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KINETICS OF THE CIS-TRANS ISOMERISATION OF CYCLOPROPANES : COMPARISON BETWEEN CAPTO-DATIVE AND DI-CAPTO RADICAL STABILISATION[1,2]

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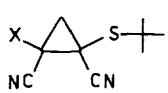
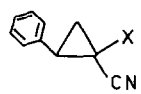
Summary : Capto-dative (*cd*) (*c* = CN, *d* = OR, SR, NR_2) compared to di-capto substitution (*c* = CN, *c'* = COOR) was found to be more efficient in lowering the activation energy of cis-trans isomerisation of cyclopropanes.

Since the formulation of the concept of capto-dative (*cd*) radical stabilisation [3] we have published our first quantitative evaluations[4,5,6], based on cis-trans isomerisation of cyclopropanes : we reported that 1c isomerises readily at 50°C with a very low activation energy (=26.9Kcal/mole). In this paper *cd* substitution is extended to amino- and methoxy nitrile and compared to di-capto substitution.

1a X = OCH_3
b = Ø
c = SØ
d = Cl
e = $COOCH_3$



1

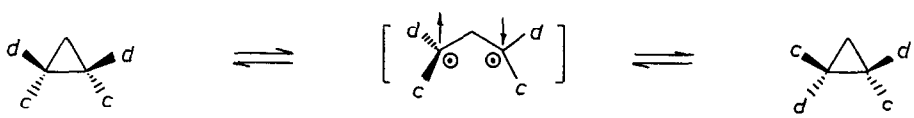


2

2a X = S

b = N O

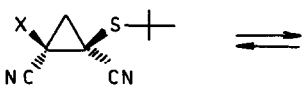
cd-Substitution stabilises particularly well the di-radical transition state[7] of the isomerisation process.



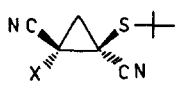
d = SR, OR, NR_2 *c* = CN, COOR

The effect of a methoxy (in 1a) or of a morpholine group (in 2b), in the *cd*-couple with a nitrile, is comparable to that of SR groups (in 1c and 2a). In contrast two geminal acceptor groups (CN and $COOCH_3$ in 1e) stabilise the transition state to a lesser extent.

The kinetic data for the cis-trans isomerisation of two sets of compounds 1a-e and 2a-b were determined in two different solvents[8]. The results are presented in tables I and II. No solvent polarity effect was detected using $CDCl_3$ and nitrobenzene or xylene-D10 and CD_3CN respectively. Any zwitterionic character in the transition state[7a] can thus be excluded.



cis



trans

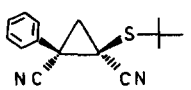
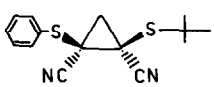
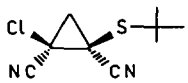
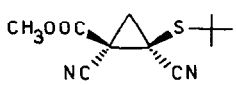
SOLVENT : $CDCl_3$	$E_{a\ c \to t}$ (Kcal/mole) ($A_{c \to t}$ sec^{-1})	$E_{a\ t \to c}$ (Kcal/mole) ($A_{t \to c}$ sec^{-1})	K=[cis]/[trans] (T °C)[9]
 (1a)	24.1 ± 0.4 (6.1×10^{10})	24.2 ± 0.5 (1.0×10^{10})	7 (58-110)
 (1b)[10]	27.0 ± 0.4 (6.3×10^{13})	26.7 ± 0.7 (7.2×10^{12})	5.3 (37 - 64)
 (1c)[10]	26.9 ± 1.0 (1.1×10^{13})	26.9 ± 1.1 (1.1×10^{12})	10 (50-95)
 (1d)	28.2 ± 1.5 (4.2×10^{12})	29.4 ± 1.1 (4.2×10^{12})	4.6 (100-138)
 (1e)	31.7 ± 0.8 (3.2×10^{13})	31.7 ± 0.7 (1.2×10^{12})	4.8 (118-150)

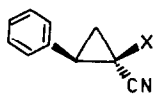
TABLE I

In both series the cis → trans and trans → cis isomerisations have nearly the same activation energy ; steric factors appear not to be predominant in these systems. This is in full agreement with X-ray analysis [11] and our previous report [4]. Indeed if steric factors of X in 1a to 1e were important, a different sequence of activation energies could be expected.

