1-disubstituted alkenes with $\underset{\sim}{2}$. The Type 3 reaction, which is the ene reaction of trisubstituted alkenes with $\underset{\sim}{2}$ and chloroacetonitrile, will be described in the following papers.[6)]

The Type 1 reaction is an abnormal Prins-type reaction and gives dichloroazirine derivatives[7)] in high yields (Table 1). In the typical procedure for the reaction of 1-octene $\underset{\sim}{1a}$ (R = n-C_6H_{13}) with $\underset{\sim}{2}$, a solution of 2 M BCl_3 in dichloromethane (1.2 ml) was added to a solution of $\underset{\sim}{2}$ (2.4 mmol) in dichloromethane (4.0 ml) at -78 °C under argon. After stirring for 10 min at this temperature, $\underset{\sim}{1a}$ (2.0 mmol) in dichloromethane (4.0 ml) was added, and the mixture was stirred at -78 °C for 2 h. Next, 0.5 M sodium carbonate solution (8.0 ml) was added and the mixture was warmed to 0 °C under stirring. The organic layer was separated, and the aqueous layer was extracted with dichloromethane. The combined dichloromethane extract was washed with sat. brine, dried ($MgSO_4$), and concentrated. The residue was purified by chromatograpy (SiO_2), giving dichloroazirine $\underset{\sim}{4a}$ in 90% yield. When the reaction was carried out at room temperature for 16 h in dichloromethane under argon, α,α,γ-trichloroalkylnitrile $\underset{\sim}{5a}$[8,9)] was obtained in 60% yield. Trichloronitrile $\underset{\sim}{5a}$ was also obtained by exposure of the isolated $\underset{\sim}{4a}$ to BCl_3 in di-

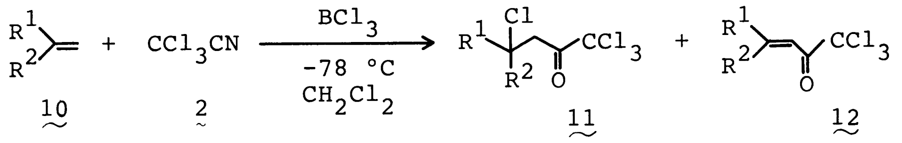


Scheme 1.

chloromethane at room temperature. This type of isomerization of the azirine to nitrile has been reported already.[10)] Using BBr_3 in place of BCl_3 gave the same product 4a, indicating that the chlorine atom at the β-position of 4a originates from the trichloromethyl group of 2. Some derivations of 4a are shown in Scheme 1.[11)]

The Type 2 reaction is the Prins-type acylation, giving α,β-unsaturated ketones and β-chloroketones in high yields (Table 2). In this case, the usual Prins-type reaction takes place through a carbenium ion intermediate. Use of BBr_3 in place of BCl_3 gave β-bromoketone (Run 2), in striking contrast to the Type 1 reaction. Namely, in the Type 2 reaction, the chlorine atom at the β-position

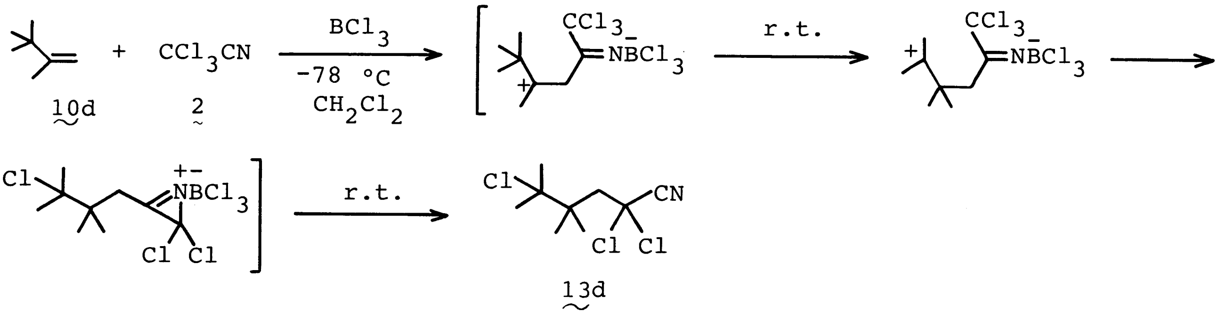
Table 2.



Run		10	Yield/%	11:12[a)]
1	10a	$R^1,R^2=-(CH_2)_5-$	92	80:20
2	"	"	90	80:20[b)]
3	10b	$R^1,R^2=-(CH_2)_3-$	91	86:14
4	10c	$R^1=R^2=C_2H_5$	80	47:53
5	10d	$R^1=t\text{-}C_4H_9$, $R^2=CH_3$	95	0:100
6	10e	$R^1=i\text{-}C_3H_7$, $R^2=CH_3$	83	12:88
7	10f	Limonene	89	0:100
8	10g	Camphene	75	0:100

a) The structure was identified by IR and NMR spectra.

b) The reaction was carried out in the presence of BBr_3 in place of BCl_3. β-Bromoketone was obtained in place of 11.



Scheme 2.

of 11 originates in the BCl_3 group.

In the case of 2,3,3-trimethyl-1-butene 10d, rearrangement of the methyl group took place with the rise in reaction temperature to room temperature from -78 °C, giving α,α,γ-trichloronitrile 13d quantitatively. This compound 13d is considered to be formed via the azirine derivative followed by isomerization as the Type 1 reaction (Scheme 2).

The Prins-type reactions reported here proceeds well only with BCl_3 or BBr_3 and not with other Lewis acids such as $AlCl_3$, $TiCl_4$, or $BF_3 \cdot OEt_2$. Unsuitable solvents were ether, THF, and benzene, and successful results were obtained in dichloromethane and chloroform.

References
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5) H. Hamana and T. Sugasawa, Chem. Lett., 1982, 1401.
6) H. Hamana and T. Sugasawa, Chem. Lett., following paper in this issue.
7) For example, 4a: IR ($CHCl_3$), 1760 cm^{-1} ($-\overset{Cl\ Cl}{\times}\!\!C{=}N$); ^1H-NMR ($CDCl_3$) δ 0.8-2.1 (n-C_6H_{13}), 3.42 (d, 2H, $-CH_2-$, J = 6 Hz), 4.30 (dq, 1H, -CHCl-, J = 6 Hz); ^{13}C-NMR ($CDCl_3$) δ 182 ($-\overset{Cl\ Cl}{\times}\!\!C{=}N$), 67 ($-CCl_3-$), 65 (-CHCl-).
8) The structure was identified by comparison with an authentic sample.[9)]
9) S. Murai and S. Tsutsumi, J. Org. Chem., 31, 3000 (1966).
10) L. Henn, D.M.B. Hickey, C.J. Moody, and C.W. Rees, J. Chem. Soc., Perkin Trans. 1, 1984, 2189.
11) The structures of 6a, 7a, 8a, and 9a were identified by IR and NMR spectra and elemental analyses.

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