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THERMAL SKELETAL REARRANGEMENTS OF DIMETHYL 1,2-HEPTALENEDICARBOXYLATES

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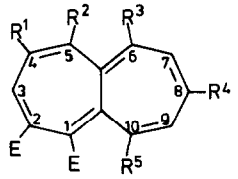
Summary: Thermolysis of dimethyl 1,2-heptalenedicarboxylates 1 leads by two different pathways to the corresponding 1,3-dicarboxylates 2 and to azulenes 3 - 5. The rearrangement of 1 into 2 presumably proceeds via a heptvalene intermediate 10.

During the course of our investigation of the dynamic behavior of chiral heptalenes[1] we were interested in studying also the thermal stability of dimethyl 1,2-heptalenedicarboxylates 1, in order to prove the reversibility of their formation by cycloaddition of azulenes with dimethyl acetylenedicarboxylate[2] and subsequent electrocyclic reaction of the first formed cyclobutene derivative. Therefore, we studied the thermolysis of numerous dimethyl 1,2-heptalenedicarboxylates 1[1,2] in boiling tetralin (207°C) and found that the bicyclic 12π-electron system reacts under these conditions by two different pathways. One of these consists of an isomerization of the 1,2-dicarboxylates 1 into the corresponding thermodynamically more stable 1,3-dicarboxylates 2 with two electron withdrawing substituents in positions of high electron density. The second route so far not observed leads to the azulenes 3, 4, and 5 by ring contraction of 1.

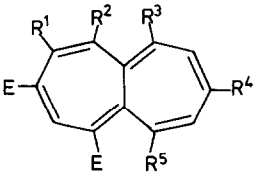
The rates of these reactions as well as the ratio of products resulting from the different pathways depend obviously strongly on the position and number of substituents of the heptalenes (Tab. 1).

While the thermolysis of the unsubstituted dimethyl 1,2-heptalenedicarboxylate 1a in boiling tetralin yields predominantly the azulenes 3a - 5a and only traces of the 1,3-heptalenedicarboxylate 2a, compounds of this type become the main products by the thermolysis of the methyl substituted heptalenes 1b - 1e (Tab. 2). Thermolysis of the 1,3-heptalenedicarboxylate 2c under the same reaction conditions shows that this rearrangement is irreversible.



1

207°C
tetralin



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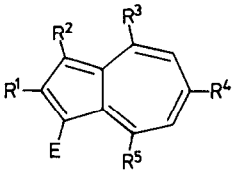

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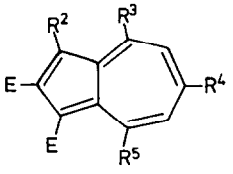

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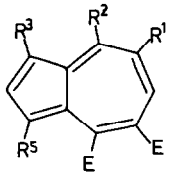


5

a: R^1-R^5=H
b: R^1-R^4=H; R^5=Me
c: R^1,R^2=H; R^3-R^5=Me
d: R^1=H; R^2-R^5=Me
e: R^2=H; R^1,R^3-R^5=Me

