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$AlCl_3$-INDUCED REACTIONS OF VINYLCYCLOPROPANES

DIMERIZATIONS AND ADDITIONS WITH REARRANGEMENT

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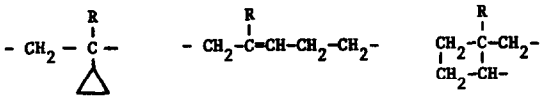
Abstract—1,1-ethano-2-methylenecyclohexane **5**, 1,1,3,3-diethano-2-methylenecyclohexane **6**, α-cyclopropylstryene **7** and its *p*-chloro and *p*-methoxy derivatives **8** and **9**, 1-methyl-1-cyclopropylethylene **10**, and 1,1-dicyclopropylethylene **11** were subjected to the action of $AlCl_3 \cdot OEt_2$ **4** in ether. Monomeric (**12–15**) and dimeric (**16, 17**) homoallylic chlorides as well as some polymeric products were obtained. The mechanism and substituents effects are discussed and spectral data (IR, PMR and MS) of the products are presented.

The reactivity of vinylcyclopropane systems towards Lewis acids has been described in the context of cationic polymerization.[1-7] Ring retained structures (**1**) from 1,2-addition and homoallylic (**2**) and cyclobutanic (**3**) structures from rearranging cyclopropylcarbinyl cations were found, and their distribution in various polymers correlated to electronic and steric properties of the substituents R, both in the starting monomers and in the intermediate cations.



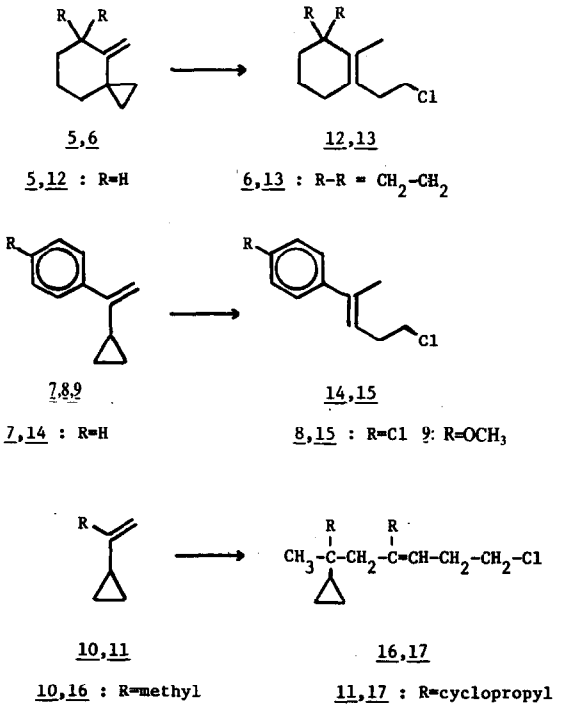
1 **2** **3**

The total conversions reported range from trace to over 90%, but complete material balance is ordinarily missing. In particular no reference is made to survival of monomeric species, whether in their initial form or as transformed products.

This study describes formation of non-polymeric products from reactions of a number of vinylcyclopropane systems with aluminium chloride etherate (**4**) in etheral solution. **4** was intentionally chosen because of accessibility in pure form,[8] with exclusion of HCl. The ether is bound to suppress polymerization by interacting both with the catalyst and with the growing chain.[9] The reagent in this solvent consists of monomeric 1:1-complex of $AlCl_3$ and diethylether.[10,11]

Equimolar quantities of a vinylcyclopropane compound and **4** were stirred at room temperature under nitrogen and strict anhydrous conditions until the organic reactant disappeared in the gas-chromatogram. No product showed in the chromatogram at this stage. The mixture was then poured into large excess of Na_2CO_3 solution, and, after extraction and drying, the product was separated by preparative GLC. This study included the following substrates: 1,1 - ethano - 2 - methylenecyclohexane (**5**), 1,1,3,3 - diethano - 2 - methylenecyclohexane (**6**), 1 - phenyl - 1 - cyclopropylethylene (**7**), 1 - (4 - chlorophenyl) - 1 - cyclopropylethylene (**8**), 1 - (4 - anisyl) - 1 - cyclopropylethylene (**9**), 1 - methyl - 1 - cyclopropylethylene (**10**) and 1,1 - dicyclopropylethylene (**11**). The results are shown in Scheme 1.

