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LEWIS ACID CATALYZED REARRANGEMENT OF VINYLCYCLOPROPANECARBONYL CHLORIDE TO CYCLOPENTENECARBONYL CHLORIDE

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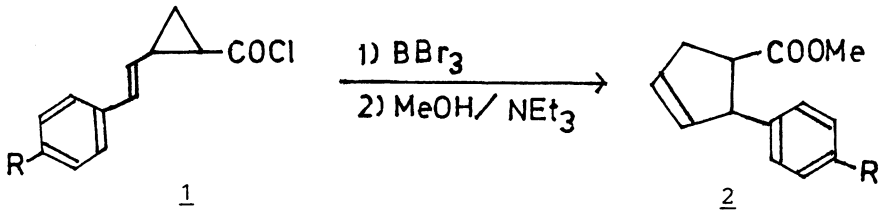
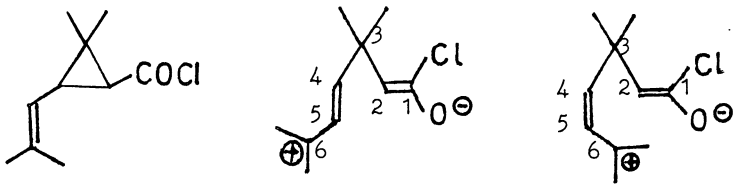
Vinylcyclopropane-cyclopentene rearrangement of 2-(2-arylvinyl)cyclopropanecarbonyl chlorides was observed upon treatment with a Lewis acid under mild reaction conditions to afford 2-arylcyclopent-3-enecarboxylates after esterification.

The methods for the vinylcyclopropane-cyclopentene rearrangement so far reported involve thermolysis, photolysis, and transition metal catalysis.[1] Base promoted rearrangement at low temperature has also been reported.[2] In this communication we wish to describe the first example of Lewis acid catalyzed vinylcyclopropane-cyclopentene rearrangement.



1 2

In our recent report on the Lewis acid catalyzed racemization of chrysanthemoyl chloride 3, the cyclopropane ring-cleaved intermediate 4a was proposed, which furnished racemized 3 through ring closure at the C_2-C_4.[3] If the intermediate 4a has a long life enough to isomerize into cis 4b, there will be a chance of the C_2-C_6 bond formation. No cyclopentene derivatives, however, were observed in the racemization of chrysanthemoyl chloride.
Therefore, replacing the methyl at the C_6 with an aryl group in order to stabilize the cation part of the intermediate, we examined the reaction of the 2-(2-arylvinyl)cyclopropanecarbonyl chlorides 1[4] with a Lewis acid.

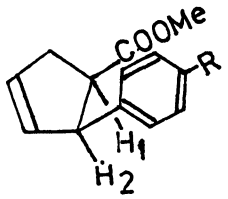


3 4a 4b

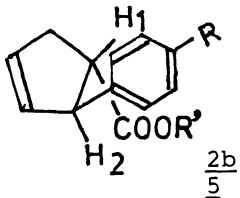
In a typical experiment, a dichloroethane solution of boron tribromide (0.06 mmol) was added to a solution of the cyclopropanecarbonyl chlolide 1 (3.00 mmol, R=OMe) in dichloroethane at room temperature. After 30 min, the reaction mixture was treated with methanol/triethylamine (5 ml/0.5 ml). Usual work-up followed by purification by silica gel column chromatography gave the cyclopentenecarboxylate 2[5] in a 61% yield as a mixture of cis and trans isomers (2a and 2b) in a ratio of 86:14.

Separation of the two isomers was carried out by selective hydrolysis. Thus, the mixture was treated with 5% aqueous NaOH at 20 °C for 10 min. The minor ester was hydrolyzed completely to give the acid 5 with 95% isomeric purity and the major ester 2a was recovered with 100% isomeric purity.

