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THE DIELS–ALDER REACTION OF STYRENE WITH *trans*-PENTA-1,3-DIENE

METHYL 2-*trans*,4-PENTADIENOATE AND DIMETHYL 2-*trans*,4-*trans*-HEXADIENEDIOATE

O. KORVER, KWA T. L. and C. BOELHOUWER

Laboratory for Chemical Technology, University of Amsterdam, Plantage Muidergracht 30.

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Abstract—The Diels–Alder reactions between styrene and *trans*-penta-1,3-diene, methyl 2-*trans*,4-pentadienoate and dimethyl 2-*trans*,4-*trans*-hexadienedioate are described. The structure of the following adducts was determined by means of IR and NMR spectrometry: *trans*-3-methyl-4-phenyl-cyclohex-1-ene, *cis*-3-methyl-4-phenyl-cyclohex-1-ene, *trans*-3-methyl-5-phenyl-cyclohex-1-ene, *cis*-3-methyl-5-phenyl-cyclohex-1-ene, *trans*-3-carbomethoxy-4-phenyl-cyclohex-1-ene, *cis*-3-carbomethoxy-4-phenyl-cyclohex-1-ene, 3-carbomethoxy-*cis*-4-phenyl-*cis*-6-carbomethoxy-cyclohex-1-ene and 3-carbomethoxy-*trans*-4-phenyl-cis-6-carbomethoxy-cyclohex-1-ene.

INTRODUCTION

THE Diels–Alder reaction between styrene and methyl sorbate gives four adducts.[1] A kinetic investigation of this reaction revealed[2] that the differences in activation enthalpy and entropy for the formation of the four adducts are very small. The relative rates of formation of the Diels–Alder adducts might be changed considerably therefore when small changes are made in the diene, dienophile or in the reaction conditions.[11] Comparison of quantitative data of the Diels–Alder reaction of styrene and methyl sorbate with those of the related dienes, viz. *trans*-penta-1,3-diene, *trans*,*trans*-hexa-2,4-diene, methyl 2-*trans*,4-pentadienoate and dimethyl 2-*trans*,4-*trans*-hexadienedioate, and of the Diels–Alder reaction of methyl sorbate with substituted styrenes should give important information on the mechanism of the Diels–Alder reaction. In order to obtain meaningful kinetic data on these reactions it was necessary to completely characterize the reaction products and, therefore, the structure and identity of the adducts was established in cases incompletely or not described in the literature. The structure and identity of the Diels–Alder adducts of methyl sorbate and styrene,[1] methyl sorbate and substituted styrenes,[10] and *trans*,*trans*-hexa-2,4-diene, and styrene[3] were established.

The Diels–Alder reaction between *trans*-penta-1,3-diene, and styrene[4] gave a 40% yield of adducts. Dehydrogenation and oxidation resulted in a mixture of 85% *o*-phenylbenzoic acid and 15% *m*-phenylbenzoic acid.

The Diels–Alder reaction between 2-*trans*,4-pentadienoic *acid* and styrene[5] yielded 58% of a mixture of *ortho* and *meta* adducts. Dehydrogenation gave a mixture of 2-phenylbenzoic acid and 3-phenylbenzoic acid in the ratio 5·7 : 1. Hydrogenation of the mixture of *ortho* adducts gave a mixture of *trans*- and *cis*-2-phenylcyclohexane-l-carboxylic acid in the ratio 17 : 1.

Diethyl 2-*trans*,4-*trans*-hexadienedioate and styrene were reported to give a 53% yield of adducts when heated 30 hr at 150° in xylene.[6]

RESULTS

Assuming that the Ph group takes an equatorial position[3] and that the configuration of the diene is retained in the adducts two racemic mixtures* can be expected from the Diels–Alder reaction between a symmetrically 1,4-disubstituted diene and styrene and four racemic mixtures* from the Diels–Alder reaction of a 1-substituted diene and styrene.

