The Thermal *cis–trans*-Isomerization of Some Substituted Tetraphenylcyclopropanes. An Assessment of the Importance of Merostabilization of a 1,3-Biradical

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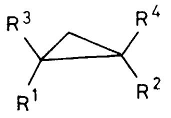
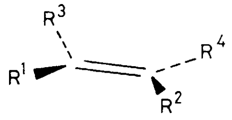
Summary The Arrhenius kinetic parameters for the thermal *cis–trans*-isomerization of 1,2-di-(*p*-methoxyphenyl)-1,2-diphenyl- (**1a**), 1,2-di-(*p*-cyanophenyl)-1,2-diphenyl- (**1b**), 1-(*p*-cyanophenyl)-2-(*p*-methoxyphenyl)-1,2-diphenyl- (**1c**), and 1,2-di-(*p*-cyanophenyl)-1,2-di-(*p*-methoxyphenyl)-cyclopropane (**1d**) give an indication of the substituent effects on the stability of the transient 1,3-biradical.

It is generally accepted that the thermal *cis–trans*-isomerization of substituted cyclopropanes usually involves homolytic cleavage of the most heavily substituted bond yielding the 1,3-biradical (trimethylene), followed by a bond rotation and subsequent rebonding.[1] Whether the 1,3-biradical is an intermediate or transition state is still a matter of some conjecture. This reaction is analogous to the thermal *cis–trans*-isomerization of alkenes which involves essential cleavage of the π-bond by a 90° rotation, through a transition state '1,2-biradical.' We have recently reported the results of a study of the kinetics of the isomerization of some substituted tetraphenylethylenes (**2a**, **b**, and **d**).[2] The variation in the activation energy correlates with parameters ($\sigma\cdot$) reflecting the substituent effect on benzylic-radical stability. A significantly lower (8 kJ mol^{-1}) barrier was observed for the unsymmetrically tetrasubstituted derivative (**2d**) which was attributed to merostabilization. This study has now been extended to substituted 1,1,2,2-tetraphenylcyclopropanes (**1a**–**d**). The results confirm the biradical nature of the transition state and give an indication of the importance of merostabilization, lowering the activation energy of this isomerization.



(1)



(2)

		m.p./°C of (**1**)	
a	*cis*	205—206	$R^1 = R^2 = 4\text{-MeOC}_6H_4$, $R^3 = R^4 = Ph$
	trans	139—141	$R^1 = R^4 = 4\text{-MeOC}_6H_4$, $R^2 = R^3 = Ph$
b	*cis*	201—202	$R^1 = R^2 = 4\text{-NCC}_6H_4$, $R^3 = R^4 = Ph$
	trans	106—110	$R^1 = E^4 = 4\text{-NCC}_6H_4$, $R^2 = R^3 = Ph$
c	*cis*	158	$R^1 = 4\text{-MeOC}_6H_4$, $R^2 = 4\text{-NCC}_6H_4$, $R^3 = R^4 = Ph$
	trans	134	$R^1 = 4\text{-MeOC}_6H_4$, $R^4 = 4\text{-NCC}_6H_4$, $R^2 = R^3 = Ph$
d	*cis*	157	$R^1 = R^2 = 4\text{-MeOC}_6H_4$, $R^3 = R^4 = 4\text{-NCC}_6H_4$
	trans	95	$R^1 = R^4 = 4\text{-MeOC}_6H_4$, $R^2 = R^3 = 4\text{-NCC}_6H_4$

The required tetraphenylcyclopropanes (**1a**–**d**) were prepared by the addition of the substituted diphenylmethylenes to the substituted 1,1-diphenylethylenes. The diphenylmethylenes were generated photochemically from the corresponding diazo-compounds.[3] The isomers were separated by medium-pressure column chromatography on silica gel. Structural assignments of (**1a**, **b**, and **c**) (*cis* and *trans*) were made primarily on the basis of ^1H and ^{13}C n.m.r. spectroscopy. The *cis*- and *trans*-isomers of (**1c**) were not so easily distinguished and the assignment, which must be considered tentative, was based upon the assumption that attraction between the cyano- and methoxy-substituted rings will cause the *cis*-isomer to be the more stable. Rates of approach to thermal equilibrium ($k_{t \to c} + k_{c \to t}$) were studied *in* degassed benzene solution over a 20 °C temperature range near 120 °C. The progress of the reaction was followed by high-pressure liquid chromatography using a calibrated u.v. detection system. Competing reactions were insignificant; even at the higher temperatures configurational equilibrium was established long before appreciable indane or propene formation.[4] The Table summarizes the thermodynamic and kinetic data for the isomerization of (**1a**—**d**). The analogous data for the isomerization of (**2a**, **b**, and **d**) are listed for comparison.[2]

TABLE. Arrhenius activation energies (E_a)[a] and pre-exponential factors (A)[a] for the thermal isomerization of (**1**) and (**2**) in benzene solution.

	K_e (*cis–trans*)	E_a kJ mol^{-1} [b]	log A[b]
(**1a**)	0·992[c]	127±5	13·1±0·6
(**2a**)	0·938[d]	148±3	12·5±0·3
(**1b**)	0·602[c]	127±3	13·4±0·4
(**2b**)	0·730[d]	147±2	12·3±0·2
(**1c**)	1·105[c]	127±4	13·3±0·5
(**1d**)	0·685[c]	118±5	12·5±0·7
(**2d**)	0·610[d]	138±5	11·8±0·5

[a] Obtained by linear least-squares analysis of the Arrhenius equation ($k_{t \to c} + k_{c \to t}$) = A exp ($-E_a/RT$). The quantity ($k_{t \to c} + k_{c \to t}$) is the sum of the rate constants for the forward and reverse reactions; therefore, the Arrhenius factors refer to the approach to equilibrium and not to the individual processes.
[b] Error limits obtained from least-squares analysis. [c] At 120 °C.
[d] At *ca.* 205 °C (see ref. 2).

Several significant points emerge from an analysis of these data. The substituent effects on the activation energy confirm the biradical nature of the transition state for the isomerization of these compounds. Comparison of the substituent effect on the isomerization of the cyclopropane with that of the analogous alkene supports the view that the reactions are similar. The strength of the cyclopropane σ-bond is less than that of the analogous alkene π-bond by about 20 kJ mol^{-1} for these derivatives. If charge separation was involved, the unsymmetrical substitution of (**1c**) would have lowered the activation barrier. The lower barrier (9 kJ mol^{-1}) for the isomerization of the tetrasubstituted derivative (**1d**) may be attributed to merostabilization of the 1,3-biradical. In addition the pre-exponential factor (log A) also decreases with this derivative, implying a more restricted transition state which is consistent with the involvement of merostabilization.

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