The monomeric compounds (**12–15**) represent *formal* 1,5-conjugated additions of HCl across the vinylcyclopropane systems, while the dimeric ones (**16, 17**) are products of similar *formal* 1,5-additions coupled with non-rearranged 1,2-selfadditions of the olefins. The yields range from 60 to 76% calculated with reference to the consumption of the organic compound. Some polymeric material was formed in every case, but a white powdery polymer, undetectable by GLC, was the sole product from **9**. The latter was devoid of cyclopropane signals in the NMR spectrum, and the integration ratio between the vinylic (*ca* τ 5.0) and methoxy (*ca* τ 6.30) signals was 1:8, suggesting that it contains a mixture of structures **2** and **3**.



5,6 → **12,13**; **5,12** : R=H; **6,13** : R-R = CH_2-CH_2

7,8,9 → **14,15**; **7,14** : R=H; **8,15** : R=Cl; **9**: R=OCH_3

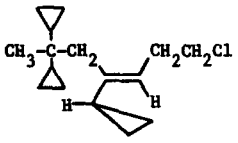
10,11 → **16,17**; **10,16** : R=methyl; **11,17** : R=cyclopropyl

Scheme 1

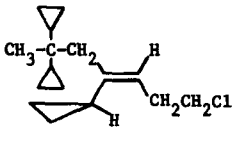
The structures of the products were deduced from the following data: (1) Elemental analysis and MS establish the molecular formulas; (2) cyclopropane signals in the IR and NMR spectra are totally or partially eliminated

(in **12**, **14**, **15** and **13**, **16**, **17**, respectively); (3) triplet resonances at τ 3.40–3.53 and quartet bands (triplet for **12** and **13**) at τ 2.40–2.68 represent the CH_2CH_2Cl groups, singlets at τ 1.30–2.05 (exception in **17**) show the vinylic Me, and the vinylic protons appear as triplets at τ 5.07–5.68 (missing in **12** and **13**); (4) absorption bands at 715–740 cm^{-1} correspond to the C–Cl stretching vibrations; (5) mass-spectral fragmentations are in accord with the proposed structures (e.g. M–CH_2Cl and M–CH_2CH_2Cl).

The monomeric products are stereochemically pure *cis* compounds. It is a trivial case for **12** and **13**, and follows from the NMR data for **14** and **15**. The spectra of the latter are simple first order patterns (in contradistinction to those of **16** and **17**, discussed below), and the chemical shifts of protons remote from the hetero atom are practically identical with those reported for analogous *cis*-acetoxy- and trifluoroacetoxy-2-pentenes.[12] Chloroheptenes **16** and **17** are *cis–trans* mixtures, their NMR spectra being easily recognized as duplicates of the characteristic bands and splitting patterns superimposed on each other (Experimental). The isomeric ratio in **16** is *ca* 1:4 (deduced from the integration figures), but the relative shifts of corresponding resonance in the two isomers are too small (0.03–0.09 ppm) to allow configurational assignment. In **17** a ratio *cis*:*trans* = 7:4 can be evaluated. The configurations were deduced by considering the relative population of the two limiting, most stable conformations of the vinylcyclopropane unit in the two isomers:[13]



17-*cis-cisoid*

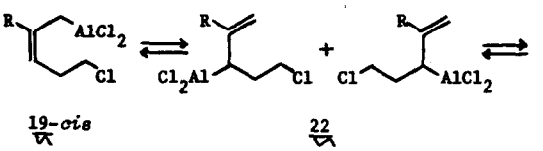


17-*trans-transoid*

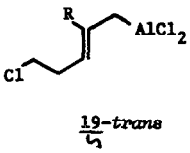
Steric interaction of the cyclopropyl with the bulky chloroethyl group would diminish the probability of the *cisoid* arrangement in the *trans* as compared to the *cis* isomer. Consequently a relative diamagnetic shifts of the vinylic and CH_2CH_2Cl protons resonances would be expected in the *cis* isomer, caused by the magnetic anisotropy of the ring, while, similarly, the other methylene and the methyl group should absorb at higher field in the *trans* isomer. Such a distribution of chemical shifts is, in fact, observed, and hence the assignment of the stereochemistry.

