

ADDITION REACTIONS OF THE TRICHLOROCYCLOPROPENYL IUM ION WITH ALKENES:  
 A NOVEL ACCESS TO CYCLOPROPENE AND CYCLOPROPENONE DERIVATIVES<sup>1</sup>

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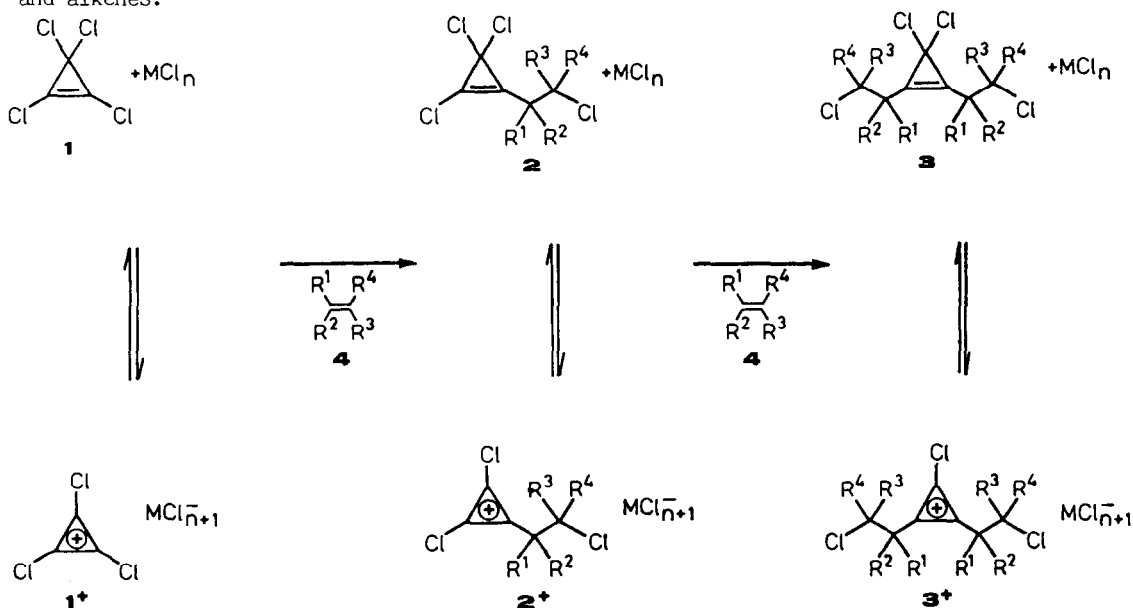
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**Summary:** Trichlorocyclopropenyl cation  $1^+$ -AlCl<sub>4</sub><sup>-</sup> reacts with alkenes in nitromethane at -35°C to give the 1:1 addition products  $2^+$ -AlCl<sub>4</sub><sup>-</sup>, which can be converted into the 2-chlorocyclopropenones **5** or the α,β-acetylenic carboxylates **6**.

Tetrachlorocyclopropene **1**, which is readily accessible from sodium trichloroacetate and trichloroethylene [2], reacts with typical alkenes under thermal conditions to give 1-chloro-1-(trichlorovinyl)-cyclopropane derivatives [3]. These products are formed *via* initial ring cleavage of **1** and successive [2+1] cycloaddition of the intermediate perchlorovinylcarbene [3]. Electrophilic additions of **1** only happen with bicyclopropylidene [4], tetraethoxyethylene, and alkenes of comparable high nucleophilicity [5]. In dichloromethane, the trichlorocyclopropenyl cation salts  $1^+$ -AlCl<sub>4</sub><sup>-</sup> or  $1^+$ -SbCl<sub>6</sub><sup>-</sup>, which are obtainable from **1** [6], give only 2:1 or 3:1 products with trichloroethylene, isobutene, 2-butene, or tetramethylethylene [5-8]. We now report on the selective formation of 1:1 adducts from  $1^+$  and alkenes.










The addition of  $1 \rightleftharpoons 1^+$  to **4** initially yields the 1:1 addition products  $2 \rightleftharpoons 2^+$ . Now the products  $2 \rightleftharpoons 2^+$  and the reactants  $1 \rightleftharpoons 1^+$  will compete for the alkene **4**, and the yield of 1:1 products will depend on the relative reactivity of these two couples. From a general analysis of such systems [9] one can derive that in this case the formation of the 1:1 products should be favoured, if an at least equivalent amount of a completely ionising Lewis acid is employed. Under such conditions, the carbenium ion  $1^+$  can be expected to be more reactive than  $2^+$  which is stabilized by an alkyl group.

However, only the 2:1 product  $3e^+$  was formed, when 0.5 - 1 equivalents of **4e** were added to a suspension of  $1^+-AlCl_4^-$  in dichloromethane. Like the results of Weiss [7], this observation can be explained by the low solubility of  $1^+-AlCl_4^-$  in  $CH_2Cl_2$ , which reduces the chance of  $1^+$  to react with **4**. Consequently, the better soluble  $2e^+$  reacts preferentially so that  $3e^+$  is formed.

Under homogeneous conditions, the expected results are obtained, however. When 0.5 equivalents of the alkenes **4a-g** are added dropwise to solutions of  $1^+-AlCl_4^-$  in nitromethane at  $-35^\circ C$ , the salts  $2^+-AlCl_4^-$  are formed exclusively. Addition of solid LiCl at ambient temperature yields the trichlorocyclopropenes **2a-g**, which can be extracted from the nitromethane solution with hexane (Tab. 1).

