

HIGH PRESSURE [4+2] AND [2+2+2] REACTIONS BETWEEN
CYCLOHEPTATRIENE AND METHYL PROPIOLATE

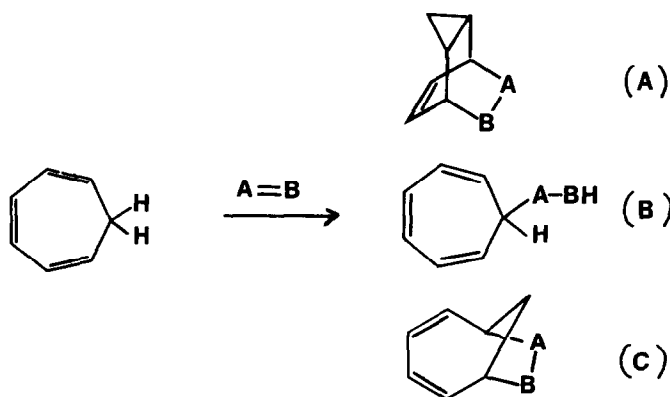
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Under high pressure conditions, cycloheptatriene reacts with methyl propiolate to afford mono-, bis- and trisadducts all retaining the norcaradiene structure. The four new compounds are formed via [4+2] and [2+2+2] cycloadditions. The latter are examples for the high pressure extension of the scope of homo-Diels-Alder reactions.

Cycloheptatriene (CHT) is an extremely interesting triene in the sense that it can react with dienophiles across the norcaradiene structure giving [4+2] adducts (route A), [6+2] cycloadducts (route C) or can undergo a ene reaction (route B) (scheme I).

Scheme I



Depending on reaction conditions and evidently on the reactive dienophile, a large variety of products can be formed¹⁻⁴. With very reactive symmetrical dienophiles (TCNE⁵, triazolinedione⁶, maleic anhydride⁷), the addition to norcaradiene is largely preferred (route A). With less reactive dienophiles, the other types

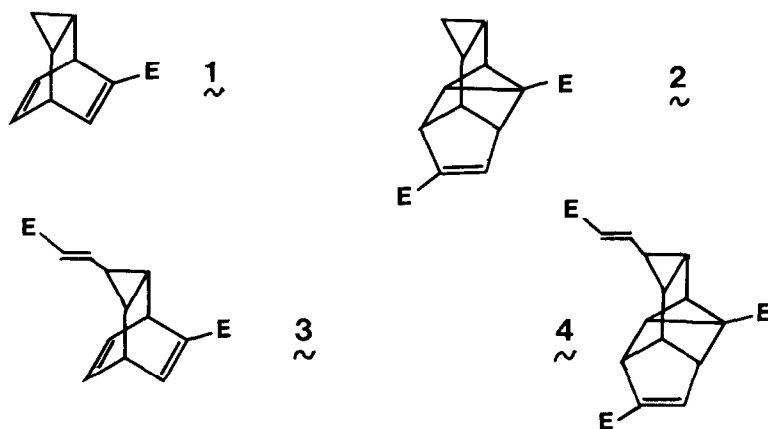
of adducts and derivatives thereof are usually observed. For example, acrylic compounds react with CHT under high temperature conditions (170-200°C) to afford norcaradiene adducts together with (C)-type adducts⁸.

We have started a high pressure study of some CHT reactions. While examining the reaction involving methyl propiolate, we could evidence several adducts with unusual structures.

At normal pressure, methyl propiolate did not react with CHT at the temperatures up to 120°C. At 180°C, after 20h, a carbonaceous mixture was recovered and analyzed by GC showing the formation of numerous products in low yield^{9,10} (propiolate conversion was about 7-8%).

At high pressure and lower temperature, the course of the reaction was different. When a CH_2Cl_2 solution of methyl propiolate with a slight excess of CHT was submitted to a 900 MPa (9 kbar) pressure at 80°C during 68h, four products were formed (total yield of purified products : 73%) in the ratio 5 : 1 : 2 : 1, which could be separated by careful column chromatography¹⁰. Their structures were established unequivocally on the basis of spectral data (1H NMR-360 MHz and MS principally) and further chemical transformations¹¹.

