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THE DIELS-ALDER REACTION BETWEEN STYRENE AND METHYL SORBATE

THE STRUCTURE OF FOUR ISOMERIC ADDUCTS

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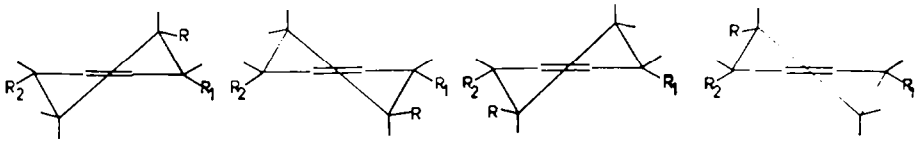
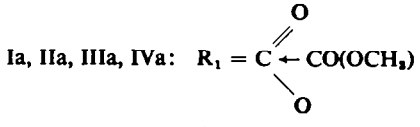
Abstract—The Diels–Alder reaction between a 1,4-disubstituted diene and a dienophile R—CH=CH_2 may give four adducts, when the configuration of the diene is retained. The four adducts (3-carbomethoxy-*cis*-4-phenyl-*cis*-6-methylcyclohexene-1, 3-carbomethoxy-*trans*-4-phenyl-*cis*-6-methylcyclohexene-1, 3-carbomethoxy-*cis*-5-phenyl-*cis*-6-methylcyclohexene-1 and 3-carbomethoxy-*trans*-5-phenyl-*cis*-6-methyl-cyclohexene-1) from the Diels–Alder reaction between methyl sorbate and styrene were isolated by means of gas chromatography and identified by NMR, mass and IR spectrometry. Some products, considered in literature as adducts, were proved to be rearrangement products by spectral methods.

THE Diels–Alder reaction between a diene R_1—CH_t=CH—CH_t=CH—R_2 ($R_1 \neq R_2$) and a dienophile R—CH=CH_2 may give four racemic mixtures,* when it is assumed that the configuration of the diene is retained in the adduct (a principle which has never been found to be violated[1,2]):



I II III IV



Ia, IIa, IIIa, IVa: R_1 = C(=O)—CO(OCH_3) (O)

$R_2 = CH_3$

R = Ph

(only the conformations with R equatorial are drawn).

One example is reported (*trans,trans*-1-phenyl-4-methyl-butadiene and acrylic

* The racemic mixtures are from now on in the text considered as one compound.

[1] J. G. Martin and R. K. Hill, *Chem. Revs.* **61**, 537 (1961).

[2] A. S. Onishchenko, *Diene Synthesis* p. 35. Israel Program for Scientific Translations, Jerusalem (1964).

acid) where three out of four of the possible products were isolated.[3] Isolation and identification of all four possible adducts, however, has not been reported so far.

The Diels–Alder reaction between styrene and methyl sorbate has been studied by Alder *et al.*[4] They isolated two acids from the hydrolysed reaction product. One (m.p. 169°) was present in major amount and possessed the carbon skeleton of Ia and IIa, the other (m.p. 220°) had the carbon skeleton of IIIa and IVa.

The Diels–Alder reaction between styrene and sorbic *acid* was studied by Deno and Johnston.[5] They isolated the acid with m.p. 169° and two unidentified acids (m.p. 120° and 145°).

Sie[6] isolated an acid having the carbon skeleton of compound Ia and IIa from the hydrolysed reaction mixture from the Diels–Alder reaction between styrene and methyl sorbate.

RESULTS

Under our conditions (24 hr, 160°, atm. press.) the Diels–Alder reaction between methyl sorbate and styrene results in a mixture, which consists of 10% starting materials, 60% non-polymeric reaction products and the remaining 30% polymeric material.

Gas chromatographical analysis of the main fraction, showed a considerable number of compounds, four of which (A, B, C and D) were proved to be Diels–Alder adducts of methyl sorbate and styrene. The others did not contain a phenyl group and are probably dimers of methyl sorbate.

The four adducts, which in the original mixture were present in the proportions A:B:C:D = 6:1:1:1, were separated and purified by means of gas chromatography.

Heating of pure A, B, C or D under reaction conditions did not produce any of the other adducts. The reaction is therefore kinetically and not thermodynamically controlled in our case. Mass spectra and NMR spectra of the adducts were determined.

