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THE DIELS–ALDER REACTION BETWEEN STYRENE AND *TRANS-TRANS* HEXA-2,4-DIENE

STRUCTURE AND CONFORMATION OF TWO ISOMERIC ADDUCTS

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Abstract—It has been shown by NMR spectrometry that the Diels–Alder reaction between styrene and *trans-trans* hexa-2,4-diene gives two adducts with retention of configuration of the diene: 3-methyl-*trans*-4-phenyl-*cis*-6-methylcyclohex-1-ene and 3-methyl-*cis*-4-phenyl-*cis*-6-methylcyclohex-1-ene. The conformation of the adducts is determined by the equatorial position of the Ph group.

Interpretation of the NMR spectra was possible with the aid of the spectra of the adducts from the reaction between *trans-trans* hexa-2,4-diene and β,β′-dideutero-styrene: 3-methyl-*trans*-4-phenyl-5,5′-dideutero-*cis*-6-methylcyclohex-1-ene and 3-methyl-*cis*-4-phenyl-5,5′-dideutero-*cis*-6-methylcyclohex-1-ene.

INTRODUCTION

THE Diels–Alder reaction between styrene and *trans-trans* hexa-2,4-diene has not been described. In the Diels–Alder reactions of hexa-2,4-diene with other dienophiles, a mixture of the *trans-trans* and *cis-trans* isomers was used and the stereochemistry of the adducts was not studied.[1]

The Diels–Alder reaction between a symmetrically 1,4-disubstituted *trans-trans* diene and a dienophile $RCH{=}CH_2$ may give two racemic mixtures,† when it is assumed, that the configuration of the diene is retained in the adducts and that the Ph group is in an equatorial position.‡ On these assumptions, the structure of the four adducts from the Diels–Alder reaction between styrene and methyl sorbate was established.[2] It is of interest, however, to ascertain independently that the substituents in the 1 and 4 position of the *trans-trans* diene are in a *cis* position to each other in the adducts and that the conformation of these cyclohexene derivatives is determined by the equatorial position of the Ph group. In this paper the validity of these assumptions has been proved by NMR spectrometry for the reaction between styrene and *trans-trans* hexa-2,4-diene. A complete interpretation of the spectra was possible with the aid of the spectra obtained from the reaction between β,β′-dideutero-styrene and *trans-trans* hexa-2,4-diene.

RESULTS

Under the conditions used (24 hr, 160°) the Diels–Alder reaction between styrene or β,β′-dideutero-styrene and *trans-trans* hexa-2,4-diene gives two components (in the ratio I:II = 5:8) which contain an aromatic group. These compounds are stable under reaction conditions. NMR data are given in Table 1.

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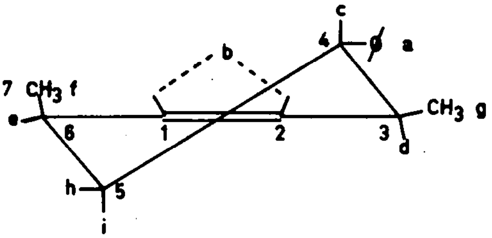
† The racemic mixtures are considered as one compound.

‡ Half chair conformations are assumed for the cyclohexene ring.

TABLE 1. CHEMICAL SHIFTS (δ) AND COUPLING CONSTANTS (J) OF THE TWO ISOMERIC ADDUCTS FROM THE DIELS–ALDER REACTION BETWEEN STYRENE AND *trans-trans* HEXA-2,4-DIENE

	Ia δ (ppm)	IIa δ (ppm)		Ia J* (c/s)	IIa J* (c/s)
H_a	7·12	7·12	J_{cd}	—	5
H_b	5·55	5·60	J_{ch}	1	3·5
H_c	2·30	3·07	J_{ci}	12	12
H_d	2·00–2·30	2·39	J_{dg}	6·5	7
H_e		2·29	J_{ef}	7	7
H_f	1·03	1·06	J_{eh}	5·5	—
H_g	0·83	0·59	J_{ei}	3	11
H_h	1·82	1·78	J_{hi}	11	11
H_i	1·63	1·49			

* Coupling with H_b is not observed.



The relative peak areas in the NMR spectra are in agreement with the expected structures for Diels–Alder adducts (Fig. 1).

