

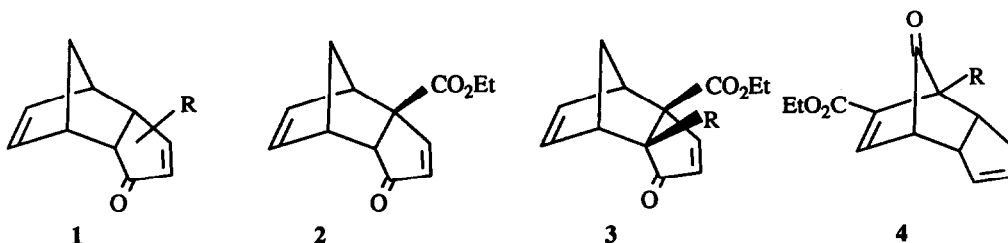
GENERATION AND REACTIONS OF 2-ALKYL-3-CARBOETHOXYCYCLOPENTADIENONES

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Abstract: Thermolysis of 6-alkyltricyclo[5.2.1.0^{2,6}]decadienone esters **3** in DMF produces 2-alkyl-3-carboethoxycyclopentadienones **8** in an efficient [4+2]cycloreversion reaction. These cyclic dienones can be trapped by cyclopentadiene to afford regioselectively tricyclodecadienones **9** in high yields.

The tricyclo[5.2.1.0^{2,6}]decadienone system **1** constitutes a potent synthetic equivalent of cyclopentadienone. Its rigid structure, the presence of a reactive α,β -enone system and the ultimate ability of the tricyclic skeleton to undergo [4+2]-cycloreversion are instrumental in the synthesis of a variety of functionalized cyclopentenones with defined stereochemistry and chirality¹. The *endo*-tricyclodecadienone system, racemic as well as optically active, is conveniently accessible via ester **2**, which in turn is readily available from the Diels-Alder adduct of benzoquinone and cyclopentadiene^{2,3}.

In a recent paper, we reported on the angular alkylation of **2** to **3** by deprotonation using LDA followed by treatment with an alkyl halide⁴. The compounds **3** showed a surprisingly low skeletal stability; at room temperature they rapidly equilibrate with bridged ketones **4**. In this communication, we demonstrate that the

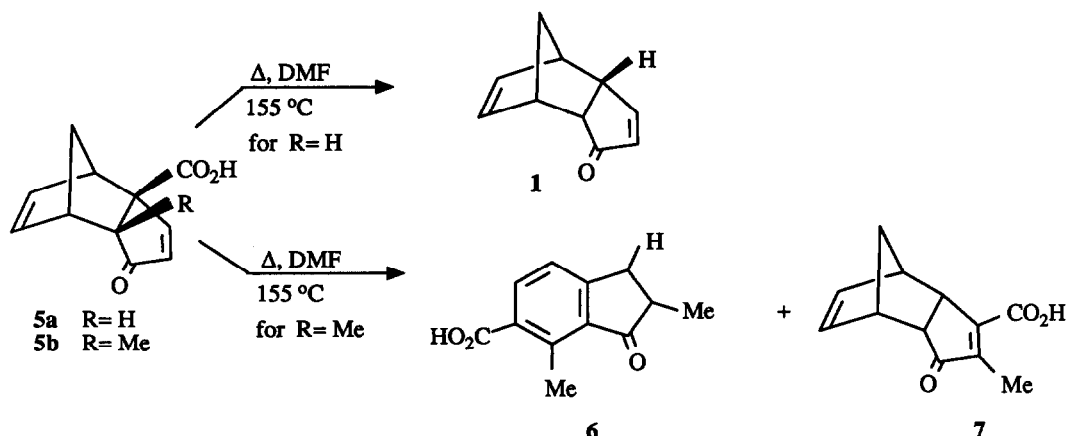


implications of angular alkylation in **2** go beyond promotion of this Cope rearrangement. The alkyl substituted esters **3/4** exhibit an unexpected and facile cycloreversion to give 2-alkylcyclopentadienone 3-carboxylates upon heating in solution⁵.

Alkyl substituted tricyclodecadienones **3**⁶ are thermally considerably less stable than the parent ester **2**. An interesting difference in thermal behaviour was encountered by comparing the parent acid **5a** and the angularly methylated acid **5b**. The acid **5a**, being a vinylogous β -keto carboxylic acid, upon heating in DMF at 155 °C readily decarboxylates to give the parent tricyclodecadienone **1** (R= H) in 83% yield^{2,3}. However, under these conditions **5b** did not give such a decarboxylation but instead produced a mixture of indanone **6** and the novel tricyclodecadienone **7** as the major products in yields of 36% and 18%, respectively⁷(Scheme D).