DISCUSSION

(a) *Mass spectra*

There are neither significant differences between the mass spectra of A and B, nor between those of C and D. Between the spectra of A and B on one hand and of C and D on the other, however, significant differences exist at m/e 170, 171 and m/e 129, 131 (Figs 1 and 2). It can be expected that the mass spectra of pairs of stereoisomers will be very similar, but that between the spectra of positional isomers there may be differences. We therefore conclude that A and B and also that C and D are pairs of stereoisomers.

The base peak of all four of the spectra is at m/e = 104, representing styrene from the retro Diels–Alder reaction. The retro Diels–Alder reaction is often an important process in the fragmentation of cyclohexene derivatives.[7]

[3] K. Alder, M. Schuhmacher and O. Wolff, *Liebigs. Ann.* **570**, 230 (1950).
[4] K. Alder, K. H. Decker and R. Lienau, *Liebigs Ann.* **570**, 224 (1950).
[5] N. C. Deno and K. Johnston, *J. Amer. Chem. Soc.* **74**, 3233 (1952).
[6] S. T. Sie, Thesis, Delft (1964).
[7] K. Biemann, *Mass Spectrometry. Organic Chemical Applications* pp. 102–103. McGraw-Hill, New York (1962).

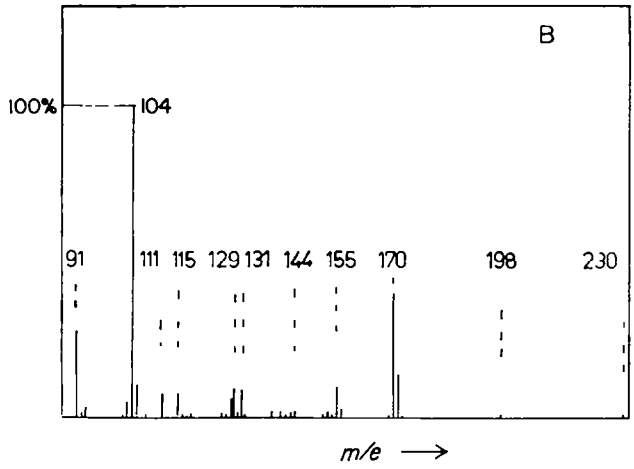


FIG. 1. Mass spectrum of compound B (IIa).

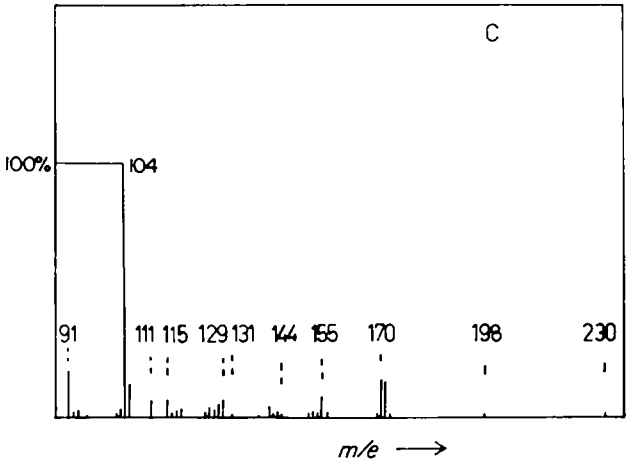


FIG. 2. Mass spectrum of compound C (IIIa).

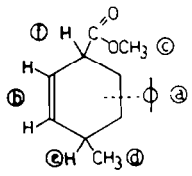
(b) *NMR spectra*

Table 1 shows the data of the NMR spectra. The relative peak areas agree with the proposed structure of the Diels–Alder adducts. The chemical shift of the methyl protons in a methyl ester is usually between $\delta = 3{\cdot}50$ and $\delta = 4{\cdot}00$.[8] The signal of the c-protons in A ($\delta = 3{\cdot}22$) therefore occurs at unusually high field. The reason for this must be the shielding effect of the ring current of the phenyl group. It is concluded therefore that A and B are the pair of stereoisomers Ia and IIa. Inspection of a Dreiding model shows that in Ia the c-protons can be in a position very close to the center of the phenyl group*, in IIa, this distance is considerably greater. It is concluded therefore that A ≡ Ia and B ≡ IIa. It is in agreement with the rule of

* Only conformations with the phenyl group in equatorial position are considered because: (1) it is the bulkiest group; (2) the —CO(OCH$_3$) and CH$_3$ groups are never in a true axial position, but at most in a pseudoaxial position, which is energetically less unfavourable.