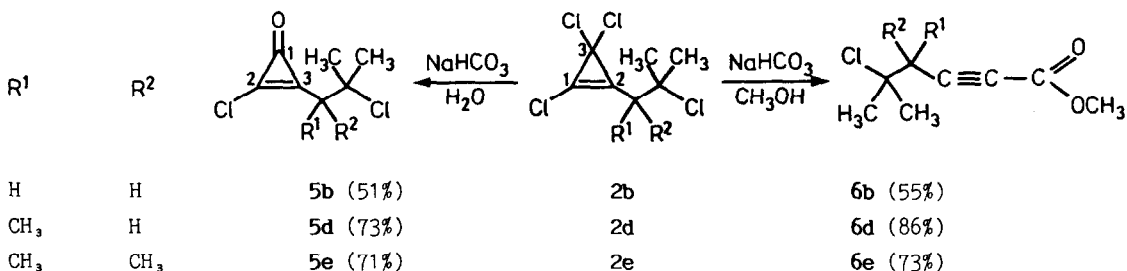
Table 1. 1,3,3-Trichlorocyclopropenes **2a-g** via  $AlCl_3$ , Initiated Addition of Tetrachlorocyclopropene **1** towards the Alkenes **4a-g**.

Alkene	Product (% Yield)	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	IR (cm <sup>-1</sup> )	<sup>13</sup> C NMR (δ)		
							C-1	C-2	C-3
 <b>4a</b>	<b>2a</b> (41)	H	H	H	CH <sub>3</sub>	1800	126.35	129.14	60.88
 <b>4b</b>	<b>2b</b> (51)	H	H	CH <sub>3</sub>	CH <sub>3</sub>	1820	126.46	129.43	65.14
 <b>4c</b>	<b>2c</b> (59)	H	H	CH <sub>3</sub>	C <sub>3</sub> H <sub>7</sub>	1816	126.41	129.48	61.15
 <b>4d</b>	<b>2d</b> (60)	CH <sub>3</sub>	H	CH <sub>3</sub>	CH <sub>3</sub>	1805	125.41	132.94	61.16
 <b>4e</b>	<b>2e</b> (56)	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	1802	124.15	135.89	61.33
 <b>4f</b>	<b>2f</b> (28)	H	H	-(CH <sub>2</sub> ) <sub>5</sub> -		1802			
 <b>4g</b>	<b>2g</b> (53)	H	-(CH <sub>2</sub> ) <sub>4</sub> -		CH <sub>3</sub>	1809	125.14	132.25	61.12

Compound **2e** was obtained in similar yield from **1** and **4e** in nitromethane, when  $\text{AlCl}_3$  was replaced by equimolar amounts of  $\text{SnCl}_4$ ,  $\text{BCl}_3$ , or  $\text{TiCl}_4$ . Its yield decreased, however, when only catalytic amounts of these Lewis acids or when catalytic or equimolar amounts of the weak Lewis acid  $\text{ZnCl}_2$  were employed.

Stirring of the cyclopropenes **2** with aqueous bicarbonate solution gave the cyclopropenones **5**, which are characterized by IR absorptions at  $1840 - 1862$  and  $1630 - 1635 \text{ cm}^{-1}$  and  $^{13}\text{C}$  NMR absorptions at  $\delta 165 - 168$  (s) and  $137 - 151$  (2 s) [10].

On the other hand, ring opening between  $\text{C}^2$  and  $\text{C}^3$  and successive elimination of  $\text{Cl}^-$  takes place when the trichlorocyclopropenes **2** are treated with a suspension of  $\text{NaHCO}_3$  in methanol. The acetylene carboxylic esters **6** thus formed show characteristic infrared bands at  $2220 - 2235$  and  $1710 - 1720 \text{ cm}^{-1}$  [11].



The formal insertion of an alkene molecule into a vinylic C-Cl bond of tetrachlorocyclopropene, which can easily be achieved by the procedure described in this letter, opens new perspectives for the use of **1** as a  $\text{C}_3$  building block [12]. Scope and limitations of this reaction are currently investigated.

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## REFERENCES AND NOTES

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- [10] IR (film): **5b**: 1842, 1636  $\text{cm}^{-1}$ . **5d**: 1862, 1636  $\text{cm}^{-1}$ . **5e**: 1861, 1631  $\text{cm}^{-1}$ .  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): **5b**:  $\delta$  32.45 (q), 43.09 (t), 64.94 (s), 140.20 (s), 151.21 (s), 161.40 (s). **5d**:  $\delta$  13.41 (q), 30.22 (q), 30.91 (q), 46.94 (d), 68.98 (s), 139.21 (s), 150.90 (s), 165.43 (s). **5e**:  $\delta$  22.15 (q), 28.67 (q), 48.75 (s), 72.88 (s), 137.27 (s), 150.46 (s), 168.74 (s).
- [11] IR (neat): **6b**: 2236, 1718  $\text{cm}^{-1}$ . **6d**: 2235, 1719  $\text{cm}^{-1}$ . **6e**: 2223, 1713  $\text{cm}^{-1}$ .  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): **6b**:  $\delta$  31.79 (q), 36.40 (t), 52.60 (q), 65.98 (s), 75.18 (s), 84.46 (s), 153.72 (s). **6d**:  $\delta$  15.80 (q), 29.07 (q), 30.92 (q), 39.74 (d), 52.47 (q), 69.88 (s), 74.92 (s), 88.86 (s), 153.72 (s). **6e**:  $\delta$  24.75 (q), 29.07 (q), 41.54 (s), 52.60 (q), 73.89 (s), 74.35 (s), 92.79 (s), 154.01 (s).
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