NMR spectra of the adducts were obtained. In every case the relative peak areas agreed with the expected structure of a Diels–Alder adduct.

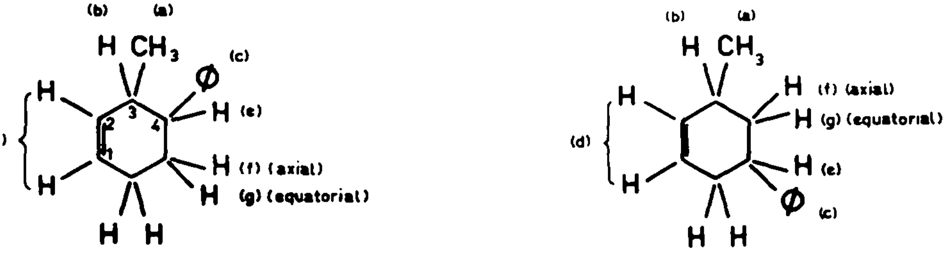
As all the adducts are stable under reaction conditions, the reaction is kinetically controlled.

A. *Diels–Alder reaction between* trans-*penta*-1,3-*diene and styrene*

Four adducts (A–D) were present in the proportion 2·7:3·8:1:1;NMR data and GLC retention data are given in Table 1 and 1a respectively.

TABLE 1. CHEMICAL SHIFTS (δ) AND COUPLING CONSTANTS (c/s) OF THE FOUR ISOMERIC ADDUCTS FROM THE DIELS–ALDER REACTION BETWEEN *trans*-PENTADIENE-1,3 AND STYRENE

Compound	H_a	H_c	H_d	H_e	J_{ab}	J_{ef}	J_{eg}	J_{eb}
A	0·83	7·11	5·69	ca. 2·25	7	—	—	—
B	0·63	7·09	5·65	3·01	7	12	3·5	5
C	1·01	7·09	5·65	—	7	—	—	—
D	1·04	7·09	5·65	—	7	—	—	—



Ia: cis
Ib: trans

IIa: cis
IIb: trans

FIG. 1

The chemical shifts of H_a for compounds A ($\delta = 0·83$) and B ($\delta = 0·63$) are similar to the chemical shift values found for the Me group next to the Ph group in 3-carbomethoxy-*trans*-5-phenyl-*cis*-6-methyl-cyclohexene-1 (δ = 0·87) and 3-carbomethoxy-*cis*-5-phenyl-*cis*-6-methyl-cyclohexene-1 (δ = 0·63)[1] and in 3-methyl-*trans*-4-phenyl-*cis*-6-methyl-cyclohexene-1 (δ = 0·83) and 3-methyl-*cis*-4-phenyl-*cis*-6-methyl-cyclohexene-1 (δ = 0·59).[3] It was concluded therefore that compound A≡Ib (*trans*-3-methyl-4-phenylcyclohex-1-ene) and compound B≡Ia (*cis*-3-methyl-4-phenyl-

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*Each racemic mixture is from now on in the text considered as one compound.

Table 1a. Relative retention of the four isomeric adducts from the Diels–Alder reaction between *trans*-pentadiene-1,3 and styrene on Apiezon L (column K 47) at 175°

Compound	Relative retention
A (*ortho, trans* isomer)	1·000
B (*ortho, cis* isomer)	1·302
C (*meta, trans* isomer)	1·203* or 1·237*
D (*meta, cis* isomer)	1·203* or 1·237*
n-dodecane	0·359
n-tetradecane	1·140

*Individual isolation of C and D was practically not feasible. Because of the ratio C:D = 1:1 no decision was made with regard to the sequence of elution of C and D.

cyclohex-1-ene). As expected the signal of H_a in Ia occurs at higher field because of the shielding effect of the Ph group.