[8] R. D. Bible, *Interpretation of NMR spectra. An Empirical Approach* p. 16. Plenum Press, New York (1965).

TABLE 1. CHEMICAL SHIFTS (δ) OF THE FOUR ISOMERIC ADDUCTS FROM THE DIELS–ALDER REACTION (REFERENCE TMS) BETWEEN STYRENE AND METHYL SORBATE (SOLVENT CCl_4).



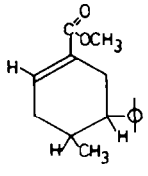
Compound	H_a	H_b	H_c	H_d[a]	H_f
A(Ia)	7·14	5·70	3·22	1·13	(3·22)[b]
B(IIa)	7·17	5·73	3·50	1·08	3·25[c]
C(IIIa)	7·17	5·74	3·63	0·87	3·08[c]
D(IVa)	7·17	5·68	3·66	0·63	3·10[c]

[a] $J_{df} = 7$ c/s in all cases.
[b] The signal is hidden under the signal of H_c.
[c] Center of multiplet.

accumulation of unsaturation for the Diels–Alder reaction[9] that Ia is the main component.

The shift of the d-protons in C and D to higher field must also arise from the shielding effect of the phenyl group. Inspection of a model shows that in IVa the d-protons are nearest to the center of the phenyl group. It is concluded therefore that C ≡ IIIa and D ≡ IVa.

The signals of the cyclohexene ring protons show a complex pattern. However, at the low field side of this region a signal for one proton (Ia: $\delta = 3{\cdot}22$, IIa: $\delta = 3{\cdot}25$, IIIa: $\delta = 3{\cdot}08$, IVa: $\delta = 3{\cdot}10$) can be clearly discerned, which can only arise from H_f or from the proton next to the phenyl group. If the signal arises from H_f it must be absent in V, when it arises from the proton next to the phenyl group it must also be present in V, because the proton would be in a similar environment and at similar distances from carbomethoxy group and double bond. Compound V, however, shows no signal between $\delta = 3{\cdot}25$ and $\delta = 2{\cdot}80$ (see section c). It is concluded therefore that the signal arises from H_f.

V 

This conclusion is in agreement with the configuration assignment given for the isomeric adducts. For it is to be expected that the signal of H_f will: (1) be simpler in Ia and IIa than in IIIa and IVa; (2) appear at lower field in Ia and IIa, than in

[9] K. Alder and G. Stein, *Angew. Chem.* **50**, 510 (1937).

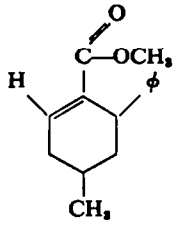
IIIa and IVa, because of the deshielding effect of the phenyl group. The NMR data show that this is indeed the case: Ia, the signal is hidden under the signal of the H_c-protons $\delta = 3{\cdot}22$; IIa, undissolved triplet $\delta = 3{\cdot}25$; IIIa and IVa, broad multiplet centered at respectively $\delta = 3{\cdot}08$ and $\delta = 3{\cdot}10$.

(c) *Comparison of the results with literature*

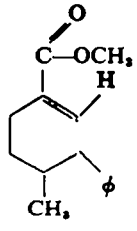
The two acids (m.p. 169° and m.p. 220°) described by Alder *et al.*[4] were isolated according to their method. The corresponding methyl esters were prepared by the diazomethane method.

The acid of m.p. 169°. Contrary to the findings of Alder *et al.* this acid was obtained in very small amount only. Its methyl ester is not identical with any of the compounds Ia, IIa, IIIa or IVa. The carbon skeleton was proved by Alder to be that of Ia and IIa. The C=O stretching vibration in the IR spectrum occurs at 1720 cm^{-1} (in CCl_4), which is typical of an α-β-unsaturated ester (in Ia, IIa, IIIa and IVa it occurs at 1740 cm^{-1}), UV absorption does not occur above 230 mμ. We therefore conclude that the acid isolated by Alder is VI. It is not possible, however, to determine whether the phenyl and the methyl group are *cis* or *trans* to each other.

VI



The acid of m.p. 220°. The carbon skeleton of this acid was proved by Alder to be that of IIIa and IVa. The NMR spectrum of the methyl ester gives the following result (in CCl_4): $\delta = 7{\cdot}19$ (5 protons, aromatic), $\delta = 6{\cdot}98$ (1 proton, olefinic, multiplet), $\delta = 3{\cdot}68$ (3 protons, methyl ester), $\delta = 0{\cdot}72$ (3 protons, methyl group, doublet, J = 6 c/s), $\delta = 2{\cdot}80 - 1{\cdot}60$ (6 protons). The C=O stretching vibration occurs at 1720 cm^{-1}. This leaves two possibilities for the structure: V and VII.



