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STEREOCHEMICAL CONTROL OF THE INTERFACIAL CYCLOPROPANE DERIVATIVES FORMATION[x]

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We have recently reported[1] that the stereochemical course of the Darzens condensation of phenylchloroacetonitrile with benzaldehyde carried out in the presence of aqueous sodium hydroxide solution and a catalyst, a tetraalkylammonium (TAA) salt (so called catalytic two-phase, CTP system[2]), is changed considerably in favour of the formation of cis-2,3-diphenylglycidonitrile, when the catalyst is absent. This phenomenon is due to the fact that in absence of the catalyst, the whole multistep process takes place at the phase boundary, whereas the catalytic reaction occures inside the organic phase. It has been found recently that numerous cyclopropane derivatives can be prepared efficiently in CTP system via addition of 2-halocarbanions to electrophilic alkenes[3].

Here we would like to report that interfacial phenomena affect strongly the stereochemical course of the formation of dicyanocyclopropane derivatives in reaction of 2-chloroalkanenitriles with 1-cyanoalkenes carried out in the two-phase system[4]. The cis to trans ratio of the products depends whether the catalyst (a TAA salt) is present or not, as shown in the table.

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[x] Reactions of Organic Anions, Part XCII; Part XCI: M.Jawdosiuk and I.Kmiotek--Skarżyńska, Polish J.Chem., in press.

Table

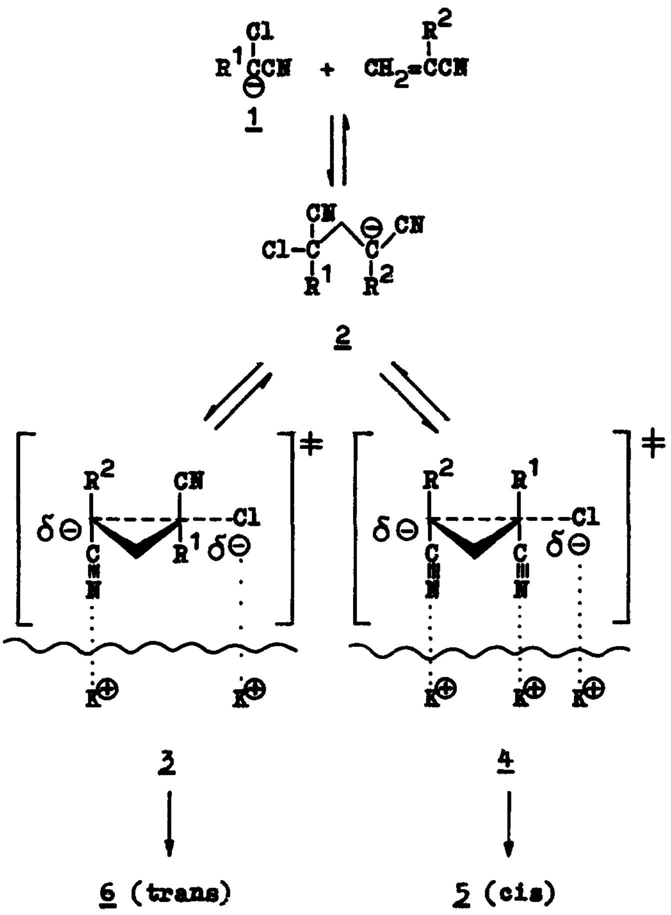
5 (cis) 6 (trans)

R^1	R^2	5 : 6 ratio			
		with cat.		without cat.	
		50 % aq NaOH	KOH solid	50 % aq NaOH	KOH solid
C_6H_5	Cl	54 : 46	-	93 : 7	-
C_6H_5	H	60 : 40	51 : 49	93 : 7	90 : 10
CH_3	CH_3	-	49 : 51	-	76 : 24
CH_3	$C_6H_5CH_2$	48 : 52	53 : 47	-	79 : 21
$(CH_3)_2CH$	CH_3	-	48 : 52	-	80 : 20

The results and the distinct regularities are rationalized as follows. In the catalytic reaction the intermediate 2-chlorocarbanions 1 and 4-chlorocarbanions 2 (see scheme) are accompanied by the TAA cation, and are located inside the organic phase. In these cases the cis to trans ratio of dicyanocyclopropanes 5 and 6 is close to 1, hence one can assume that the free energies of the transition states 3 and 4 are roughly equal.

On the other hand, in the absence of the catalyst, both these intermediate carbanions are located in the interfacial region. In this situation in the transition state 4, there are interactions of two cyano groups and the leaving chloro substituent with alkali metal cations located at the phase boundary. In the transition state 3, such interactions are considerably hindered by the trans mutual location of the cyano groups and the hydrophobic substituents R^1 (see scheme). For these reasons, the transition state 4 is additionally stabilized as compared to the transition state 3, and as a result the predominant formation of the cis isomere of the dicyanocyclopropane derivatives 5 is observed.

Scheme



The different stereochemical course of the formation of dicyanocyclopropanes in the two-phase system in the presence and absence of the catalyst, and similar phenomena in the case of the Darzens condensation[1], can serve as a direct independent piece of evidence that carbanions are indeed formed and react at the phase boundary. These results give a strong support for the mechanistic picture of reactions of carbanions in the two-phase system we have presented in our earlier papers[2a,5].

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4. In some cases noncatalytic reactions carried out in the presence of aqueous sodium hydroxide solution are very slow, hence the solid powdered potassium hydroxide was frequently used instead of aqueous sodium hydroxide. Cross-checking experiments have shown that this change does not effect the stereochemical results (see the table).
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