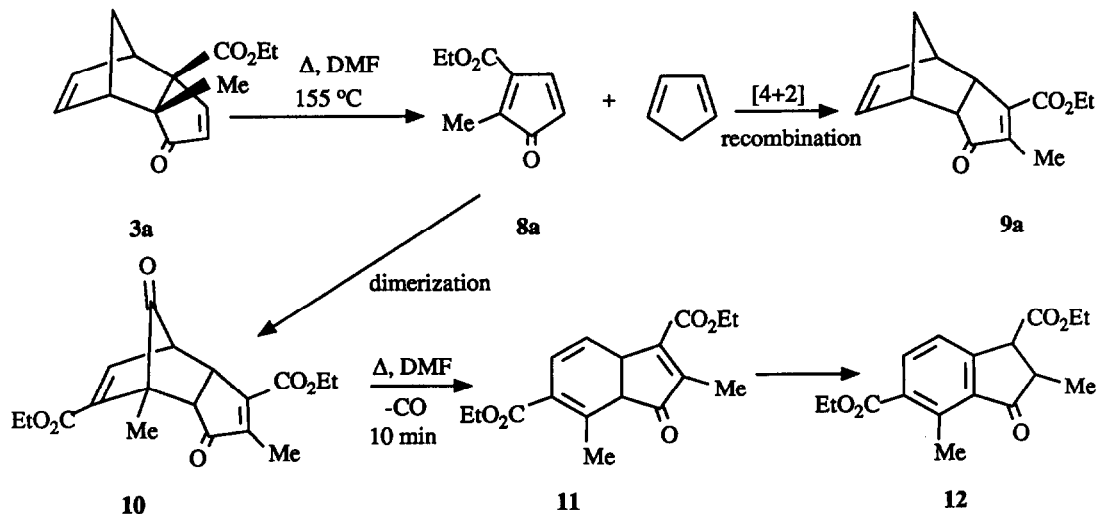
Under similar thermal conditions, methyl substituted ethyl ester **3a** was rapidly converted into a mixture of

Scheme I



indanone ester **12** and tricyclic β -enone ester **9a** in yields of 38% and 19%, respectively (Scheme II). The concurrent formation of **12** and **9a** during the thermolysis of **3a** in DMF can readily be rationalized by assuming a [4+2] cycloreversion as the initial step involving the formation of cyclopentadienone **8a** and cyclopentadiene (Scheme II). Subsequently, **8a** rapidly recombines with cyclopentadiene to afford tricyclodecadienone **9a** having a reversed regiochemistry compared to the starting material. On the other hand, its stability is apparently sufficient to find another cyclopentadienone molecule to dimerize with. This dimerization results in the regioselective formation of tricyclic diketone **10**. Under the thermal conditions applied, subsequent decarbonylation occurs to form dihydroindenone **11** which aromatizes to indanone **12**. In case of the dicarboxylic acid analogue of **12** subsequent decarboxylation leads to **6**

Scheme II



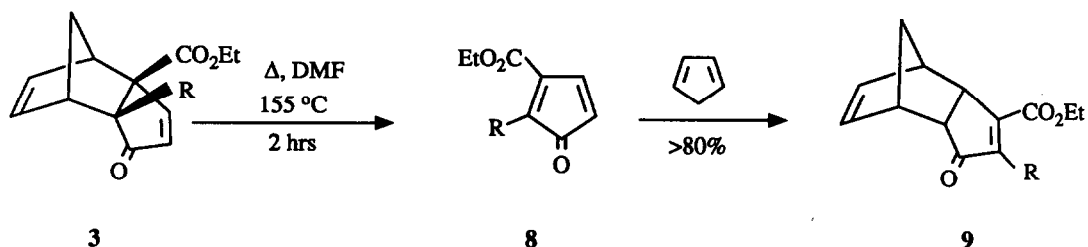
The intermediacy of free cyclopentadienone **8a** was unambiguously proven by a crossed Diels-Alder reaction with cyclopentadiene. The addition of a twentyfold excess of this diene to the solution of **3a** in DMF and heating this mixture again at 155°C for 2.5 hrs afforded 4-methyltricyclodecadienone 3-carboxylic ethyl ester **9a**

in the excellent yield of 81%.

