Tetrahedron Letters,Vol.24,No.7,pp 715-718,1983 0040-4039/83/070715-04$03.00/0
Printed in Great Britain

LOW TEMPERATURE EQUILIBRATION OF CYCLOPROPANES BY LEWIS ACID CATALYSIS

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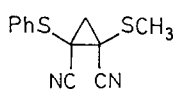
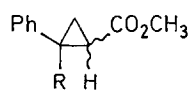
Summary: Under the influence of Lewis acids the cis/trans-equilibration of methyl 2-trimethylsiloxy cyclopropanecarboxylates occurs even at -78°C. It involves the heterolytic cleavage of a C-C bond and seems to be governed by steric effects.

Usually cis-trans-isomerization of cyclopropanes involves homolytic cleavage of one bond yielding 1,3-diradicals [1]. The high temperature of more than 400°C necessary to induce this process in 1,2-dideuteriocyclopropane [2] can be lowered to about 50°C if geminal "capto-dative" substituted cyclopropanes like (1) are chosen [3]. We here want to demonstrate that vicinal acceptor-donor substituted cyclopropanes as (2) equilibrate by Lewis acid catalysis via a heterolytic cleavage even at -78°C.

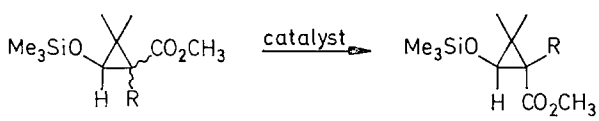


(1)



(3)

a: R = H
b: R = CH_3



cis/trans-(2) trans-(2)

a: R = H, b: R = D, c: R = Me, d: R = n-Bu
e: R = Allyl, f: R = Benzyl

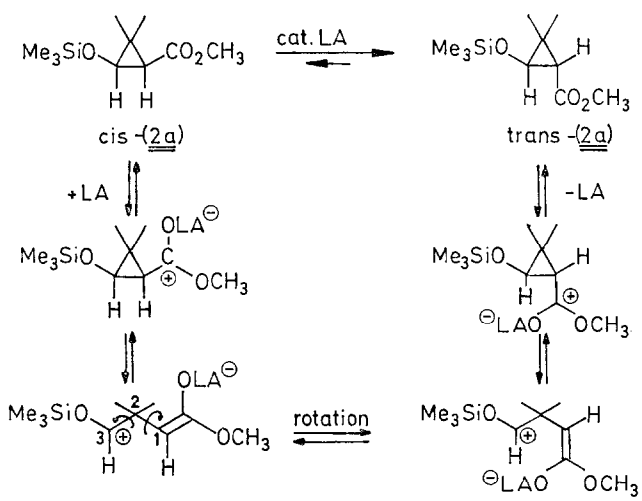
Treating a 25:75 cis-trans mixture of methyl 3,3-dimethyl-2-trimethylsiloxycyclopropanecarboxylate (2a) [4] with a catalytic amount (0.04 equiv) of trimethylsilyl nonafluorobutanesulfonate [5] for 14 h at room temperature [6] provides pure trans-(2a) in 94 % yield after filtration through a pad of alumina (activity III, neutral) and distillation. According to ^1H and ^{13}C spectrometry the configurational purity is higher than 99 % [7]. We found that this isomerization occurs even at -78°C (0.04 equiv $Me_3SiOSO_2C_4F_9$, CH_2Cl_2, yield 78 %). Similarily

other Lewis acidic catalysts like Me_3SiI, $TiCl_4$ or $ZnCl_2$-etherate can be employed in the same fashion.

Also cis-trans mixtures of the 1-substituted derivatives (2b) - (2f) [8] (table I) can efficiently be converted to the pure (> 98 %) trans compounds using Me_3SiI (0.1 - 0.3 equiv, 20°C). These results rule out the rather unlikely possibility of an epimerisation at C-1 by deprotonation-protonation [9]. On the other hand cyclopropaneesters (3a) and (3b) lacking the strong electron donating trimethylsiloxy group so far failed to equilibrate even under forced conditions [10].

A mechanism for this - to our best knowledge - unprecedented mild isomerization is suggested in scheme I: coordination of the Lewis acid LA to the carbonyl oxygen and subsequent ring opening gives a siloxy stabilized homoallyl carbenium ion [11], which can rotate around bond 1,2 and/or bond 2,3 [12]. Ring closure and expulsion of LA recreates the cyclopropaneester and finally leads to the thermodynamic equilibrium between the cis and trans isomers [13].

Scheme I:

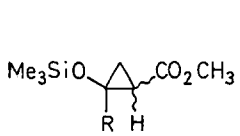


Our results indicate that this equilibrium is governed by steric effects mainly or exclusively, as a preference for the trans position of the largest substituents [14] at C-1 and C-2 respectively is observed. This causes formation of pure trans compounds in the (2)-series as shown, and clean cis isomer (> 99 %) with cyclopropane (4d) on the other hand where the huge t-butyl group is forced trans to the methoxycarbonyl function (table I) [15]. The bicyclic system (5) also gave the pure cis compound under the influence of $TiCl_4$. Between these extremes are cyclopropanes (4a) - (4c). Here the second substituent at C-2 has a similar size as the Me_3SiO-group thus giving mixtures of cis-trans isomers.