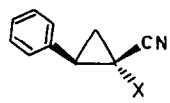
The kinetic results suggest a similar stabilisation for *cd* radicals R - C(OCH$_3$)(CN) and R - C(SPh)(CN), and for the R - C(Ph)(CN) radical.

Although chlorine is a poor donor and the least efficient radical stabilising substituent considered here, the activation energy for 1d (*c* = CN, *d* = Cl) is still lower than for di-capto substitution (1e , *c* = CN, *c'* = $COOCH_3$).

From the data for 2a and 2b (Table II) we can conclude that t-butyl thio and morpholine substituents in a *cd* couple afford a similar degree of stabilisation in the diradical transition state.



cis



trans

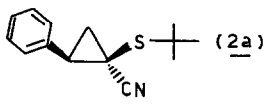
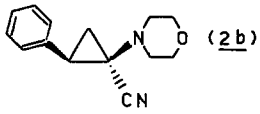
SOLVENT : xylene-D10	$E_{a\ c\to t}$ (Kcal/mole) ($A_{c\to t}$ sec^{-1})	$E_{a\ t\to c}$ (Kcal/mole) ($A_{t\to c}$ sec^{-1})	K=[cis]/[trans] (T°C) [9]
 (2a)	34.3 ± 0.8 (1.0×10^{13})	34.0 ± 1.9 (2.1×10^{12})	3.6 (155-187)
 (2b)	34.2 ± 0.1 (1.4×10^{13})	34.1 ± 0.1 (6.0×10^{12})	1.9 (150-187)

TABLE II

The correlation between radical stabilisation energies by substituent effect and the activation energies of cyclopropane geometrical isomerisation is already established [2,7]. However, small variations of 1-2 Kcal/mole in the activation energies by changing only one substituent X out of three or four could be justified by differences in the ground state energies ; but there is no obvious reason to expect ground state destabilisation of four or of seven Kcal/mole replacing the ester group of 1e, by a chlorine 1d or a methoxy 1a.

In conclusion our results indicate the following order of radical stabilisation :

d-C(CN) > Ph-C(CN) > Cl-C(CN) > ROOC-C(CN) > Ph-C(H) *d* = OR, SR, NR_2

This sequence does not correspond to the simple additivity of individual capacities [12] of substituents to stabilise an adjacent radical and underlines the importance of the *cd* effect.

In quantitative terms the comparison of the E_a's for 1,1,2,2-tetramethylcyclopropane (E_a = 54.4 Kcal/mole)[13] and of bis-*cd* substituted cyclopropanes 1a and 1c (Ea=24-27 Kcal/mole) permits the estimation of 14-15 Kcal/mole for the *cd* radical stabilisation energy, which is even higher than for diphenyl substitution (cf. 1,2-Di(p-cyanophenyl)-1,2-diphenylcyclopropane E_a = 30.4 Kcal/mole[5]).

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8. Synthesis of the new cyclopropanes will be reported later ; the cis and trans isomers have been separated by column chromatography. The kinetics were followed by ^{1}H-NMR on a Varian XL-200 spectrometer, on 0.1-0.2 molar solutions, and are first order in each case. Equilibria and rate constants have been determined for at least four different temperatures in each solvents.

9. The K-values given here are averages with the appropriate temperature in parentheses.

10. Optimised value from ref. 4.

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12. See for ex. : a) J.W. Timberlake, A.W. Garner, M.L. Hodges, Tetrahedron Lett. 1973, 309 ; b) M.F. Dube, J.W. Timberlake, Tetrahedron 36, 1753 (1980); c) S. Dinçtürk, R.A. Jackson, J. Chem. Soc. Perkin II 1981, 1127

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