E: CO_2Me

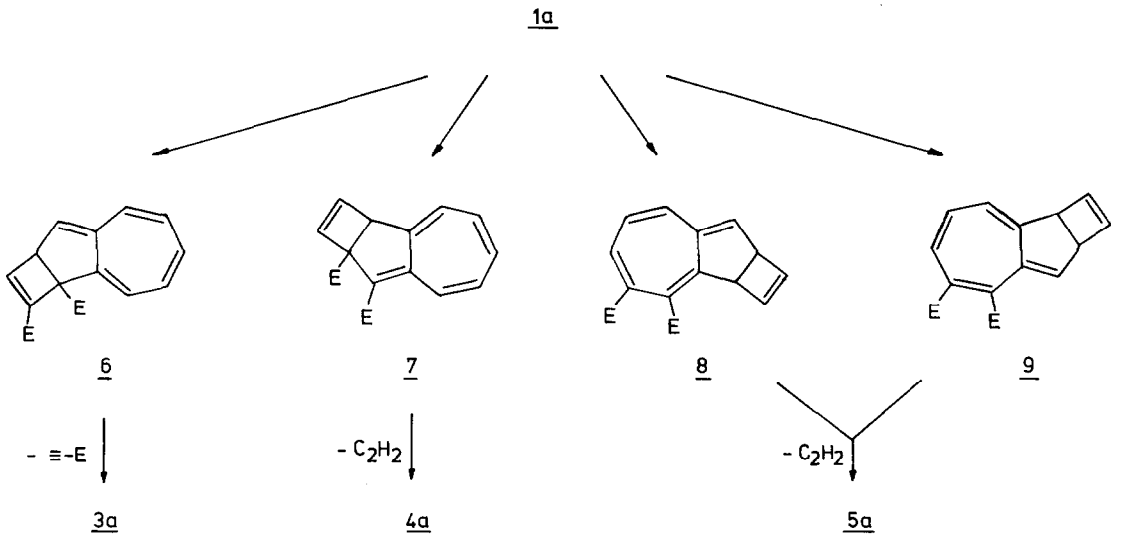
Tab. 1: Product ratios for the conversion of 1 into 2 - 5

	reaction time [h]	conversion [%]	yields[a] [%] 2	3	4	5
1a	6	70	1	1[4]	30[2]	8[5]
1b	16	36	10	1	2	-
1c	24	12	55	-	2[2]	-
1d	72	6	13[6]	-	1	-
1e	60	10	66	-	-	-

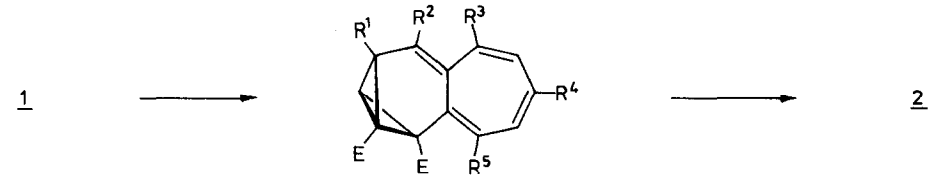
a) yields based on conversion of 1

For the formation of the azulenes 3 - 5 from heptalenes 1 we assume an isomerization to the cyclobutenes 6 - 9 and subsequent cycloreversion of an alkyne, which would be a reverse of the heptalene synthesis from azulenes and dimethyl acetylenedicarboxylate.[2]

The isomerization of 1 to 2 proceeds formally by migration of the ester group in 2-position, while all methylsubstituents retain at their position. Migration of the methyl group in 5-position of 1d to the corresponding dimethyl 3,6,8,10-tetramethyl-1,2-heptalenedicarboxylate, previously postulated by Hansen et al.[7], has been revealed to be a misassignment[8] of the double bond isomers of 1d[1]. Also, for the claim of these authors[6], according to which the rearrangement of 1 into 2 should be induced by a reversible addition of a radical, we obtained



no indication. The isomerization can be explained rather simple by an intramolecular $[\pi 2_a+\pi 2_s]$-cycloadditon of 1 to the heptvalene 10 and subsequent $[\sigma 2_a+\sigma 2_s]$ ring opening to 2[9]. Alter-



10

native mechanisms, as also discussed by Paquette et al.[10] for the isomerization of cyclooctatetraenes, cannot explain the observed substitution pattern of isolated products, e.g. the exclusive formation of 2d from 1d or 2e from 1e.

Tab. 2: Physical Data of compounds 2a-e, 4b and 4d[11]

2a: brown-red oil[a]; ^{1}H NMR: δ= 3.77, 3.81(2s; 3H each, 2 CO_2Me), 5.48(d, J= 7.6Hz; 1H, 5-H), 5.58(d, J= 7.5Hz; 1H, 10-H), 5.89(d, J= 9.8Hz; 1H, 6-H), 6.25, 6.54(2m; 2H and 1H, 7/8/9-H), 7.54(dd, J= 7.6, 1.1Hz; 1H, 4-H), 7.78(s; 1H, 2-H).

