

CONFORMATION OF 1,2 - DISUBSTITUTED CHLORMETHYL CYCLOHEXENES

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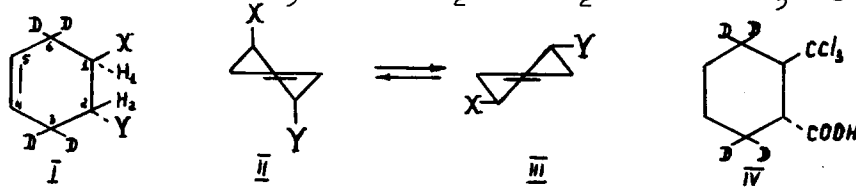
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Our previous work (1) showed that diequatorial conformation III is preferable for a large number of trans-1,2-disubstituted cyclohexenes of type I with exception of acid chloride Ia which has abnormally low coupling constant $J_{H_1H_2}$ in the PMR spectra (2).

The aim of this work was the conformational analysis of some cyclohexenes of type I containing CCl_3 Ia-d, $CHCl_2$ I e, CH_2Cl I f and CH_3 I g groups.



I	a	b	c	d	e	f	g
X	CCl_3	CCl_3	CCl_3	CCl_3	$CHCl_2$	CH_2Cl	CH_3
Y	$COCl$	$COOH$	$COOCH_3$	NO_2	$COOH$	$COOCH_3$	NO_2

All compounds were prepared from 1,1,4,4- d_4 - butadiene and the corresponding trans-dienophiles (3). Acid Ib was prepared by hydrolysis of acid chloride Ia. Constants of the compounds obtained and respective PMR data are presented in Table 1. The PMR spectra of 10 M% solutions were recorded using Varian HA-100 spectrometer with double irradiation at the deuteron resonance frequency 9.209662 c/s, TMS was used as an internal standard.

Inspection of Table indicated that all compounds with CCl_3 group have

Table 1
 Constants and PMR Data of the Compounds Ia - g

Compound I X	Y	b.p. °C/mm (m.p. °C)	n_D (°C)	δ_{H_1} ppm	δ_{H_2} ppm	Proton system	$J_{H_1H_2}$ c/s	% III $\pm 15\%$
CCl ₃	COCl	106/1	1.5349 (19,5)	3.44	3.53	AB	5,9	46
CCl ₃	COOH	(74-5)	-	3.44	3.28	AB	6,2	49
CCl ₃	COOCH ₃	90-6/1	1.5130 (23)	3.21	2.99	AB	7.2	61
CCl ₃	NO ₂	112-6/1	1.5323 (20)	3.68	5.00	AX	6.3	51
CHCl ₂	COOH	(129)	-	2.52	2.72	AB	9.95	93
CH ₂ Cl	COOCH ₃	58-9/6	1.4542 (23)	2.3	2.6	AB	9.6	89
CH ₃	NO ₂	74-6/5	1.4708 (20)	2.25	4.30	AX	10.7	(100)

low coupling constants. It is quite logical to connect such lowering of coupling constants $J_{H_1H_2}$ at least in part with an increase in the content of diaxial form II in the conformational equilibrium. Such conformational abnormality of CCl₃ - derivatives is not affected by varying other substituent at C₂, although a decrease in the number of chlorine atoms in going from CCl₃ to CHCl₂, CH₂Cl and CH₃ makes disappear this effect. Thus, this peculiarity should be associated just with the presence of the bulky CCl₃ group. This effect holds only for cyclohexene derivatives because the saturated compound IV was also studied and found to exist in the diequatorial conformation ($J_{H_1H_2} = 10.1$ c/s, $\delta_{H_1} = 2.98$ ppm, $\delta_{H_2} = 2.72$ ppm).

The position of conformational equilibrium can be estimated using the Eliel equation: $J_{H_1H_2} = n J^{aa} + (1-n) J^{ee}$, where n is mole fraction of ee-conformer, J^{aa} , J^{ee} - coupling constants in ee- and aa-conformer.

The major difficulty in estimating the conformational equilibrium using the above equation relates to a necessarily somewhat arbitrary selection of the standard J^{aa} and J^{ee} constants. Figure 1 shows the dependence of calculated content of diequatorial conformation III upon the values $J_{H_1H_2}$ based on the use of the various sets of standard constants.

Table 1 lists the data calculated with the "optimal set" ($J^{aa} = 10.5$ c/s,

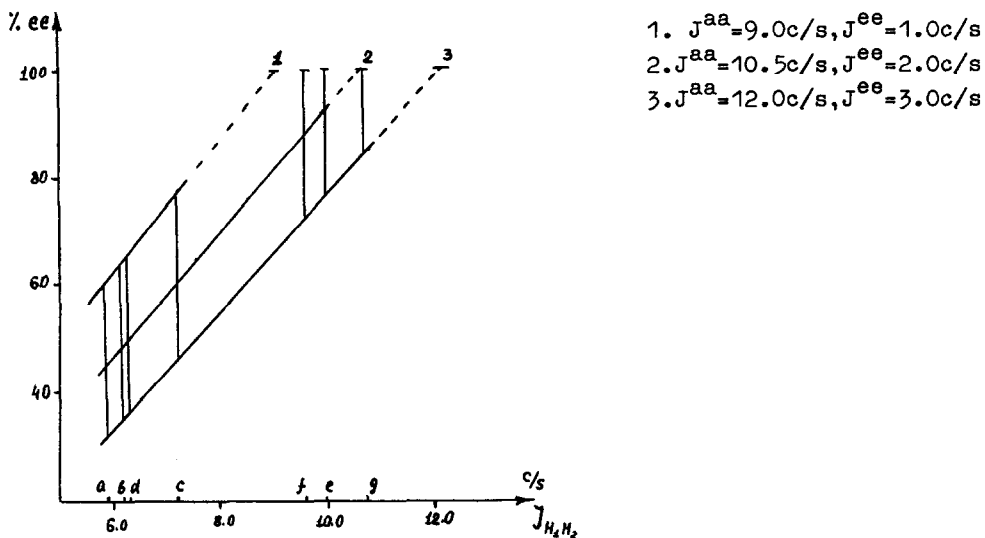


Fig. 1. Content of Diequatorial Conformation III upon the Value $J_{H_1H_2}$ on Various Sets of Standard Constants

$J^{ee} = 2 \text{ c/s}$). For comparison we estimated the position of the conformational equilibrium of compound I d from the dipole moment data ($\mu_{\text{exper.}} = 3.08\text{D}$, $\mu_{\text{calc.}}^{aa} = 1.57 \text{ D}$, $\mu_{\text{calc.}}^{ee} = 3.64 \text{ D}$). Hence the content of the diequatorial conformation III for I d is 65%. The agreement between the data obtained by two methods is quite good allowing for the uncertainty in standard values of J^{aa} and J^{ee} and the influence which the electronegativity of the substituent exerts on the coupling constants.

Thus, for trans - 1,2 - disubstituted cyclohexenes with CCl_3 group the portion of diequatorial form is sharply diminished. In our opinion this abnormality can be generally interpreted in term of the dipole-dipole and (most likely) steric repulsion of the bulky substituents in the diequatorial conformation III.

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R E F E R E N C E S

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