

THE ENE REACTION OF TRISUBSTITUTED ALKENES WITH ELECTRON-DEFICIENT  
NITRILES IN THE PRESENCE OF BORON TRICHLORIDE

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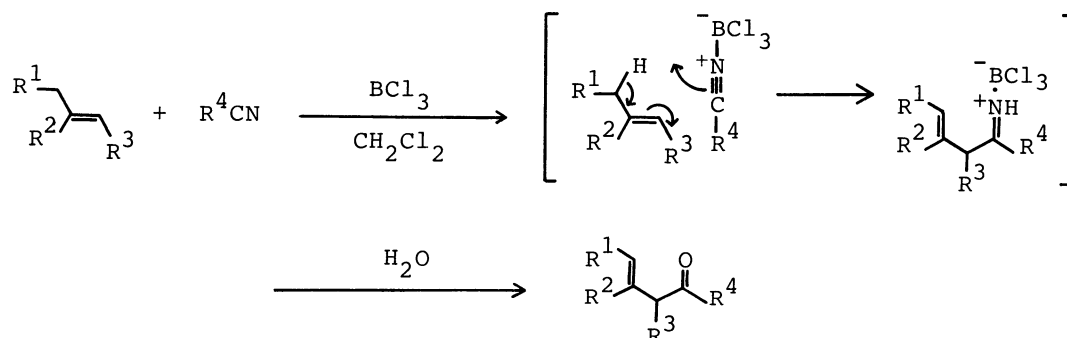
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The ene reaction of trisubstituted alkenes with electron-deficient nitriles proceeds smoothly in the presence of boron trichloride to afford  $\beta,\gamma$ -unsaturated ketones in high yields. Investigation of the stereochemistry of the ene products suggests that this ene reaction is a concerted one. Similar reactions of cyclic trisubstituted alkenes are also described.

Although the ene reaction is one of the simplest and most versatile reactions in organic chemistry like the related Diels-Alder reaction, it is less known because of its high activation energy.<sup>1)</sup> Since the enophile, like the dienophile in the Diels-Alder reaction, should be electron-deficient, complexation of Lewis acids to enophiles containing basic groups should accelerate the ene reaction. Recently, Snider found that the ene reaction of aldehydes proceeds well in the presence of  $\text{Me}_2\text{AlCl}$ .<sup>2)</sup> Reported here, for the first time, is the ene reaction of nitriles.

In the preceding paper, we reported that monosubstituted and 1,1-disubstituted alkenes react with trichloroacetonitrile in the presence of boron trichloride ( $\text{BCl}_3$ ) (Type 1 and 2 reactions, respectively).<sup>3)</sup> In this communication, we report on the Type 3 reaction of trisubstituted alkenes with trichloroacetonitrile 2 and chloroacetonitrile 3 in the presence of  $\text{BCl}_3$ . This first example of the ene reaction of nitriles gave  $\beta,\gamma$ -unsaturated ketones in high yields (Table 1). Chloroacetonitrile 3 reacted as smoothly as trichloroacetonitrile 2, but the reaction of aliphatic nitriles was unsuccessful. The procedure was similar to that reported for the Type 1 reaction of monosubstituted alkenes with 2.<sup>3)</sup> In

Table 1. Type 3 Reaction (The Ene Reaction)



Run	Alkene	R <sup>4</sup>	Reaction conditions	Product <sup>a)</sup>	Yield/%	B <sub>p</sub> /°C (mmHg)
1		CCl <sub>3</sub>	-78 °C, 2 h		72	46-49 (3)
2	"	CCl <sub>3</sub>	-78 °C, 2 h		70 <sup>b)</sup>	—
3	"	CH <sub>2</sub> Cl	r.t. 20 h		74	63 (10)
4		CCl <sub>3</sub>	-78 °C, 2 h		76	92 (7.5)
5	"	CH <sub>2</sub> Cl	4.5. 20 h		70	91 (17)
6		CCl <sub>3</sub>	-78 °C, 2 h		74	42-44 (0.2)
7	"	CH <sub>2</sub> Cl	r.t. 20 h		70	94-95 (18)
8		CCl <sub>3</sub>	-78 °C, 2 h		74	58 (2)
9	"	CH <sub>2</sub> Cl	r.t. 20 h		71	76 (9)
10		CCl <sub>3</sub>	-78 °C, 2 h		74	50 (0.17)
11	"	CH <sub>2</sub> Cl	r.t. 20 h		72	81-82 (9.5)
12		CCl	-78 °C, 2 h		13	—

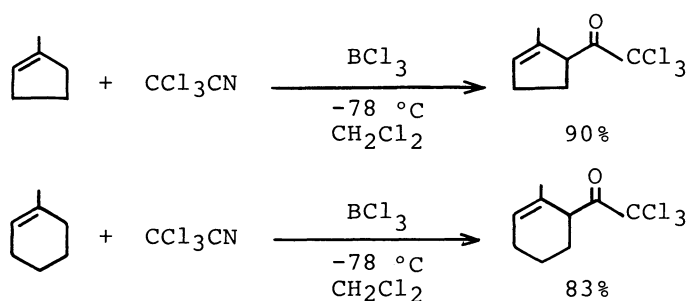
a) The structures were identified by IR and NMR spectra and elemental analyses.

b) The reaction was carried out in the presence of Na<sub>2</sub>CO<sub>3</sub> powder.

the reaction of **3**, the ene products could be obtained by stirring the reaction mixture at room temperature for 16 h.

From the standpoint of the reaction mechanism, the term "ene reaction" is ambiguous. It has sometimes been used to refer not only to those reactions which are concerted, but also to a reaction which forms an ene product, be it by a stepwise or concerted process. Snider concluded that in the ene reaction of aldehydes catalyzed by  $\text{Me}_2\text{AlCl}$ , a zwitterionic intermediate is formed.<sup>2)</sup> Support for this zwitterionic mechanism came from the formation of chloroalcohols. However, in our case, the reaction must be concerted, because the reactions of (E)- and (Z)-3-methyl-2-pentenes and (E)- and (Z)-3,4-dimethyl-2-pentenes with **2** and **3** proceed with exclusive stereoselectivity (Runs 4, 5, 6, 7, 10, 11, and 12). In these reactions, the exclusive abstraction of a hydrogen from the alkyl group syn to the vinylic hydrogen took place and no chlorinated products were obtained. Furthermore, no reaction of tetrasubstituted alkenes with **2** occurred. These results suggest that the abstraction of a hydrogen from the alkyl group anti to the vinylic hydrogen is completely hindered sterically and that these reactions are concerted. Consequently, in the reaction of (Z)-2,3-dimethyl-2-pentene, the ene product was produced in a low yield, because it can only donate its crowded isopropyl hydrogen (Run 12).

In the reaction of cyclic trisubstituted alkenes, only trichloroacetonitrile could react and  $\beta,\gamma$ -unsaturated ketones were obtained in high yields (Scheme 1). These results are analogous to those reported for the  $\text{ZnCl}_2$ -catalyzed Friedel-Crafts acylation of cyclic alkenes with acetic anhydride.<sup>4)</sup> In this case, it cannot be concluded whether the reaction proceeds via a stepwise mechanism with a zwitterionic intermediate or a concerted mechanism.



Scheme 1.

In this ene reaction only  $\text{BCl}_3$  and  $\text{BBr}_3$  could be used and the suitable solvents were dichloromethane and chloroform. Using other Lewis acids and other solvents did not give successful results. Studies on the synthetic utility of the ene products are now in progress.

#### References

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