2b: brown-red oil[a]; ^{1}H NMR: δ= 1.66(s; 3H, 10-Me), 3.78, 3.86(2s; 3H each, 2 CO_2Me), 5.62(dd, J= 7.3, 0.8Hz; 1H, 5-H), 6.03(dd, J= 10.1, 0.5Hz; 1H, 6-H), 6.20-6.42(m; 3H, 7/8/9-H), 7.65(d, J= 7.3Hz; 1H, 4-H), 7.93(s; 1H, 2-H).

2c: brown crystals, m.p. 118-122°C; ^{1}H NMR: δ= 1.59(s; 3H, 10-Me), 1.98(d, J= 1.2Hz; 3H, 8-Me), 2.11(d, J= 1.0Hz; 3H, 6-Me), 3.76, 3.83(2s; 3H each, 2 CO_2Me), 5.94(d, J= 7.1Hz; 1H, 5-H), 6.02(br.s; 1H, 9-H), 6.18(br.s; 1H, 7-H), 7.68(dd, J= 7.1, 0.9Hz; 1H, 4-H), 7.91(s; 1H,2-H); UV(dioxane): λ_{max}(lgε) = 224sh(4.31), 279(4.25), 324sh(3.58), 434(3.13)nm.

2d: brown-red crystals; m.p. 127-128°C; ^{1}H-NMR: δ= 1.59(s; 3H, 10-Me), 1.84(s; 3H, 5-Me), 1.98 (d, J= 1.2Hz; 3H, 8-Me), 2.01(d, J= 1.1Hz; 3H, 6-Me), 3.74, 3.84(2s; 3H each, 2 CO_2Me), 6.09, 6.12(2br.s; 1H each, 7/9-H), 7.67(s; 1H, 4-H), 7.87(s; 1H, 2-H); UV(n-hexane): λ_{max}(lgε)= 208(4.39), 227(4.31), 279(4.31), 318sh(3.59), 413(3.06)nm.

2e: red crystals; m.p. 129°C; ^{1}H NMR: δ= 1.57(s; 3H, 10-Me), 1.97(d, J= 1.2Hz; 3H, 6-Me), 2.09 (d, J= 1.1Hz; 3H, 8-Me), 2.26(d, J= 0.9Hz; 3H, 4-Me), 3.74, 3.81(2s; 3H each, 2 CO_2Me), 5.73(br.s; 1H, 9-H), 5.98(br.s; 1H, 7-H), 6.12(br.s; 1H, 5-H), 7.79(s; 1H, 2-H); UV(dioxane): λ_{max}(lgε)= 278(4.33), 325sh(3.68), 412sh(3.11)nm.

4b: blue crystals; m.p. 64-65°C; ^{1}H-NMR (100 MHz): δ= 2.92(s; 3H, Me), 3.06, 4.03(2s; 3H each, 2 CO_2Me), 7.10-7.40(m; 2H, 5/7-H), 7.50-7.70(m; 1H, 6-H), 7.74(s; 1H, 1-H), 8.46(d, J= 10.0Hz; 1H, 8-H).

4d: blue crystals; m.p. 148-149°C; ^{1}H-NMR: δ= 2.54(s; 3H, 6-Me), 2.78(s; 3H, 4-Me), 2.88(s; 3H, 8-Me), 3.02(s; 3H, 3-Me), 3.91(2s; 3H each, 2 CO_2Me), 6.98, 6.99(2s; 1H each, 5/7-H); UV(dioxane): λ_{max}(lgε)= 229sh(4.18), 253(4.44), 302sh(4.64), 309(4.69), 347sh(3.77), 358(3.82), 370sh(3.60), 581(2.88)nm.

a) could not been obtained as pure compounds so far.

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