The results presented here differ from the reported Lewis-acids-induced reactions of vinylcyclopropanes in three main respects: First, the very meaningful suppression of the polymerization process (except for **9**), which is due to the reduction of the catalytic efficiency of anhydrous $AlCl_3$ by the coordination of ether molecules.[14] Second, the formation of monomeric homoallylic chlorides (**12–15**) in absence of free HCl. The exclusion of HCl is evidenced also by lack of co-catalysis with $AlCl_3$[15] (which should enhance polymerization) and by the non-occurrance of these products prior to hydrolysis.† Third, the hitherto unknown type of dimeric products (**16** and **17**),‡ where the reaction is both regiospecific in the "head-to-tail" sense for the dimerizations and stereoselective in the rearrangement mode of the vinylcyclopropane systems.

To rationalize these observations we propose the intermediacy of an organoaluminum species **19** which is polarized in opposite sense relative to the equilibrating dipolar structures (**21**) suggested for cationic polymerization.[2–4,6] Compound **19** arises, presumably, from addition of the Al–Cl bond across the vinylcyclopropane system *via* a pericyclic transition-state **18** (Scheme 2). The allylic carbon-metal bond in **19** is particularly suited for *anionic* addition to a polarized olefin,[16,17] leading to the dimeric species **20**, which, in turn, are not reactive enough for further chain-growth due to the loss of the allylic resonance participation. The same intermediate could exhibit *cis-trans* isomerization,§ which, in fact, occurs concurrently with dimerization.



19-*cis* **22**



19-*trans*

We could not detect any products arising from **22**. Apparently the preferred charge localization on a primary rather than a secondary C-atom and the greater steric accessibility to the olefin attack in the dimerization step tips the balance in favor of **19**.

The effect of substitution on the reaction mode is in consonance with this general scheme. The most powerful electron-donating anisyl group favors the formation of the carbon *cationic* moiety **21**, which polymerizes in high yield. In the case of **5** and **6**, it is the bulky *spiro* structure which sterically precludes the dimerization, thus terminating the reaction at the monomeric stage (**12** and **13**). The non-occurrance of dimerization in **7** and **8** is most likely due to electronic effects, namely the olefinic bond is too weakly polar for further addition. The observed *cis* stereospecificity can be explained either in terms of the geometry of the transition-state **18**, or as the result of a thermodinamically-controlled process.[13] The influence of the methyl and cyclopropyl is apparently intermediary between the anisyl and the *p*-chlorophenyl substituents, enhancing dimerization (to **16** and **17**) but not polymerization. Precedents to formation of *cis–trans* mixtures in homoallylic rearrangements of these systems have been recorded.[13]