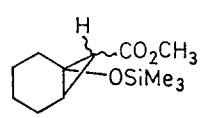
Table I. Equilibration of siloxy-substituted methyl cyclopropanecarboxylates with Lewis acids

	before equilibration cis : trans[a]	equivalents of catalyst	after equilibration cis : trans[a]	yield[b]
(2a)	25 : 75	0.04 Me_3SiONf[c]	< 1 : > 99	94
(2b)	25 : 75	0.11 Me_3SiI	< 2 : > 98	67
(2c)	10 : 90	0.13 Me_3SiI	< 1 : > 99	93
(2d)	19 : 81	0.35 Me_3SiI	< 2 : > 98	94
(2e)	18 : 82	0.32 Me_3SiI	< 1 : > 99	76
(2f)	35 : 65	0.29 Me_3SiI	< 2 : > 98	91
(4a)	25 : 75	0.03 $TiCl_4$	26 : 74	93
(4b)	42 : 58	0.02 $TiCl_4$	36 : 64	88
(4c)	74 : 26	0.08 $TiCl_4$	61 : 39	75
(4d)	48 : 52	0.05 $TiCl_4$	> 99 : < 1	70
(5)	55 : 45	0.03 $TiCl_4$	> 99 : < 1	79

[a] Ratio determined by ^1H and/or ^{13}C NMR. Control experiments showed that the ratios are reproducable to within ± 2 %. [b] Isolated yield of purified product after bulb-to-bulb distillation. [c] Nf = $SO_2C_4F_9$.



(4)



(5)

a: R = Me, b: R = Vinyl
c: R = Ph, d: R = t-Bu

In addition to the mechanistic aspect the importance of the equilibration method described lies in the efficient availability of configurationally pure siloxysubstituted methyl cyclopropanecarboxylates. Ways of opening the ring under transmission of the stereochemistry are currently studied in our laboratory [16].

References and Notes

1. J. A. Berson, "Rearrangements in Ground and Excited States", P. de Mayo, Ed., Academic Press: New York, 1980, Vol. 1, p 311.
2. J. A. Berson, L. D. Pedersen, B. K. Carpenter, J. Am. Chem. Soc. 1976, 98, 122.
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4. H.-U. Reissig, E. Hirsch, Angew. Chem. 1980, 92, 839; Int. Ed. Engl. 1980, 19, 813.
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6. The reaction was performed in $CCl_4/HN(SiMe_3)_2$ = 20:1; thus the actual catalyst might be $\overset{\oplus}{H}N(SiMe_3)_3\ \overset{\ominus}{O}_3SC_4F_9$. The secondary amine was added to prevent partial hydrolysis to the 1,4-dicarbonyl compounds [4]. However, the isomerization is also observed without amine and does not occur without Lewis acid!
7. trans-(2a): ^{1}H NMR (C_6H_6) δ = 0.11 (s, $SiMe_3$), 1.18, 1.22 (2s, 2 Me), 1.58, 3.84 (2d, J = 3 Hz, trans cyclopropane H), 3.49 (s, CO_2Me); ^{13}C NMR ($CDCl_3$) δ = -0.6 (q, $SiMe_3$), 18.0, 19.5 (2q, Me), 28.8 (s, C-3), 34.0 (d, C-1), 63.9 (d, C-2), 50.9, 171.6 (q, s, CO_2Me).
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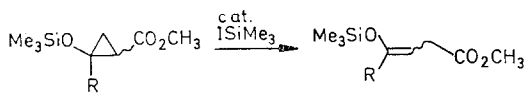
9. D. S. Seigler, J. J. Bloomfield, J. Org. Chem. 1973, 38, 1375.
10. For ring opening reactions of cyclopropanecarboxylates with Lewis acids see: Y. Morizawa, T. Hiyama, H. Nozaki, Tetrahedron Lett. 1981, 22, 2297. S. P. Brown, B. S. Bal, H. W. Pinnick, Tetrahedron Lett. 1981, 22, 4891. M. E. Alonso, M. Gómez, S. P. de Sierraalta, S. P. Jano, J. Heterocyclic Chem. 1982, 19, 369.
11. The ketene acetal moiety of this intermediate can be trapped by external electrophiles like carbonyl compounds: H.-U. Reissig, Tetrahedron Lett. 1981, 22, 2981.
12. We hope to distinguish between these rotation modes by studying suitable model compounds substituted at C-3.
13. A similar mechanism has been mentioned and disfavoured for the acid catalyzed racemization of methyl 1-cyano-2,2-diphenyl-cyclopropanecarboxylate: E. W. Yankee, F. D. Badea, N. E. Howe, D. J. Cram, J. Am. Chem. Soc. 1973, 95, 4210. Although not discussed this mechanism might also be involved in the rearrangement of other cyclopropane derivatives: H. Kunz, Z. Naturforsch. 1976, 31b, 1676. H. Quast, J. Stawitz, Tetrahedron Lett. 1976, 3803. T. Sasaki, S. Eguchi, M. Ohno, Bull. Chem. Soc. Jpn. 1980, 53, 1469.
14. For substituent parameters see: R. Knorr, Chem. Ber. 1980, 113, 2441, T. Fujita, T. Nishioka, Progr. Phys. Org. Chem. 1976, 12, 49.
15. Cyclopropanes not dialkylated at C-3 like (4) and (5) have to be equilibrated with $TiCl_4$. $ISiMe_3$ or $C_4F_9SO_3SiMe_3$ lead to a proton transfer in the ring opened species (scheme I) and give a structural rearrangement to silyl enol ethers, e. g.:



H.-U. Reissig, I. Böhm, unpublished results.

16. Support of this work by the Fonds der Chemischen Industrie and by the Deutsche Forschungsgemeinschaft is gratefully appreciated.

(Received in Germany 19 November 1982)