Cis configuration for the major isomer 2a was established on the basis of the NMR data and the chemical behavior: 1) The H_1 signal of the major isomer 2a appears at lower field (3.54 ppm) than that of the minor isomer 2b (around 2.8 ppm);[6] 2) The coupling constant $J_{1,2}$ of the major isomer 2a is 9 Hz while that of the minor isomer 2b is ca. 5 Hz; 3) The major isomer 2a was converted into thermodynamically more stable 2b. Treatment of 2a with NaOMe in methanol at 60 °C for 4 h gave a 14/86 mixture of cis/trans isomers (2a/2b), which is considered to be an equilibrium mixture;[7] 4) Sterically less hindered ester 2b was hydrolyzed faster than 2a as described above.



2a



2b; R'=Me
5 ; R'=H

As for the Lewis acid catalyst, $AlCl_3$ and BCl_3 worked as efficiently as BBr_3.

The reactivity of the cyclopropanecarbonyl chloride 1 is dependent upon the substituent on the phenyl ring (Table 1).

Electron-donating group favored the reaction. The starting molecule was consumed completely within 30 min to give the cyclopentene derivative 2 (entries 1,2). In the absence of the electron-donating group the reaction became sluggish and did not go to completion under the same reaction conditions (entry 3). Electron-withdrawing group suppressed the rearrangement. The starting compound 1 was consumed gradually on prolonged contact with a Lewis acid, but the cyclopentene 2 was not detected (entry 4).

At the early stage of the reaction , cis-trans isomerization of the cyclopropane molecule (1a/1b) was observed irrespective of the substituent on the phenyl ring as shown in Table 2. This fact is consistent with our previous observation of the racemization of chrysanthemoyl chloride.

Table 1. Synthesis of 2: Effect of the substiuent R

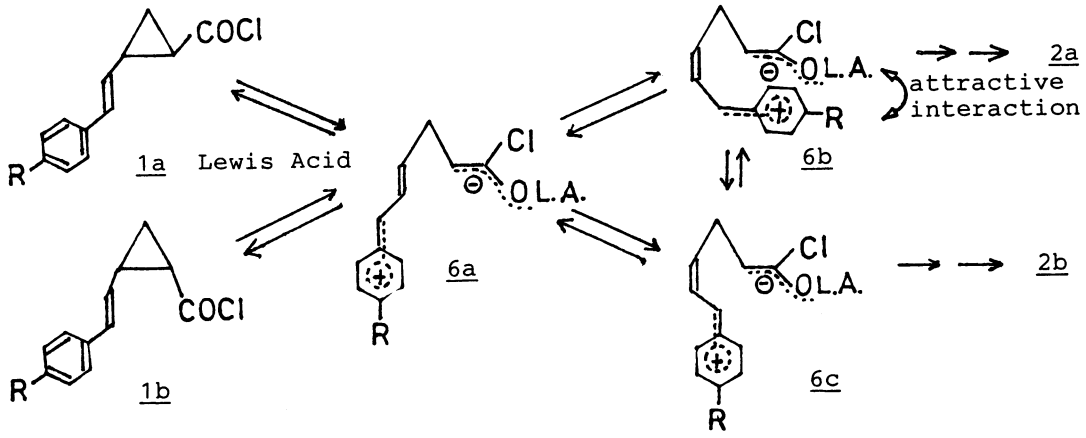
No	R	BBr_3(mol%)	Time/min	Conv./%[a]	Yield/%[b]	cis/trans[c]
1	OMe	2.0	30	100	61	86/14
2	Me	10.0	30	100	51	82/18
3	H	20.0	30	17	d)	81/19
4	Cl	20.0	30	0	--	-----

a) Consumed 1 was estimated by gas chromatography.
b) Isolated yield of the methyl ester.
c) Determined by gas chromatography.
d) Not isolated.

