CATALYST EFFECTS ON THE STEREOSELECTIVITY OF ADDITION OF TETRACHLOROMETHANE TO 1,3-CYCLOHEXADIENE

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The stereoselectivity of addition reaction of tetrachloromethane with conjugate cyclodienes represented by 1,3-cyclohexadiene has been studied in respect to the type of catalyst. In all addition reactions the product of 1,4-addition, i.e. 1-chloro-4-(trichloromethyl)cyclohex-2-ene was formed exclusively consisting of two isomers (**1a**, **1d**). Copper–amine complexes gave higher isomeric ratio **1a** : **1d** (up to 3.7) than ruthenium complex (1.3) at the same conditions (80 °C). Moreover, it was found that isomeric ratio was temperature dependent and the highest value (6.4) was obtained at lower temperature (20 °C). The results proved both catalyst and ligand effects on stereoselectivity of addition reaction of conjugated cyclic dienes. This supports a non-chain reaction mechanism because isomeric ratios of chain reactions are catalyst independent.
Key words: Addition; Stereoselectivity; Ligand effects.

Recently we reported catalyst effects on the stereoselectivity of addition reactions between tetrachloromethane and *cis*-cycloalkenes[1]. Both the nature of the central metal atom and the ligands were found to effect stereoselectivity and this provides valuable information about the mechanism of addition reactions. Addition reactions to conjugated cyclodienes, e.g. 1,3-cyclohexadiene may provide more isomers of the corresponding 1 : 1 adduct and therefore it is a convenient model reaction from the point of view of a study of catalyst effects on stereoselectivity.

Reaction between 1,3-cyclohexadiene and tetrachloromethane in the presence of $[RuCl_2(PPh_3)_3]$ has been only briefly reported in the literature[2]. However, the stereochemistry of the 1 : 1 adduct was not determined.

EXPERIMENTAL

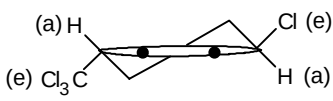
All reactions were carried out under an atmosphere of argon. Reagents were purified by standard methods immediately prior to use. GC analysis was performed on an HP 5890 A instrument with an HP Ultra-1 capillary column. ^1H and ^{13}C NMR spectra of the products were measured on a Varian

XL 200 spectrometer with $CDCl_3$ as solvent. Mass spectra were recorded on GC-MS instrument Finnigan MAT, model ITD 800.

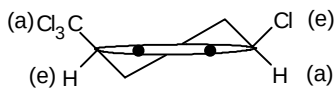
Typically, tetrachloromethane, 1,3-cyclohexadiene and the catalyst in the molar ratio 5 : 1 : 0.02 were weighed into a glass ampoule. The copper catalyst was prepared in situ from cuprous chloride and an appropriate amine in the molar ratio 1 : 2. The reaction mixture was magnetically stirred and heated at a given temperature (80, 60, 20 °C) in an oil bath. Samples of the reaction mixture were taken through a septum at regular intervals and analysed by GC (70 °C, 20 °C/min–230 °C) in respect of the isomeric ratio of the 1 : 1 adduct. Reaction times varied from 2 to 5 h except for temperatures of 60 °C (7 h) and 20 °C (20 days). The ratio of the two isomers of the 1 : 1 adduct did not change in the course of the reaction with most amine ligands and high conversion of 1,3-cyclohexadiene was obtained (87–100%). In the case of some amines (cyclohexylamine, di-n-butylamine) the ratio changed at high conversion, presumably as a consequence of the lower stability of the corresponding copper complexes. In these cases isomeric ratios are reported at lower conversions (10–60%). In a preparative experiment with [CuCl(2-propylamine)$_2$] as catalyst 1 : 1 adduct, i.e. 1-chloro-4-(trichloromethyl)cyclohex-2-ene (**1**) was isolated in 72% yield (molar ratio = 2.5 : 1 : 0.02, 80 °C, 2 h, conversion 100%, purity 98%). GC analysis of the product showed two peaks at retention time 9.613 min (minor) and at retention time 9.760 min (major). Both peaks correspond to two isomers of the product with practically identical mass spectra: EI, 70 eV, 0–100% relative intensity: 79 (100), 115 (38), 161 (33), 234 (31), 125 (25), 39 (23), 232 (21) and 163 (20). Both isomers are characterised by the molecular ions with *m/z* 234, 232 and 236, by $(M - Cl)^+$ fragments (197 and 199) and by $(M - Cl - HCl)^+$ fragments (161 and 163). The base peak 79^+ correspond to cyclohexene ring fragment (C_6H_7). NMR analysis of the product: major isomer – ^{13}C NMR (δ, ppm): 131.29 (CH=CH), 127.95 (CH=CH), 102.93 (CCl_3), 56.66 (CHCl or ($CHCl_3$), 52.61 (CHCl or $CHCl_3$), 30.48 (CH_2), 20.84 (CH_2); minor isomer – ^{13}C NMR (δ, ppm): 133.79 (CH=CH), 127.08 (CH=CH), 103.11 (CCl_3), 55.70 (CHCl or $CHCCl_3$), 54.07 (CHCl or $CHCl_3$), 32.22 (CH_2), 25.66 (CH_2); both isomers – ^1H NMR (δ, ppm): 6.05–6.15 (m, CH=CH), 4.50–4.70 (m, CHCl), 3.15–3.40 (m, $CHCCl_3$), 1.80–2.60 (m, CH_2–CH_2).