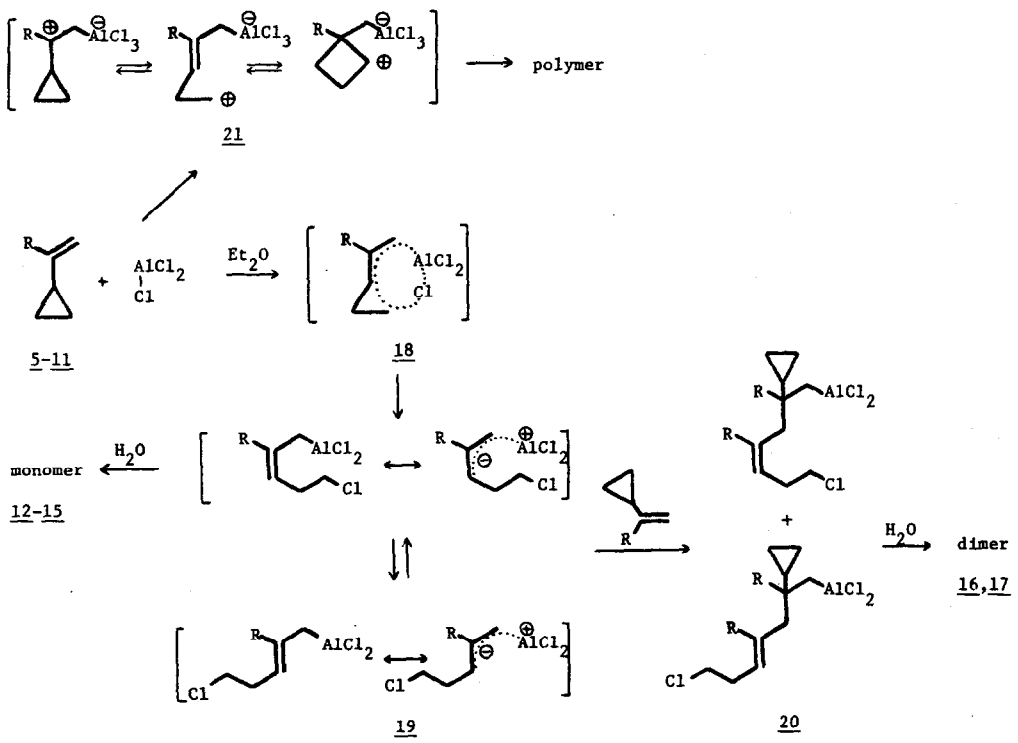
EXPERIMENTAL

Yields calculations are based on the amount of vinylcyclopropane compound present in the preparatively isolated materials. IR spectra were obtained neat with Perkin–Elmer 237 spectrophotometer. NMR spectra were determined in CCl_4 solutions with TMS as internal standard on a Jeol JMN–C–60H spec-

†In an experiment with HCl added intentionally the product formation could be monitored by GLC simultaneously with the consumption of the substrate.

‡Note that these are *not* the known self-dimerization products of allylaluminum compounds.[16]

§Allylaluminum compounds were shown to undergo allylic rearrangement,[16,17,18] during which *cis–trans* isomerization could take place.



Scheme 2

trometer; the chemical shifts are reported in τ values and J couplings in Hz units. MS were taken on a Varian MAT CH-5 spectrometer. GLC were carried on a Varian-Aerograph A-90-P3 gas-chromatograph (TCD) with a 6 ft × 1/4 in., 10% SE-30 on Chromosorb W. column at appropriate temperatures in the 100–180° range and He flow rate of 20–50 ml/min.

The starting materials were prepared by literature procedures—**5** and **6**;[19] **7**, **8** and **9**;[20] **10**;[21] **11**.[22]

General procedure. Aluminum chloride monoetherate[8] (5 mmole) was distilled (100–105°/0.5 mm) into a round-bottomed flask equipped with a magnetic stirring bar, and the flask was sealed with a rubber septum under N_2. 8 ml of dry ether were added by injection, followed by a soln of the vinylcyclopropane compound (5 mmole) in 2 ml dry ether. The mixture was stirred at room temp. until the substrate was consumed (20–30 min, determined by GLC). The mixture was then poured into excess Na_2CO_3aq., the organic layer separated and the aqueous phase extracted with additional ether. The combined etheral soln was washed with water and dried over $MgSO_4$. The solvent was removed in vacuum and the product separated by GLC from the residue.

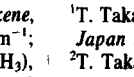
1 - *Methyl* - 2 - (2 - *chloroethyl*) - 1 - *cyclohexene*, **12**, yield: 62%; IR: 740 (C–Cl) cm^{-1}. NMR: τ 8.60–7.90 (8H, m), 8.38 (3H, s, CH_3), 7.60 (2H, t, J 7.5, CH_2CH_2Cl), 6.58 (2H, t, J 7.5, CH_2Cl); MS: *m/e* 158, 160 (100:33, M^+), 109 ($M-CH_2Cl$); 95 ($M-CH_2CH_2Cl$, base peak); 81 ($M-CH_2Cl-C_2H_4$, retro Diels–Alder); 67 ($M-CH_2CH_2Cl-C_2H_4$, retro Diels–Alder). (Found: C, 67.98, H, 9.49, Cl, 22.30. Calc. for $C_9H_{15}Cl$: C, 68.14, H, 9.46, Cl, 22.40%).