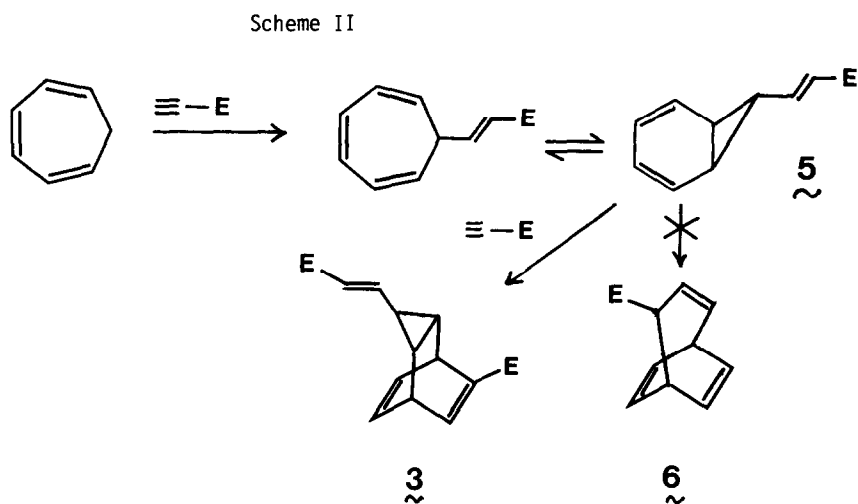
All four products were shown to contain the norcaradiene structure. The first and major product eluted from the column was easily identified as the monoadduct 1 (yield : 41%). The second (yield : 8%) was the pentacyclic bisadduct 2. The third product 3 (yield : 16%) was also a bisadduct, however with a different structure. The last 4 was a trisadduct (yield : 8%), (E = CO_2CH_3):



The formation of the adducts can be rationalized in following way : 1 is the normally expected [4+2] adduct, 2 results from a homo-Diels-Alder reaction between the homoconjugated diene 1 and methyl propiolate¹¹. There are four possible adducts, however only adduct 2 is formed as can be predicted by FMO theory¹². The formation of 4 is believed to proceed in a similar manner through reaction of 3 with the acetylenic bond. These reactions are of theoretical interest, since it has been stated that the scope of the homo-Diels-Alder reaction is limited to bicycloheptadiene systems, since the less reactive bicyclo octadienes give virtually no homo-Diels-Alder adducts¹³. Application of high pressure may thus be a way to

circumvent the low reactivity in such systems¹⁴.

Finally **3** is probably formed according to a sequential process, via an initial ene-reaction (route B) followed by a [4+2] addition of methyl propiolate on the norcaradiene structure **5** (Scheme II).



It should be emphasized that **6** was not obtained. In contrast, the corresponding reaction with the more reactive symmetrical acetylenedicarboxylate dimethyl ester gives **7** via \times rearrangement of the initial ene adduct¹⁵, no Diels-Alder product corresponding to structure **3** was observed. The other product of the reaction is **8** which does not undergo a homo-Diels-Alder reaction probably because the blocking effect of the ester groups¹⁶



We conclude that high pressure considerably promotes addition of acetylenic bonds to trienes with norcaradiene character. The readily formed adducts are reactive enough under pressure conditions to undergo further additions leading to polyadducts, all containing the norcaradiene structure. These reactions are apparently fairly concerted because their facile pressure synthesis¹⁴ Other CHT reactions are currently under investigation.

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- 9) Due to the low yield, the products were not separated. However, their GC retention times were different of those of the products obtained in the high pressure runs, except for 1 which is formed in 3% yield in normal pressure conditions.
- 10) Experimental details will be reported in a forthcoming publication encompassing numerous high pressure additions on cycloheptatriene.
- 11) The formation of 2 was proved independently by reacting 1 with methyl propiolate (900 MPa, 80°C, 24h). 2 was formed in 50% yield demonstrating the synthetic utility of the pressure variable in achieving reluctant homo-Diels-Alder reactions.
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