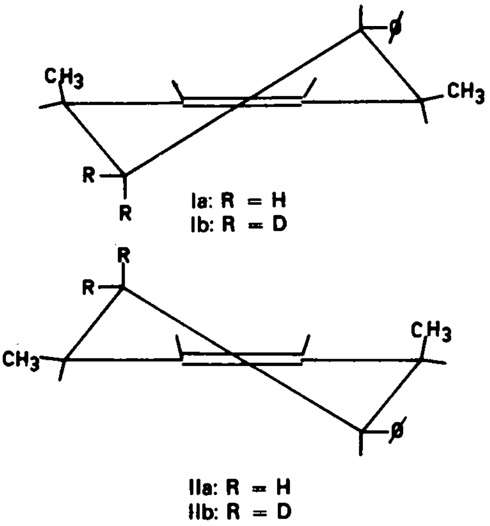


FIG. 1.

From the NMR spectra of compounds Ib and IIb the chemical shifts of H_c, H_d and H_e can be determined. The coupling constants J_{cd} cannot be deduced from the spectra of the deuterated compounds, because the signal of H_c coincides with those of H_d and H_e in the spectrum of Ib, whereas in the spectrum of IIb the signal of H_c is broadened (by coupling with the deuterium atoms) and structureless.

The chemical shift differences between the signals of H_c in I and II provide important information. It is known that the chemical shift of a proton H_x in a system H_x—C_1—C_2—Y depends on the dihedral angle between $H_xC_1C_2$ and C_1C_2Y.[3] In *cyclohexane* systems, therefore, the difference in chemical shift between compounds with an equatorial or an axial substituent Y is far less when H_x is in an equatorial position (the change in the dihedral angle being small) than when H_x is in an axial position (the dihedral angle changing from 60° to 180°). When H_x is in an axial position its signal is shifted to lower field when the dihedral angle passes from 60° (Y equatorial) to 180° (Y axial), the shift difference being 0·70–0·80 ppm when Y = Me.[3] No data are reported for *cyclohexene* derivatives. The difference in chemical shift (0·75 ppm) between the signals of H_c in I ($\delta = 2{\cdot}30$) and II ($\delta = 3{\cdot}07$) indicates that the results obtained in *cyclohexane* derivatives may be used also in the *cyclohexene* derivatives investigated. The results show that H_c is a proton in axial position with an equatorial Me group on the neighbouring carbon atom in I and an axial Me group on the neighbouring carbon atom in II.

In the NMR spectra of Ia and IIa the signals of H_i and H_h (which are missing in the deuterated compounds Ib and IIb) can be located. Assuming that the axial proton H_i absorbs at higher field than the equatorial proton H_h as in cyclohexanes,[4] the coupling constants given in Table 1 can be obtained. Coupling constants in agreement with the established axial position of H_c can only be determined when it is assumed that the axial proton H_i absorbs at higher field than the equatorial proton H_h. As $J_{ci} = 12$ c/s in both I and II, the dihedral angle between $H_iC_5C_4$ and $H_cC_4C_5$ is close to 180°[5] and therefore is in agreement with the axial position of H_c in both I and II. The chemical shift difference between H_c in I and II and the value of 12 c/s for J_{ci} in I and II are in agreement only with the configuration around C_3, C_4 and C_5 as shown in Fig. 1 for Ia and IIa, respectively (Ph group equatorial in both adducts and Me group *trans* and *cis*, respectively, to the Ph group). This is confirmed by the value of $J_{cd} = 5$ c/s for compound II, which implies a dihedral angle of about 60° between $H_dC_4C_3$ and $H_cC_3C_4$.

The difference in chemical shift between the signals of H_g in I and II is ascribed to a difference in shielding effect of the Ph group. From an inspection of Dreiding models it is clear that H_g absorbs at higher field in the *cis* compound II ($\delta = 0{\cdot}59$) than in the *trans* compound I ($\delta = 0{\cdot}83$) because the Me group in II is shielded by the aromatic ring. Nearly the same chemical shift values are found for the Me group in 3-carbomethoxy-*cis*-5-phenyl-*cis*-6-methylcyclohexene-1 ($\delta = 0{\cdot}63$) and 3-carbomethoxy-*trans*-5-phenyl-*cis*-6-methylcyclohexene-1 ($\delta = 0{\cdot}87$).[2]

There are two possibilities for the configuration around C_5 and C_6: H_e may be in a pseudo axial or pseudo equatorial position. For I a pseudo equatorial position of H_e means that the configuration of the diene is retained during the Diels–Alder reaction, for II, however, H_e must be in a pseudo axial position if the configuration of the diene is retained.