VII

The base peak in the mass spectrum is at m/e 118 (Fig. 3). This is the mass of a methylstyrene, which can arise from a retro Diels–Alder reaction from V only. It is concluded therefore that the ester is V. It is not possible to determine whether the phenyl and the methyl group are *cis* or *trans* to each other.

Deno and Johnston[5] isolated three acids from the reaction between sorbic *acid* and styrene: (1) The acid with m.p. 169°. (2) An unidentified acid with m.p. 145°, which we did not obtain* when repeating the experiments of Deno and Johnston. (3) An

* We did obtain a product melting in the range 143–145°, which proved to be a mixture of the acids with m.p. 169 and 220°.

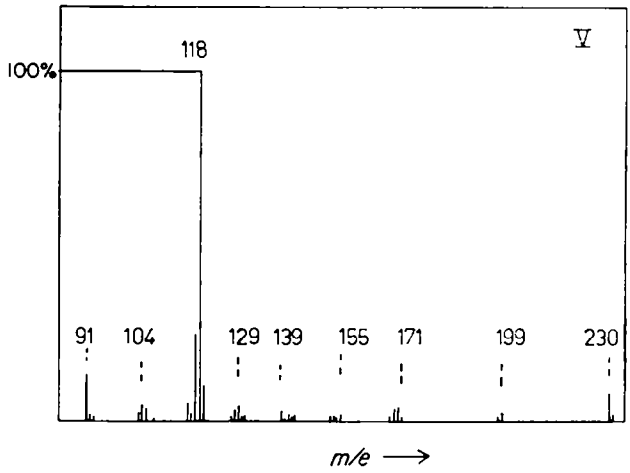


FIG. 3. Mass spectrum of compound V.

unidentified acid with m.p. 120°. We isolated this acid in small amount. It does not contain a phenyl group and might be a dimer of sorbic acid.

In the experiments of Alder, isomerization of one of the adducts to V or VI might have occurred during the base catalysed hydrolysis or thermally during the reaction proper. Because Deno isolated the same acid (VI) as did Alder, without hydrolysis, thermal isomerization does indeed take place under the reaction conditions of both Alder and Deno (200°). GLC analysis of Alder's not hydrolysed reaction mixture shows a considerably larger number of compounds than our own reaction mixture.

EXPERIMENTAL

(a) *Reaction conditions*

10 g styrene, 10 g methyl sorbate and 0·5 g hydroquinone were heated 24 hr at 160°. The reaction mixture was distilled under red. press. The fraction boiling at 125°/1 mm (n_D^{25} = 1·5200) contained Diels–Alder adducts and dimers of methyl sorbate.

(b) *Gaschromatographical separation and purification*

On diethyleneglycolsuccinate (DEGS) columns four fractions containing aromatic compounds could be separated according to Fig. 4. The primary fractions were contaminated by non-aromatic esters (probably dimers of methyl sorbate). They were purified on an Apiezon L column. The products for mass spectra were purified until better than 99·9%.

The following products were obtained:
A1: purity 95%; d^{20} = 1·06; analysis IR, NMR, GLC.
A2: purity 99·9%; analysis mass spectrum, GLC.
B1: purity 99·7%; d^{20} = 1·04; analysis IR, NMR, GLC.
B2: purity 99·9%; analysis mass spectrum, GLC.
C: purity 99·9%; colourless hexagonal plates; m.p. 40°; d^{20} = 1·06 (of metastable liquid); analysis IR, NMR, mass spectrum, GLC.
D1: purity 80%*; d^{20} = 1·08; analysis NMR, GLC.
D2: purity 99·9%; analysis IR, mass spectrum, GLC.

* On standing for some time at room temperature in a glass vessel there appeared two new components in the gas chromatogram. Possibly some migration of the cyclohexene double bond occurred under this condition.

The four compounds A, B, C and D could conveniently be determined on two types of columns.* Two normal alkanes were used as standards. The relative retention volumes at 150° are given in Table 2.

TABLE 2. RELATIVE RETENTION VOLUME OF THE FOUR ISOMERIC ADDUCTS AT 150°.