The occurrence of dimer **10** as precursor for indanone **12** could be proven independently by subjecting **3a** to gas phase thermolysis (450 °C, 4.10^{-2} torr)⁸. Dimer **10** turned out to be the major product in this thermolysis. Its structure could unequivocally be established by X-ray analysis⁹. Subsequent heating of **10** in DMF caused rapid decarbonylation to give indanone **12** as the sole product (90% yield).

The thermal behavior of **3a** in DMF appeared to be typical for 6-alkyl substituted tricyclodecadienone 2-carboxylates. In all four other cases studied, the thermolysis proceeded smoothly to generate the corresponding 2-alkylcyclopentadienone esters **8b-e**, which were again efficiently trapped with the excess cyclopentadiene present, to afford tricyclic enones **9b-e** in yields over 80% (Scheme III). This efficient generation of **8** and its smooth regiospecific cycloaddition reaction with cyclopentadiene makes this thermolysis of practical utility. The obtained tricyclic α -alkyl, β -carboethoxy enones **9** are currently being exploited as synthons for sarkomycin derivatives¹⁰.

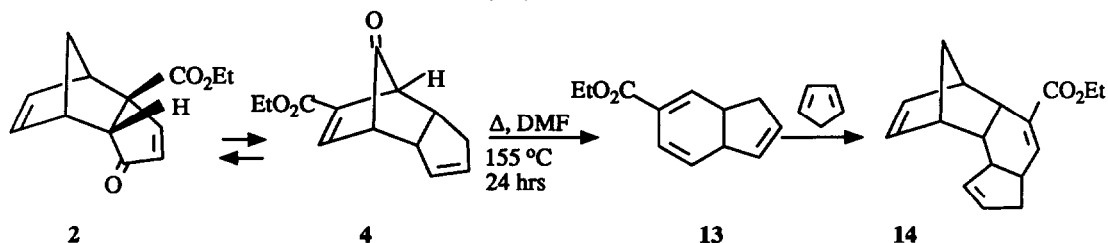
Scheme III



R: a CH₃, b C₂H₅, c n-C₇H₁₅, d CH₂CH=CH₂, e CH₂C₆H₅

In contrast to the angularly alkylated tricyclodecadienone carboxylates **3**, parent ester **2** appeared to be thermally relatively stable when heated in DMF. Complete conversion of **2** was only observed after 24 hours yielding an intractable mixture. However, when the thermolysis of **2** was carried out in the presence of an excess of cyclopentadiene with the aim to trap possible cyclopentadienone intermediates, the formation of tetracyclic ester **14** was observed (35%). It is quite clear that a deviating reaction took place. The rationale for the formation of **14** is outlined in Scheme IV and involves the cheletropic decarbonylation of the Cope isomer of **2**, followed by Diels-Alder reaction of the intermediate dihydroindene **13** with cyclopentadiene¹¹.

Scheme IV



In conclusion, the introduction of an alkyl group at the 6-position in tricyclic ester **2** drastically alters its thermal behavior in DMF. Whereas in ester **2** thermal fragmentation proceeds through decarbonylation, the angularly alkylated species **3** exclusively fragmentate by a [4+2]-cycloreversion. The ease at which the alkyl substituted cyclopentadienone esters **8** are formed in this latter reaction suggests a considerable stabilization of these cyclic dienones due to alkyl substitution¹². This enhanced thermodynamic stability is apparently sufficient

to favor the cycloreversion reaction of either 3 or 4 over the alternative decarbonylation of the Cope rearrangement product 4. It should be noted that whereas generally tricyclodecadienones of the type 1 undergo thermal decarbonylation^{4,13}, the thermal cycloreversion encountered here for 3/4 furnishing cyclopentadienones has no precedent.

Notes and References

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6. It is obvious that in all thermal experiments with 3, the actual starting material consists of an equilibrium mixture of 3 and 4⁴.
7. Satisfactory elemental composition (combustion analyses or exact mass determinations) and spectral data were obtained for all new compounds.
8. Details on this gas phase thermolysis will be published in due time.
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11. Cf. C.S. Baxter and P.J. Garratt, *Tetrahedron* **27**, 3285 (1971).
12. The enhanced thermodynamic stability of these cyclopentadienones 8 may be the result of a capto-dative interaction between the vicinal ester function and methyl group. See for instance: R. Gompper and G. Seybold, *Angew. Chemie* **19**, 805 (1968).
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