This is confirmed by the chemical shift of the axial proton H_e ($\delta = 2{\cdot}25$ in A, $\delta = 3{\cdot}01$ in B). It is known that the chemical shift of a proton in a system $H—C_1—C_2—X$ depends on the dihedral angle between HC_1C_2 and C_1C_2X.[7] For the system $H_eC_4C_3X$ in a cyclohexene derivative, with X = Me and a Ph group at C_4, it has been shown that the signal of H_e is shifted 0·75 ppm to lower field when this dihedral angle changes from 60° (H_e axial, Me pseudo-equatorial) to 180° (H_e axial, Me pseudo-axial).[3]

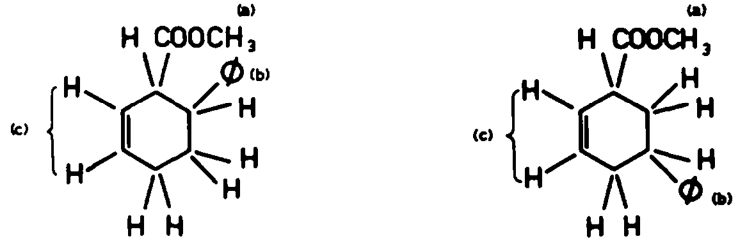
The coupling constant J_{eb} (5 c/s) which can be evaluated for adduct B is also indicative of the *cis* position of the Me group relative to the Ph group (H_e axial and $J_{eb} = 5$ c/s implies a dihedral angle of about 60° between $H_bC_3C_4$ and $H_eC_4C_3$, according to Karplus' rule[8]). Isomers C and D were not isolated individually. The chemical shift values of H_a ($\sigma = 1{\cdot}01$ and $\sigma = 1{\cdot}04$) in the NMR spectrum of the reaction mixture are similar to the chemical shift values found for the Me group (*meta* to the Ph group) in 3-methyl-*trans*-4-phenyl-*cis*-6-methyl-cyclohex-1-ene ($\delta = 1{\cdot}03$) and 3-methyl-*cis*-4-phenyl-*cis*-6-methyl-cyclohex-1-ene ($\delta = 1{\cdot}06$).[3] In 3-carbomethoxy-*cis*-4-phenyl-*cis*-6-methyl-cyclohex-1-ene (or its Ph substituted analogs, derived from the Diels–Alder reaction of *meta* and *para* substituted styrenes[10]) the signal is always at lower field than in 3-carbomethoxy-*trans*-4-phenyl-*cis*-6-methyl-cyclohex-1-ene[1] (or its Ph substituted analogs, derived from the Diels–Alder reaction of *meta* and *para* substituted styrenes[10]). It was concluded therefore that C ≡ IIb (*trans*-3-methyl-5-phenyl-cyclohex-1-ene) and D ≡ IIa (*cis*-3-methyl-5-phenyl-cyclohex-1-ene).

B. *Diels–Alder reaction between methyl* 2-trans,4-*pentadienoate and styrene*

The adducts E and F were not isolated individually but the mixture was analysed. The NMR spectrum suggested the presence of four adducts in the proportion E:F:G:H = 1:1·8:0·01:0 01. NMR data and GLC retention data are given in Table 2 and 2a respectively. The chemical shifts of the H_a proton in adducts E ($\delta = 3{\cdot}48$) and F ($\delta = 3{\cdot}28$) are consistent with adducts IIIb and IIIa (compare the chemical

TABLE 2. CHEMICAL SHIFTS (δ) OF THE FOUR ISOMERIC ADDUCTS FROM THE DIELS–ALDER REACTION BETWEEN METHYL 2-*trans*,4-*trans*-PENTADIENOATE AND STYRENE

Compound	H_a	H_b	H_c
E	3·48	7·20	ca. 5·87
F	3·28	7·20	ca. 5·86
G	3·63	—	—
H	3·68	—	—



III a : cis
III b : trans

IV a : cis
IV b : trans

FIG. 2

TABLE 2A. RELATIVE RETENTION OF THE FOUR ISOMERIC ADDUCTS FROM THE DIELS–ALDER REACTION BETWEEN METHYL 2-*trans*,4-*trans*-PENTADIENOATE AND STYRENE ON APIEZON L (column K 47) AND DEGS (column K 40) AT 175 °C.