	DEGS	Apiezon L
n-Tetradecane	0·071	0·34
n-Hexadecane	0·148	0·89
A	1·00	1·00
B	1·05	1·05
C	1·24	1·25
D	1·94	1·92

Conditions for chromatography. chromatograph, F & M, Model 810–15; detector, flame ionization detector; recorder, Honeywell, −0·05 to 1 mV, 1 sec.

Column 1. Primary separations were done on this column [5-m × 1·3 cm i.d. copper coiled tube filled with chromosorb P (45/60 mesh) coated with DEGS (20:80)]. Carrier gas He at 400 ml/min with a post-column splitter (1:10). Sample size 50–250 μl. Column efficiency was about 4000 theoretical plates.

Column 2. This column [8-m × 0·5 cm i.d. copper coiled tube filled with Diatoport P (60/80 mesh) coated with DEGS (5:95)] was used particularly for the critical separations of A and B. Carrier

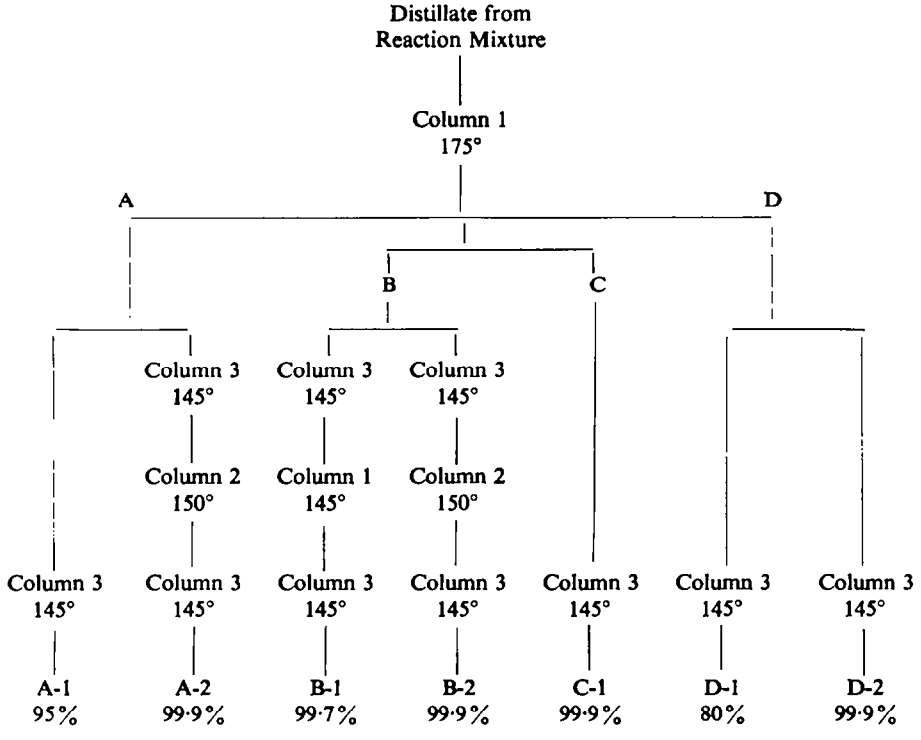


FIG. 4. GLC separation and purification of the adducts.

* A detailed study of the gas chromatographic behaviour of these and related compounds is in progress.

gas was He at 100 ml/min with a post-column splitter (1:10). Sample size 0·1–2 μl. Column efficiency was about 10,000 theoretical plates.

Column 3 [2-m × 0·5 cm i.d. copper coiled tube filled with Diatoport S (60/80 Mesh) coated with Apiezon L (10:90)] was used at 145° to remove methyl sorbate dimers and DEGS from the primary fractions. Carrier gas was helium at 100 ml/min with a postcolumn splitter (1:10). Column efficiency about 2000 theoretical plates. Sample size 0·1–10 μl.

(c) *Spectra*

Mass spectra* (AEI Ms 2H mass spectrometer equipped with a heated inlet system; ionising potential 70·00 eV). NMR† spectra (Varian A-60 NMR spectrometer; solns about 1M in CCl_4; TMS as internal standard). IR spectra (Perkin–Elmer 137 spectrophotometer; solns about 0·04M in CCl_4).

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* Mass spectra were measured by Messr. W. J. Rooselaar and J. D. van Wageningen.

† NMR spectra were measured by Miss L. Boshart.