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THE MECHANISM OF OLEFINIC CYCLIZATIONS. A CASE OF π- PARTICIPATION

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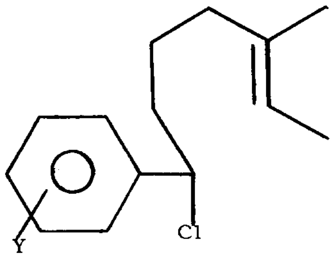
We report the following partial results of an investigation on π- participation because of their relevance to the mechanism of nonenzymic, biogenetic-like olefinic cyclizations[1].

A series of 1-aryl-5-methyl-trans-2-heptenyl chlorides I and an analogous series of chlorides II with a saturated aliphatic chain were prepared and their solvolysis rates measured.



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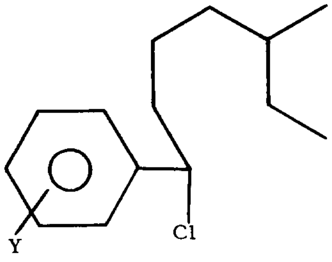

II

The results are given in Table I. The calculated ratios of first order constants for analogous compounds of the two series are given in Table II.

The data reveal a significant rate acceleration due to the olefinic double bond[2] in all

Table I

Solvolysis Rates of 1-Aryl-5-methyl-trans-2-heptenyl Chlorides I and of 1-Aryl-5-methylheptyl Chlorides II

Y	Solvent[a]	Temp.	k_I (sec^{-1})[b]	k_{II} (sec^{-1})[b]
p-OCH_3	96%E	5°	$2.97x10^{-3}$ (1)	$3.00x10^{-3}$ (1)
	96%E	10°	$5.36x10^{-3}$ (4)	$5.29x10^{-3}$ (3)
	96%E	25°	$2.80x10^{-2}$	$2.59x10^{-2}$
p-CH_3	96%E	40°	$1.46x10^{-4}$ (2)	$6.11x10^{-5}$ (1)
	96%E	50°	$3.49x10^{-4}$ (1)	$1.75x10^{-4}$ (2)
	96%E	25°	$3.54x10^{-5}$	$1.10x10^{-5}$
	80%E	25°	$2.81x10^{-4}$ (2)	$1.26x10^{-4}$ (1)
H	80%E	40°	$9.53x10^{-5}$ (5)	$1.12x10^{-5}$ (1)
	80%E	50°	$2.26x10^{-4}$ (3)	$3.98x10^{-5}$ (3)
	80%E	25°	$2.34x10^{-5}$	$1.45x10^{-6}$
	97%T	25°		$5.15x10^{-4}$ (2)
p-Br	80%E	40°	$2.20x10^{-5}$ (5)	
	80%E	50°	$6.38x10^{-5}$ (5)	
	80%E	25°	$3.89x10^{-6}$	
	97%T	25°	$1.93x10^{-3}$ (1)	$1.02x10^{-4}$ (1)
m-Br	97%T	40°		$1.37x10^{-5}$ (2)
	97%T	50°		$2.91x10^{-5}$ (5)
	97%T	25°	$2.34x10^{-4}$ (1)	$4.02x10^{-6}$

a) %E = volume percent aq. ethanol, %T = weight percent aq. 2,2,2-trifluoroethanol. b) Rate constants are the mean of 3-5 measurements. Uncertainties are standard errors, e.g. $2.97x10^{-3}$ (1) means $(2.97 \pm 0.01) \times 10^{-3}$. Rate constants listed without the standard deviation are extrapolated values.

Table II

Relative Rate Ratios k_I/k_{II} at 25° and Percent of I Reacting via Neighboring Group Assisted Route

Compounds Y	k_I/k_{II}	$(Fk_\Delta/k_t) \times 100$ for I
p-OCH_3	1.1	9
p-CH_3	2.2-3.2	55-70
H	16.2	94
p-Br	18.9	95
m-Br	58	98

cases except for the p-anisyl substituted compound. Using the well known equation[3] $k_t = k_c + Fk_\Delta$ the percent I reacting by way of the anhimerically assisted route $(Fk_\Delta/k_t) \times 100$ was calculated and the results are given in Table II.

Hammett plots for the two series gave the following results. For series II, $\rho^+ = -6.3$ (correlation coeff. 0.997) which is the same value as with α-arylethyl chlorides[4]. For series I, $\rho^+ = -3.9$ (correlation coeff. 0.998) with the point for p-OCH_3 compound deviating significantly from the correlation line[5]. The line drawn from the latter point to the point for the p-tolyl compound is parallel to the correlation line for series II.

The relatively small negative value of ρ^+ for series I indicates a larger dispersal of positive charge in the reaction transition state as compared with series II, which is consistent with nucleophylic participation of the olefinic double bond in the rate determining step. The break in the $\rho^+\sigma^+$ correlation line indicates a change in mechanism[5]. It appears that chlorides with a better electron releasing aryl group than p-tolyl solvolyze without π-participation and by the same mechanism as the chlorides of series II or

α-arylethyl chlorides.

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