Compound	Relative retention	
	Apiezon L	DEGS
E (*ortho, trans* isomer)	1·00	1·000
F (*ortho, cis* isomer)	1·00	1·036
G (*meta, trans* isomer)	—	ca. 0·81
H (*meta, cis* isomer)	—	ca. 0·81
n-tetradecane	0·36	0·11
n-hexadecane	1·11	0·27

The compounds E and F were eluted simultaneously from the Apiezon L column. On the DEGS column partial resultion of E and F was achieved, two small peaks at relative retentions of approximately 0·81 probably are the *meta*-isomers G and H.

shifts of the proton in the carbomethoxy group in 3-carbomethoxy-*trans*-4-phenyl-*cis*-6-methyl-cyclohex-1-ene (δ = 3·50) and 3-carbomethoxy-*cis*-4-phenyl-*cis*-6-methyl--cyclohex-1-ene (δ = 3·22) respectively[1]).

It was concluded therefore that compound E ≡ IIIb (*trans*-3-carbomethoxy-4-phenyl-cyclohex-1-ene) and compound F ≡ IIIa (*cis*-3-carbomethoxy-4-phenyl-cyclohex-1-ene). Two signals in the NMR spectrum of the reaction mixture suggest the presence the H_a proton in adducts G and H (δ = 3·63 and δ = 3·68 respectively): Their chemical shifts correspond to the chemical shifts found for the ester Me group in 3-carbomethoxy-*trans*-5-phenyl-*cis*-6-methyl-cyclohex-1-ene (δ = 3·63) and 3-carbomethoxy-*cis*-5-phenyl-*cis*-6-methyl-cyclohex-1-ene (δ = 3·66).[1]

It is suggested, on a tentative basis, that compound G ≡ IVb (*trans*-3-carbomethoxy-5-phenyl-cyclohex-1ene) and compound H ≡ IVa (*cis*-3-carbomethoxy-5-phenyl-cyclohex-1-ene). Titov and Kuznetsova[6] found a larger amount of *meta* adducts in the reaction mixture of 2,4-pentadienoic *acid* with styrene. It is not clear why there should be a considerable difference between acid and ester.

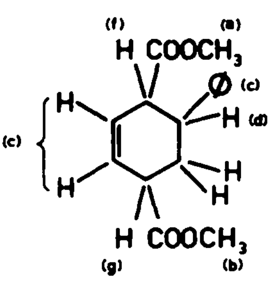
C. *Diels–Alder reaction between dimethyl* 2-trans,4-trans-*hexadienedioate and styrene*

The two possible adducts were present in the proportion I:J = 1:2. NMR data and GLC retention data are given in Table 3 and 3a respectively.

TABLE 3. CHEMICAL SHIFTS (δ) OF THE TWO ISOMERIC ADDUCTS FROM THE DIELS–ALDER REACTION BETWEEN DIMETHYL 2-*trans*,4- *trans*-HEXADIENEDIOATE AND STYRENE

Compound	H_a	H_b	H_c	H_d	H_e	J_{df}*
I	3·52	3·65	ca. 5·90	3·08	7·18	12 c/s
J	3·23	3·68	ca. 5·90	3·00	7·18	5 c/s

* The coupling constants and some of the chemical shifts were evaluated from the spectra of adducts from β,β-di-deuterostyrene and hexadienedioic ester. The signals of H_f and H_g could not be detected because they coincide with the signals of H_a and H_b.



Va: all cis

Vb: -Φ trans to both -COOCH$_3$

FIG. 3

TABLE 3A. RELATIVE RETENTION OF THE TWO ISOMERIC ADDUCTS FROM THE DIELS–ALDER REACTION BETWEEN DIMETHYL 2-*trans*, 4-*trans*-HEXADIENEDIOATE AND STYRENE ON APIEZON L (Column K 12) AT 200°

Compound	Relative retention
I (*trans* isomer)	1·00
J (*cis* isomer)	1·19
n-tetradecane	0·12
n-hexadecane	0·30

The adducts I and J decomposed during prolonged analysis. They were therefore chromatographed rapidly on a short column.

