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CAPTO-DATIVE SUBSTITUENT EFFECT ON THE CIS-TRANS ISOMERISATION OF CYCLOPROPANES[1].

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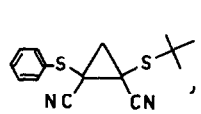
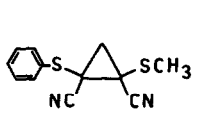
Summary. Very low activation energies were found for the cis-trans isomerisation of capto-datively substituted cyclopropanes.

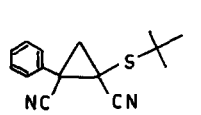
It has been shown that the activation energy for the cis-trans isomerisation of cyclopropanes is considerably decreased by substituents able to stabilise a diradical transition state (or an intermediate diradical) [2]. In order to get more information as to the magnitude of the capto-dative (*cd*) substituent effect [3] on the stabilisation of free radicals, the geometrical isomerisation of the following four cyclopropanes was investigated.



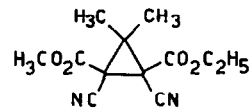
I



II



III



IV

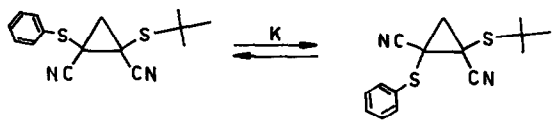
In the case of I, II and III, the kinetics [4] can already be followed at temperatures as low as 50°. In contrast, IV does not isomerise at temperatures up to 220°, and even then, it decomposes without isomerisation.

The rate constants for the forward an reverse reaction kinetics : the integrates expression is the usual one [5] :

$$\ln[(AK-B)/(A_oK-B_o)] = (k_{c,t} + k_{t,c})t$$

where A and B are the %ages of the cis and trans isomers at any given time of the reaction respectively and A_o and B_o, the respective starting %ages. The equilibrium constants ($K = \frac{k_{c,t}}{k_{t,c}}$) were measured for each temperature. The values of the slope ($k_{t,c} + k_{c,t}$) were determined by the least-squares treatment of the kinetic data. The unimportance of the solvent polarity was checked for I, excluding any ionic reaction.[6] Those results are presented in Table 1.

Table 1



K = 10 (independent of the temperature)

Solvent	ε	A x 10^{-11} (sec^{-1}) cis → trans	A x 10^{-11} (sec^{-1}) trans → cis	E_a (Kcal.mol^{-1}) cis → trans	E_a (Kcal.mol^{-1}) trans → cis
$CDCl_3$	4.8	103.5	8.07	26.8	26.7
	34.8	28.0	410.0	27.9	28.2

The relative unimportance of the steric factors are shown in Table 2, where the activation energies for the isomerisation of I and II in $CDCl_3$ are compared.

Table 2

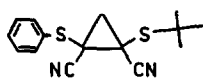
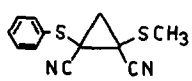
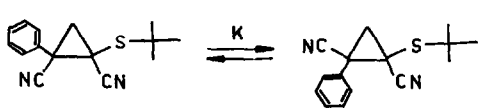
	Ea (Kcal.mol^{-1}) cis → trans	Ea (Kcal.mol^{-1}) trans → cis
	26,8	26,7
	25,3	25,8

Table 3 shows the Arrhenius parameters for the isomeration of III, and the equilibrium constants measured at 5 different temperatures.

Table 3



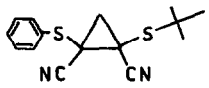
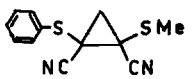
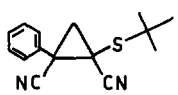
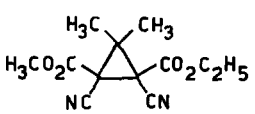
A x 10^{-14} cis → trans	A x 10^{-14} trans → cis	E_a (Kcal.mol^{-1}) cis → trans	E_a (Kcal.mol^{-1}) trans → cis
0.27	1.01	26.6	28.6

Solvent : $CDCl_3$

K	T°C
3.59	96
4.28	80
4.51	64
5.09	57
5.63	49

The results, together with some of the literature data are summarised in table 4.

Table 4

		E_a (Kcal.mol^{-1})	Reference
		65.1	7
		47.0	5
		33.5	8
	(I)	26.8 *	this work
	(II)	25.5 *	this work
	(III)	27.6 *	this work
	(IV)	at 220°C decomposition without isomerisation	this work

* Average value between $E_{a_{cis \rightarrow trans}}$ and $E_{a_{trans \rightarrow cis}}$.

It is worthwhile to note the very low activation energies reported in table 4, for I, II and III, and the absence of isomerisation of IV at temperatures up to 220°C. Since we have good reasons to believe that the mechanism is a biradical one [5,6], all those results are in good agreement with the fact that a captodatively substituted radical (-$\dot{C}$(SR)(CN)) is better stabilised than a radical centered on a carbon atom carrying two accepting groups (-$\dot{C}$(CO_2CH_3)(CN)). Other types of cyclopropanes are being investigated in order to be able to generalise the (*cd*)stabilisation effect. Those results will be discussed in a later paper, together with the synthesis of the new cyclopropanes.

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(b) for theoretical support of our concept, see also :
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M. Klessinger, Angew. Chem. 92, 937 (1980)
Angew. Chem. Int. Ed. Engl., 19, 908 (1980)

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