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TRIMERIZATION OF CYCLOHEPTA-2,6-DIEN-1-ONE.

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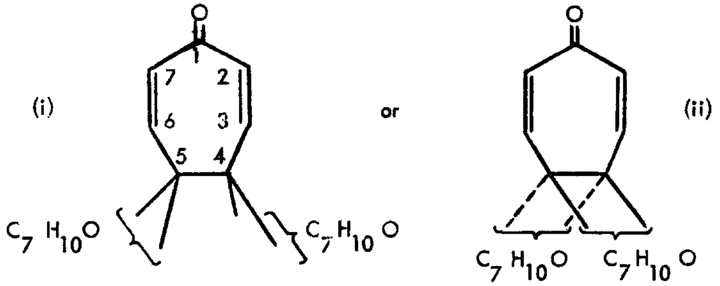
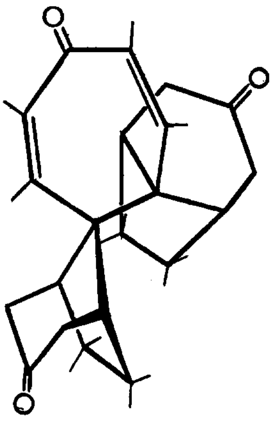
In the course of our investigation of the addition of various nucleophilic reagents to cyclohepta-2,6-dien-1-one (*I*)[1-3], the reaction with active methylenic compounds was performed. During this research, it was found that compound *I* can act as the addend as well as the acceptor in a Michael-type addition reaction, thus yielding, in the presence of $KOBu^t$ a crystalline trimer (*II*); $C_{21}H_{24}O_3$, m.p. 181°-182° (acetone), m/e 324 ($M^{\oplus}$), IR 3000, 2980, 2940, 1700 (C=O), 1675, 1600 (C=C-C=O), 1420, 1400, 1340, 1140, 1020, 990, 950, 895, 880,870, 780, 690 cm^{-1}, NMR at high field δ 1.45-1.88 (m ,4H), 1.90-3.10 (m ,16H) and at low field an AA'BB' pattern, δ_A 5.73 (2H) and δ_B 6.28 (2H) (irradiation of each half of the AA'BB' pattern changed the other one into a singlet). This AA'BB' pattern indicates, together with the other spectral data, that a 4,5-tetra-substituted-cyclohepta-2,6-dien-1-onic system is part of the trimer (*II*) i.e. the γ-positions in this dienonic system are the ones through which the connection to the other parts of the molecule (*II*) are achieved, (the latter finding is in contrast to the known behaviour of such systems under basic conditions)[4].

In the trimer, one molecule of *I* is connected to the two others in one of the following two ways:

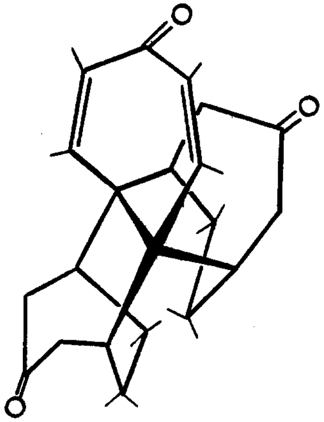


i.e. in (i) C-4 should be connected to one additional cycloheptanonic unit and C-5 to the other, to give two bicyclo[3.2.1]octanic systems, while in (ii) C-4 and C-5 together are connected to both two units to form bicyclo[3.2.2]octanic systems.

Three possible structures can be suggested for (i) or (ii) according to the relative position in which the two bicycloheptanonic units are connected in *II*, e.g. structures *III* (type i) and *IV* (type ii) are two of the possibilities.



III



IV

Inspection of Dreiding models of the six possible trimers reduces the probability of four of them, because of overcrowding in the structure (some of the distances between spatial near carbon atoms are not more than ~0.6-1.4 Å) and severe rigidity which does not allow conformational mobility (see below).

The complexation of the trimer with Eu(dpm)$_3$ in CCl$_4$[5], gave rise to the following shifts for a ca.0.15 Eu(dpm)$_3$/substrate ratio: δ 2.52(s, $\Delta W_{\frac{1}{2}}$=6Hz, 8H), 3.50 (m, $\Delta W_{\frac{1}{2}}$=9Hz, 4H), 4.26(d, J=18Hz, 4H) 4.98(d, J=18Hz, 4H) (the latter two signals attributed to the protons α-to the carbonyl, as they disappear on deuteration, seem to be the AB part of an ABX system, the J_{AX} and J_{BX} values of which are difficult to measure because of line broadening) and the dienonic AA'BB' system; δ_A6.26 (m, 2H) and δ_B6.63 (m, 2H).

Of most significance is the simplicity of the above spectrum which seems to indicate both conformational mobility, as well as the two bicyclic parts of *II* being identical. Furthermore, great similarity of the shifts to those observed in other bicyclo[3.2.1]octanic systems could be seen. This fact by itself cannot remove from consideration the [3.2.2] systems as a part of *II*, but structure *III* is tentatively preferred in our opinion, on the basis of the above consideration and Dreiding models inspection.

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