Assuming that the Ph group is an equatorial position,[3] the proton H_d is axial, $J_{df} = 12$ c/s implies therefore that H_f is in pseudo-axial position and $J_{df} = 5$ c/s implies that H_f is in pseudo-equatorial position. It was concluded therefore that compound J $\equiv$ Va (3-carbomethoxy-*cis*-4-phenyl-*cis*-6-carbomethoxy-cyclohex-1-ene) and I $\equiv$ Vb (3-carbomethoxy-*trans*-4-phenyl-*cis*-6-carbomethoxy-cyclohex-1-ene), where it has been assumed for the detailed configuration that the two carbomethoxy groups are *cis* to each other according to the rule of retention of configuration of diene.

This was confirmed by a comparison of the chemical shift for H_a in compounds I (δ = 3·52) and J (δ = 3·23) with the chemical shift of the protons of the carbomethoxy group in 3-carbomethoxy-*trans*-4-phenyl-*cis*-6-methyl-cyclohex-1-ene (δ = 3·50) and 3-carbomethoxy-*cis*-4-phenyl-*cis*-6-methyl-cyclohex-1-ene (δ = 3·22)[1]: In the all-*cis* compounds the signal is at higher field because of the shielding effect of the Ph group.

EXPERIMENTAL

trans-Penta-1,3-diene and 2-*trans*,4-*trans*-hexadienedioic acid were commercially available.

trans-2,4-Pentadienoic acid was synthesized from malonic acid and acrolein[9]. Methyl esters were prepared by the diazomethane method. β,β-Dideutero-styrene was prepared as described in Ref. 4.

Reaction conditions. The reactions were carried out by heating equimolar amounts of diene and dienophile in a 100 ml stainless steel autoclave at 160° for 48 hr in a N_2 atm with addition of 0·1 g hydroquinone. Press was 10–20 atm.

GLC purification

1. *Trans*-penta-1,3-diene adducts: a fraction boiling at 75–80°/0·5 mm.
2. *Trans*-2,4-pentadienoic ester adducts: a fraction boiling at 130–133°/3 mm.
3. Hexadienedioic ester adducts: the crude reaction mixture.

Gaschromatographic conditions· Chromatograph F&M, model 810-15; Detector: hydrogen flame ionization; recorder: Honeywell, −0·05 to +1·00 mV, 1 second; carrier gas: He at 100 ml/min measured at atm press. A post-column splitter (1 : 10) was used for preparative work; sample size 10 to 50 mg.

Column K 47. 9·00 m × 0·435 cm i.d. coiled stainless steel tube filled with Apiezon L on Chromosorb P-DMCS (100–120 Mesh) (5:95); column efficiency was *circa* 12,000 theoretical plates; analysis temp

175°; analysis time 300 min for compound B (Table 1a) and 600 min for compounds E and F (Table 2a); sample size 0·10 mg.

Column K 12. 2·00 m × 0·455 cm i.d. coiled copper tube filled with Apiezon L on Diatoport S (45–60 Mesh) (5:95); column efficiency was *circa* 2300 theoretical plates; analysis temp 200°; analysis time 12 min for compound J (Table 3a); sample size 0·01 mg.

*Column K*40. 8·00 m × 0·455 cm i.d. coiled copper tube filled with diethyleneglycol succinate (DEGS) on Diatoport P (60–80 Mesh) (5:95); column efficiency was *circa* 10,000 theoretical plates; analysis temp 175°; analysis time 65 min for compound E and F (Table 2a); sample size 1 mg.

NMR spectra (Varian A-60 NMR spectrometer; Solutions circa 1 M in CCl_4; TMS as internal standard).

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