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SOLVOLYSIS OF *cis*- AND *trans*-CHRYSANTHEMYL 3,5-DINITROBENZOATES. THE CONJUGATIVE TRANSMISSION ABILITY OF CYCLOPROPANE RING[1)]

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The solvolysis of the titled compounds was investigated. The *trans*-isomer was solvolyzed 5.5 times faster than the *cis*-isomer at 100°C, but the product compositions were similar. From these results, *cis*- and *trans*-homopentadienyl cations were postulated as the intermediates.

Much attention has been paid recently to the ring-opening reactions of the chrysanthemyl system into non-head-to-tail monoterpenes as a biogenetic model study.[2)] As previously reported by us,[3)] it seems of interest to compare the character of "solvated" carbonium ion with that of "hot" one in chrysanthemyl system. Furthermore, a recent theoretical study on *trans*-vinylcyclopropylmethyl cation indicates the presence of a transmission of conjugation with the cation through the cyclopropane ring to the vinyl group.[4)] Thus, comparative solvolysis study between *cis*- and *trans*-chrysanthemyl systems is instructive in view of the conjugative transmission ability of the cyclopropane ring. A recent communication by Poulter et al.[5)] on the solvolysis of N-methyl-4-(chrysanthemyloxy)pyridinium iodide prompted us to report our results in the solvolysis of *cis*- and *trans*-chrysanthemyl 3,5-dinitrobenzoates (*cis*-I-DNB and *trans*-I-DNB).

The solvolysis of *cis*- and *trans*-I-DNB was carried out in 75% (vol/vol) aqueous dioxane at 70-100°C, which was followed the first order kinetic. The kinetic parameters were calculated for both *cis*- and *trans*-I-DNB as summarized in Table 1. For product studies, 2,6-lutidine was used to neutralize the 3,5-dinitrobenzoic acid. The main products were yomogi alcohol (II)[6)], artemisia alcohol (III)[7)], and artemisia triene (IV)[8)], all of which might be produced *via* the 1,3-bond fission of the cyclopropane ring. Besides, santorina triene (V)[9] and santorina alcohol (VI)[2] both as the 1,2-bond fission products were obtained in 0.5 and 0.2% yields from *trans*-I-DNB, and 2 and 1% yields from *cis*-I-DNB (Table 2). The yields of IV increased as the reaction time prolonged due to dehydration of primarily produced II under the solvolysis conditions as evidenced by a blank test.

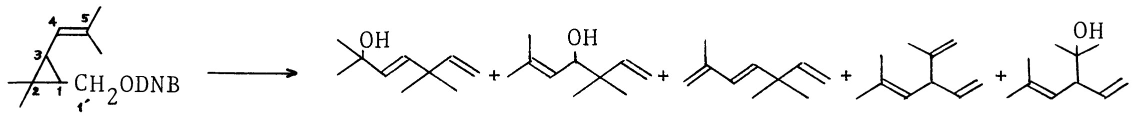
Table 1. Solvolysis Rate Constants of *trans*-I-DNB and *cis*-I-DNB

Compds.	Temp. (°C)	k (sec^{-1})	Ea (kcal/mol)	$\Delta S^{\ddagger}$ (eu)	$k_{rel.}$
trans-I-DNB	70.0	3.91×10^{-6}			
	80.0	1.08×10^{-5}			
	90.0	3.21×10^{-5}			
	100.0	1.02×10^{-4}	27.8	-5	5.5
cis-I-DNB	70.0	5.55×10^{-7}			
	80.0	1.51×10^{-6}			
	90.0	5.39×10^{-6}			
	100.0	1.85×10^{-5}	28.8	-6	1

Table 2. Product Composition of Solvolysis[a] and Deamination[b] in Chrysanthemyl System

Compds.	Time (hr)	Temp. (°C)	Product Composition (%)[c]			
[Solvolysis]				II	III	IV
trans-I-DNB	5.5	100		56	8	35
	9.5			53	8	38
	30.5			41	6	52
cis-I-DNB	9.5	100		50	7	40
	30.5			43	7	47
	50.5			34	7	56
	104.0			15	5	77
[Deamination]			I-Ac		III-Ac	IV
trans-VII	5.0	80	30		27	38
cis-VII	5.0	80	25		23	48

[a] Inspection by nmr and ir spectra revealed that neither *trans*- nor *cis*-I-DNB undergoes isomerization or interconversion *via* ion-pair return during the course of reaction. [b] Taken from Ref. 3. [c] Estimated from relative peak areas on glpc.



(I)-DNB (II) (III) (IV) (V) (VI)

Above results revealed that the 2-methyl-1-propenyl group interacted considerably with the intermediate carbonium ion through the cyclopropane ring. The reaction rate (Table 1) was apparently enhanced by the 2-methyl-1-propenyl group at C^3 in comparison with other cyclopropylmethyl system.10) This is in good contrast with a phenyl substituent which could be realized by the slight rate acceleration;11) this difference should be attributable to the conjugative ability of the substituents; i.e., 2-methyl-1-propenyl group can take a preferred bisected conformation but phenyl group can only insufficiently. Furthermore, it is to be noted that the solvated carbonium ion generated in the solvolysis was attacked by a nucleophile at C^1- and C^3-positions instead of C^3- and C^5-positions for the "hot" carbonium ion generated by deamination of chrysanthemylamine (VII) (Table 2).

Another interesting feature of this solvolysis reaction is that the *trans*-I-DNB was solvolyzed 5.5 times faster than the *cis*-I-DNB. This fact indicates the presence of a better transmission of the conjugation in the *trans*-configuration than in the *cis*-one, and also reflects on the more energetically favored pπ-interaction in the *trans*-isomer than in the *cis*-one.

According to the Schleyer's method, the rate enhancement due to 2-methyl-1-propenyl group can be estimated as ca. 15 factor for *trans*-I-DNB, and ca. 3 for *cis*-I-DNB.12) However, these values seem to be too small as the acceleration factor by the 2-methyl-1-propenyl group, considering the observed selective 1,3-bond fission. The present results could be rationalized by postulating considerable charge delocalization between C$^{1'}$ and 2-methyl-1-propenyl group at C^3 more than between C$^{1'}$ and $C_2^2(CH_3)_2$ at the transition state.

Conclusively, the kinetic data and the product compositions in the solvolysis of *cis*- and *trans*-I-DNB suggest that the 2-methyl-1-propenyl group alters the transition conformation of the intermediate cyclopropylmethyl cation to homopentadienyl cation instead of the normal bisected one, as illustrated in Figure 1.

trans *cis*

Fig. 1.

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