RESULTS AND DISCUSSION

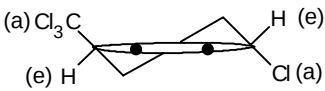
Addition of tetrachloromethane to 1,3-cyclohexadiene was carried out in the presence of ruthenium [$RuCl_2(PPh_3)_3$] and copper [CuCl(amine)$_2$] complexes. The results are summarised in Table I. In all addition reactions the product of 1,4-addition, i.e. 1-chloro-4-(trichloromethyl)cyclohex-2-ene (**1**) was formed exclusively in agreement with the literature[2]. No 2 : 1 adduct has been detected. GC, MS and NMR analysis of



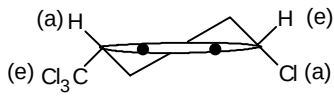
1a



1b



1c



1d

the product showed the formation of two isomers. Their ratio significantly differed for the ruthenium (1.3) and copper (3.0, amine is n-propylamine) complexes. The results indicate that the stereoselectivity of the addition reaction is catalyst dependent, i.e. the type of central metal atom of the complex plays an important role.

In order to investigate any ligand effect on stereoselectivity we examined copper complexes with a number of amines as ligands at 80 °C. Copper complexes with tertiary amines (trimethylamine, triethylamine) were completely inactive. Secondary amines gave the lowest isomeric ratio (1.2). Primary amines gave higher isomeric ratios dependent on the nature of alkyl group. The highest isomeric ratio was obtained with 2-propylamine (3.7). The results indicate that as the bulk of the alkyl group increases a lower ratio of isomers is formed (n-octyl 2.0, *tert*-butyl 1.6).

In an attempt to maximise the isomeric ratio, the effect of temperature was examined. It was found that lower reaction temperatures lead to an increase in isomeric ratio. A value of 6.4 was obtained when the reaction was carried out at room temperature (20 °C).

1,4-Substitued cyclohexenes usualy adopt half-chair structures and are thus in principle, existing in four isomeric forms: *trans*-diequatorial (**1a**), *cis*-axial-CCl_3-equatorial-Cl (**1b**), *trans*-diaxial (**1c**) and *cis*-axial-Cl-equatorial-CCl_3 (**1d**). Attempts to unequivocally identify two isomers formed were not fully successful, since the ^{1}H NMR coupling patterns were insufficiently resolved, event at 270 MHz. Attempted spin decoupling experiments did not further clarify the issue. However, molecular models

TABLE I
Catalyst effect on stereoselectivity of addition of tetrachloromethane to 1,3-cyclohexadiene

Catalyst		Temperature, °C	Isomeric ratio[a]
$RuCl_2(PPh_3)_3$		80	1.3
$CuClL_2$	L = n-propylamine	80	3.0
	L = 2-propylamine	80	3.7
		60	4.7
		20	6.4
	L = n-butylamine	80	2.4
	L = 2-methylpropylamine	80	2.6
	L = *tert*-butylamine	80	1.6
	L = di-n-butylamine	80	1.2
	L = n-octylamine	80	2.0
	L = cyclohexylamine	80	2.7

[a] The isomeric ratio (presumably **1a** : **1d**) corresponds to a constant value in the region of conversions of 1,3-cyclohexadiene 10–87% and 10–60%, respectively.

suggest that when the CCl_3 group on C4 occupies an axial position, it experiences severe steric interaction with the C3 axial hydrogen atom. The interaction between the chlorine atom in an axial site on C1 and the axial hydrogen atom on C3 is considerably less. However, it is clear that steric repulsions are minimised when both the CCl_3 group and the Cl atom occupy equatorial sites (**1a**) and maximised when both groups occupy axial sites (**1c**). Thus, we suggest that **1a** is the preferred product in this reaction. We are not entirely certain of the geometry of the minor product, but suggest that it is likely to be **1d**. This assignment is supported also by the results of semiempirical AM1 calculations[3] according to which the most stable product corresponds to **1a** isomer while the configuration **1d** was found to be less stable and isomers **1b**, **1c** were of the lowest stability. Such steric effects would be expected to be even greater in the cases of the 1-bromo-4-trichloromethyl and 1-bromo-4-tribromomethyl compounds. In agreement with this, we have obtained these compounds in yields similar to those observed for 1-chloro-4-(trichloromethyl)cyclohex-2-ene, but with isomeric ratios of 1.5 and 3.35, respectively. In none of these reactions we have been able to separate these mixtures by preparative GC in sufficient purity for NMR analysis of the individual isomers.

In conclusion, the results proved both catalyst and ligand effects on stereoselectivity of the addition reaction of conjugated cyclic dienes as represented by 1,3-cyclohexadiene. This supports a non-chain mechanism of reaction as was recently reported[1]. Moreover, modification of the isomeric ratio by catalyst, ligand and temperature to reach the highest value opens up the possibility of employing these reactions for stereospecific synthetic purposes, for example in the field of liquid crystals.

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