3 - (2 - *Chloroethyl*) - 2 - *methyl* - 1,1 - *ethano* - 2 - *cyclohexene*, **13**, yield: 76%; IR: 3070, 1010 (cyclopropane), 720 (C–Cl) cm^{-1}; NMR: τ 9.48 (4H, $A_2'B_2'$, cyclopropane), 8.70 (3H, s, CH_3), 8.65–8.10 (4H, m), 8.10–7.75 (2H, m, cyclic allylic), 7.60 (2H, t, J 8.0, CH_2CH_2Cl), 6.60 (2H, t, J 8.0, CH_2Cl), MS: *m/e* 184, 186 (100:33, M^+), 135 ($M-CH_2Cl$), 121 ($M-CH_2CH_2Cl$), base peak), 107 ($M-CH_2Cl-C_2H_4$, retro Diels–Alder), 93 ($M-CH_2CH_2Cl-C_2H_4$, retro Diels–Alder). (Found: C, 71.31, H, 9.27, Cl, 19.28. Calc. for $C_{11}H_{17}Cl$: C, 71.53, H, 9.28, Cl, 19.20%).

cis - 2 - *Phenyl* - 5 - *chloro* - 2 - *pentene*,[23] **14**, yield: 66%; IR: 735 (C–Cl) cm^{-1}. NMR: τ 7.95 (3H, s, CH_3), 7.37 (2H, q, J 7.0, CH_2CH_2Cl), 6.47 (2H, t, J 7.0, CH_2Cl), 4.32 (1H, tq, J_{H,CH_2} 7.0, J_{H,CH_3} 1.5, vinyl), 2.82 (5H, broad single band); MS: *m/e* 180, 182 (100:33, M^+), 131 ($M-CH_2Cl$), 91 (tropilium, base peak).

cis - 2 - (4 - *Chlorophenyl*) - 5 - *chloro* - 2 - *pentene*,[24] **15**, yield: 57%; IR: 730 (C–Cl) cm^{-1}, NMR: τ 7.97 (3H, s, CH_3), 7.38 (2H, q, J 7.0, CH_2CH_2Cl), 6.47 (2H, t, J 7.0, CH_2Cl), 4.38 (1H, tq, J_{H,CH_2} 7.0, J_{H,CH_3} 1.5, vinyl), 2.80 (4H, broad single band).

cis – trans - 2,4 - *Dimethyl* - 2 - *cyclopropyl* - 7 - *chloro* - 4 - *heptene*, **16**, yield: 68%; IR: 3080, 1015 (cyclopropane), 720 (C–Cl) cm^{-1}; NMR: τ 9.95–9.65 (4H, m, cyclopropane CH_2), 9.60–9.00 (1H, m, cyclopropane CH), 9.28(s) + 9.23(s) (4:1, 6H, CH_3), 8.28(s) + 8.19(s) (4:1, 3H, allylic CH_3), 8.03(s) + 7.95(s) (4:1, 2H, isolated CH_2), 7.54 (2H, diffuse q, J 7.0, CH_2CH_2Cl), 6.59(t) + 6.56(t) (1:4, 2H, J 7.0, CH_2Cl), 4.88 (1H, diffuse t, J 7.0, vinyl). (Found: C, 71.83, H, 10.70, Cl, 17.20. Calc. for $C_{12}H_{21}Cl$: C, 72.00, H, 10.50, Cl, 17.50%).

cis–trans - 2,2,4 - *Tricyclopropyl* - 7 - *chloro* - 4 - *heptene*, **17**, yield: 76%; IR: 3080, 1015 (cyclopropane), 715 (C–Cl) cm^{-1}; NMR: τ 9.96–8.33 (15H, m, cyclopropane), 9.50(s) + 9.45(s) (4:7, 3H, CH_3), 8.10(s) + 7.78(s) (4:7, 2H, isolated CH_2), 7.50(q) + 7.32(q) (7:4, 2H, J 7.0, CH_2CH_2Cl), 6.60(t) + 6.47(t) (7:4, 2H, J 7.0, CH_2Cl), 4.93(t) + 4.63(t) (7:4, 1H, J 7.0, vinyl). MS: m/e 252, 254 (100:33, M^+), 109 ( , base peak). (Found: C, 75.87, H, 10.20, Cl, 13.93. Calc. for $C_{16}H_{25}Cl$: C, 76.01, H, 9.97, Cl, 14.02%).

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