Table 2. Cis-trans isomerization of 1 (1a/1b)

R	Reaction time: Initial cis/trans[a]	5 min[b] cis/trans[a]
Me	24/76	9/91
H	26/74	11/89
Cl	23/77	8/92

a) Determined by gas chromatography.
b) Cis/trans ratio of recovered 1 in the reaction mixture.



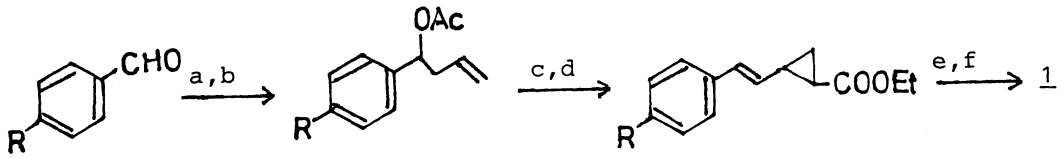
Scheme 1. Plausible reaction pathway.

These results support our initial assumption: Equilibrium between 1a and 1b through 6a is a quick step and the formation of the cis intermediate (6b or 6c) is a slow step. Electron-donating group on the phenyl ring is necessary to make the intermediate 6a stable enough to bring about the cis-trans isomerization.

The predominancy of the cis product 2a over the trans product 2b may be explained in terms of the attractive interaction between the cationic phenyl moiety and the anionic carbonyl moiety in the intermediate 6b as depicted in Scheme 1.

References

1) T. Hudlicky, T. M. Kutchan, and S. M. Naqvi, Org. Reac. 33, 247 (1985).
2) For example, see: R. L. Danheiser, C. Martinez-Davila, and J. M. Morin, Jr., J. Org. Chem., 45, 1340 (1980); L. Skattebol, Tetrahedron, 23, 1107 (1967).
3) G. Suzukamo, M. Fukao, and T. Nagase, Chem. Lett., 1984 1799.
4) Cyclopropanecarbonyl chorides 1 were prepared from the correspondig aldehydes according to the following procedure.



a; allylmagnesium chloride, b; acetic anhydride/triethylamine,
c; ethyl diazoacetate/ anhydrous cupric sulfate, d; p-toluenesulfonic acid,
e; aqueous sodium hydroxide, f; thionyl chloride.
Data for 1 (R=Me, trans/cis=75/25); NMR($CDCl_3$) δ (ppm)=1.20-1.90 (m, 2H), 2.05-2.62 (m, 2H), 2.32 (s, 3H), 5.68 (dd, J=17.0 Hz, 9.0 Hz, 0.75H, (trans)), 6.00 (dd, J=17.0 Hz, 9.0 Hz, 0.25H, (cis)), 6.56 (d, J=17.0 Hz, 0.75H, (trans)), 6.62 (d, J=17.0 Hz, 0.25H, (cis)), 7.16 (m, 4H);
IR (neat) 2928, 1774, 1516, 1058cm^{-1}.

5) Data for 2a (R=Me); NMR($CDCl_3$) δ (ppm)=2.28 (s, 3H), 2.43-2.68 (m, 1H), 2.80-3.00 (m, 1H), 3.21 (s, 3H), 3.39-3.69 (m, 1H), 4.20 (bd, J=9 Hz, 1H), 5.69 (m, 1H), 5.92 (m, 1H), 7.02 (s, 4H); IR (gas) 2951, 1755, 1173cm^{-1}; MS m/e 216 (M^+).
Data for 2b (R=Me); NMR ($CDCl_3$) δ (ppm)=2.32 (s, 3H), 2.60-3.32 (m, 3H), 3.68 (s, 3H), 4.10 (m, 1H), 5.70 (m, 1H), 5.81 (m, 1H), 7.11 (s, 4H); IR (gas) 2959, 1755, 1169cm^{-1}; MS m/e 216 (M^+).
6) D. Y. Curtin, H. Gruen, and B. A. Shoulders, Chem. Ind., 1958 1205.
7) The isomeric ratio was not changed under the same conditions for another 3 h.

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