The values of J_{ie} for I (3 c/s) and II (11 c/s) and Karplus relation[5] indicate that H_e

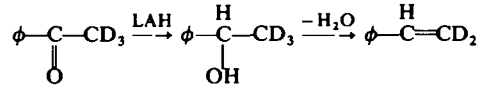
is in a pseudo equatorial position in I and in a pseudo axial position in II. Therefore the configuration of the diene is retained during the reaction.

The dihedral angle between $C_7C_6C_5$ and $H_iC_5C_6$ is about 60° in II and about 180° in I. The situation around carbon atoms C_5 and C_6 cannot, however, be compared with the situation around carbon atoms C_4 and C_3 or the analogous situation in the compounds studied in Ref. 3, where the *two* carbon atoms considered carry a substituent. The change in chemical shift of H_i between I ($\delta = 1{\cdot}63$) and II ($\delta = 1{\cdot}49$) is in the expected direction,[3] although it is much smaller. The equatorial proton H_b absorbs at about the same field in I and II,[3] as expected.

It may be concluded that the Diels–Alder reaction between *trans-trans* hexa-2,4-diene and styrene at 160° gives the two possible adducts with retention of configuration of the diene. The conformation of the cyclohexene derivatives is determined by the equatorial position of the Ph group. Adduct I is 3-methyl-*trans*-4-phenyl-*cis*-6-methylcyclohex-1-ene, adduct II is 3-methyl-*cis*-4-phenyl-*cis*-6-methylcyclohex-1-ene.

EXPERIMENTAL*

a. *Reaction conditions.* 2 g *trans-trans* hexa-2,4-diene (K and K Laboratories, Plainview, New York), 2 g styrene or β,β′-dideutero-styrene and 0·1 g hydroquinone were heated 24 hr at 160° under N_2. β,β′-dideutero-styrene was prepared according to Beachel and Nemphos:[6]



$$\phi\text{—}\underset{\overset{\|}{O}}{C}\text{—}CD_3 \xrightarrow{LAH} \phi\text{—}\underset{OH}{\overset{H}{C}}\text{—}CD_3 \xrightarrow{-H_2O} \phi\text{—}\overset{H}{C}{=}CD_2$$

Dehydration was effected by heating the carbinol with $KHSO_4$. The product contained 97% (by NMR) of deuterium in the β-position. Acetophenone-d_3 was prepared according to den Hertog and Kooyman.[7] Styrene was purified according to Ref. 2.

b. *Gaschromatographical separation and purification.* On an Apiezon L column two components containing aromatic compounds could be separated. The following products were obtained:

Ia: purity 98% $n_D^{25} = 1{\cdot}5222$; IIa: purity 98% $n_D^{25} = 1{\cdot}5277$; Ib: purity 99%; IIb: purity 99%.

The four compounds Ia, IIa, Ib and IIb could be determined conveniently on an Apiezon L column. Two normal alkanes were used as standards. The relative retention volumes at 150° are given in Table 2. No significant differences of the relative retention volumes between the deuterated and non-deuterated compounds was noted.

TABLE 2. RELATIVE RETENTION VOLUME OF THE ADDUCTS FROM THE DIELS–ALDER REACTION BETWEEN STYRENE AND *trans-trans* HEXADIENE-2,4 ON APIEZON L AT 150°

n-Tetradecane	0·87
n-Hexadecane	2·39
Ia, Ib	1·00
IIa, IIb	1·30

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* The authors are grateful for the competent cooperation of Mrs. M. den Dulk.

Conditions for Chromatography

Chromatograph	Aerograph Autoprep Model 705
Detector	Hydrogen Flame Ionization
Recorder	Leeds & Northrup, Speedomax W −0·05 to 1 mV, 1 sec
Column Dimensions	5·70 m × 0·8 cm i.d. aluminium coiled tube
Solid support	Anakrom AS (50/60 mesh)
Stationary phase	Apiezon L (5:95)
Temperature	150°
Carrier Gas	N_2 at 300 ml/min with a post column splitter (1:10)
Column Efficiency	About 2000 theoretical plates
Sample size	0·5 and 25 mg
Analysis time	15 min

c. *NMR spectra* (Varian A-60 spectrometer; solns about 1 M in CCl_4; TMS internal standard).

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