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CIS-TRANS ISOMERIZATION OF ALLOOCIMENE WITH DIENOPHILES AND OTHER π-ACIDS.

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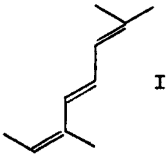
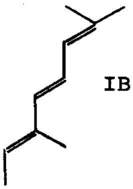
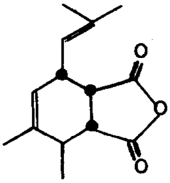
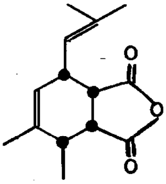
Contradictory results have been reported for the addition of maleic anhydride (MA) to the isomeric alloocimenes IA (b.p.$_{12}$ 73°C) and IB (b.p.$_{12}$ 79°C). According to several authors2) IA and IB yield the same adduct IIB (m.p. 83-84°C). The formation of IIA (m.p. 38°C5)) from IA, and of IIB from IB, however, has been described by others3,4). We have re-investigated this reaction and found, that the apparently contradictory results can be explained by a competing isomerization of IA to IB.


IA


IB

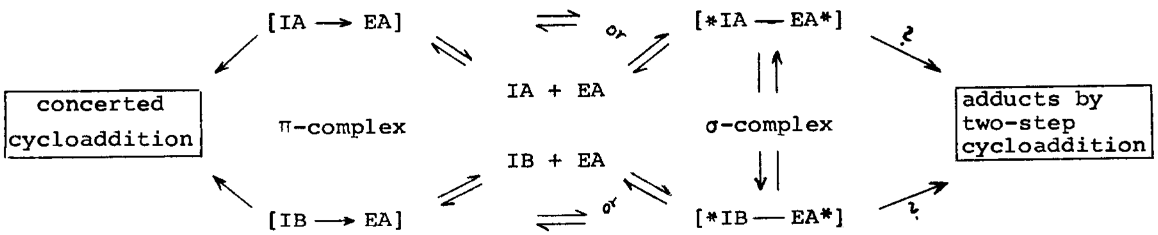

IIA


IIB

The reaction of IB with MA is several orders of magnitude faster than that of IA; IA (> 97% by v.p.c.) was obtained from mixtures of IA and IB by removing IB as IIB with the calculated amount of MA (in benzene). IB (> 95 %) was separated from IA by fractional distillation. Catalytic amounts of iodine convert either pure IA or IB at room temperature in minutes to a 1:2 mixture of IA and IB, which seems to correspond to the thermodynamic equilibrium, indicating a free energy difference of ~ 0.4 kcal/mol.

IIA is produced as an oil5) by refluxing IA and MA in benzene. However, in the exothermic reaction (self-heating to 180°C) of 0.21 mol IA and 0.11 mol MA (neat) 0.08 mol IIB was formed, and the recovered alloocimene was found to be a mixture of 44 % IA and 56 % IB, corresponding to a total conversion of 2/3 IA into IB. (No IIB was formed from IIA by heating to 185°C.) Also rearrangement occurs, if IA and MA are combined in methyl benzoate at 170°C. Generally, in the reaction of IA and MA without dilution, the ratio of the two reactants determines the temperature reached by self-heating and thus the product composition. IIB is obtained from MA and IB either by reaction in solution or by combining the neat reactants; in the latter case (self-heating !) recovered excess alloocimene contains IA.

This effect of MA can be attributed to its electron acceptor properties as a π-acid, since succinic acid, succinic anhydride, diethyl succinate, tributylamine, dibenzoylperoxide and azobisisobutyronitrile failed to rearrange IA ⟶ IB under comparable conditions. Solutions of MA and I display an orange color due to charge transfer absorption (CTA). As shown in the table a variety of π-acids (EA) are efficient for the isomerization IA $\rightleftharpoons$ IB, some even without adduct formation. The position of the maximum of CTA seems to parallel the efficiency of structurally related π-acids in rearranging IA. In those cases where the cycloaddition of the π-acid to IB is slow compared with the cis-trans-isomerization, 1:2 mixtures of IA and IB are obtained on starting with either pure IA or IB (e.g. with dichloromaleic anhydride, tetraethyl ethylenetetracarboxylate). Obviously an intermediate is formed which allows for thermodynamic equilibration. We believe this intermediate to be a σ-complex[6] and propose the following scheme to explain the observations:



Formation of the σ-complex via the π-complex[7] would account best for the parallelism of CTA_{max} and rearranging efficiency found, although we can not exclude from this alone the direct formation of the σ-complex from the reactants. [Since the degree of charge separation in the σ-complex may depend on the nature of EA, the symbol * has been used to describe any species within the range between a zwitterion and a diradical.] Whether some II stems from a two-step cycloaddition reaction involving the σ-complex is a question, which demands further investigation8) (for a comprehensive discussion of this basic problem see Lit.9)).

The ionization potential (I.P.) of alloocimene can be estimated from CTA_{max} with tetrachloro-p-quinone10) to be $\sim$ 7.5 eV; whether such a low I.P. is important for the facility of cis-trans isomerizations by π-acids is currently under investigation.

EA	CTA_{max} (eV) [in CCl_4]	IA $\rightleftharpoons$ IB 78°C [in CCl_4]	 160°C [neat]
Diethyl maleate	i.a.	-	-
Tetraethyl ethylene-tetracarboxylate	i.a.	+	+++
Dimethyl maleic anhydride	3.3 (Sh.)	-	-
Maleic anhydride	3.3	-	++
Dichloro maleic anhydride	2.8	++	+++
Dibromo maleic anhydride	2.8	++	+++
Tetracyanoethylene	1.85 (in benzene)	Lit.11)	
p-Benzoquinone	i.a.	-	-
Tetrachloro-p-benzoquinone	2.0	+	++
Tetrachloro-o-benzoquinone	$\sim$ 2	++	
2.4.6-Trinitro-toluene	2.9 (Sh.)	-	
Tetrachloro phthalic anhydride	2.8	-	
Picric acid	2.6 (Sh.)	++	

Sh. = shoulder; i.a. = increased absorption of the π-acid, no CTA_{max} observed; +,++,+++ = increasing relative efficiency in rearranging IA.

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5) According to v.p.c. analysis4) crystalline adducts melting in the range 36 - 42°C actually are 2:1 mixtures of IIA and IIB.

6) Also an equilibrating radical-ion pair resulting from an electron transfer in the π-complex should be discussed as an intermediate in the isomerization IA $\rightleftharpoons$ IB. While such a process seems less favourable than the σ-complex formation for our thermal reaction out of energetic considerations, it may, however, be important in photochemical reactions.

7) The π-complex can be also regarded as an intermediate in the DIELS-ALDER reaction:
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11) According to a private communication a detailed report on this system will be given by J.Sauer and C.Rücker.