A Convenient Synthesis of 7-Substituted Norbornadienes

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7-Substituted norbornadienes were conveniently synthesized from the adduct of nickelocene and dimethyl acetylenedicarboxylate.

Bicyclo[2.2.1]heptadienes with a substituent at C-7 have long been recognized as being useful synthons for the preparation of various complex molecules of theoretical as well as practical interest.[1] However, a general route for the synthesis of these highly interesting intermediates was lacking.[2] We now report a convenient synthesis from the readily available organonickel compound (**3**).

Compound (**3**) has been known for more than two decades,[3] and its *X*-ray structure has been determined.[4] More recently, some optically active analogues of (**3**) were also synthesized.[5] Surprisingly, no report has been made of the reactions of (**3**) other than its hydrogenation which gives 2,3-dimethoxycarbonylnorbornane.[3] It has been well established that the transition metal–alkyl σ-bond can readily be cleaved, which makes them useful in organic synthesis.[6] Thus, we felt that (**3**) could be a useful starting material for the preparation of various 7-substituted bicyclo[2.2.1]heptadienes.

On treatment with *N*-bromosuccinimide in the presence of azobisisobutyronitrile at 80 °C, (**3**) was rapidly transformed into a mixture of (**1a**)† and (**2a**) (1:4) in 61% yield. The isomeric ratio was determined by the proton n.m.r. spectrum. The olefinic protons of the *syn* isomer (**1**) usually show

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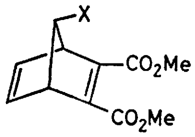
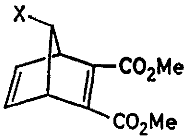
† All new compounds exhibited satisfactory spectroscopic and analytical data consistent with the proposed structures.

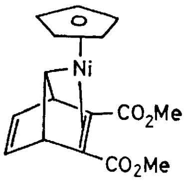


(1)

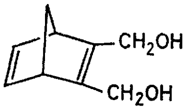


(2)

a; X = Br
b; X = Cl
c; X = OH
d; X = CO_2Me



(3)



(4)

absorption at higher field than those of the *anti* isomer (**2**).‡ In addition, only *syn* isomer (**1**) exhibits typical nuclear Overhauser enhancement upon irradiation at δ *ca.* 4.0 which is assigned to the absorption of C-7-H.

In a similar manner, the chloro-derivatives (**1b**) and (**2b**) (*ca.* 1 : 1) were obtained in 47% yield from the reaction of (**3**) with *N*-chlorosuccinimide in the presence of azobisisobutyronitrile. Compound (**3**) was also converted into the 7-hydroxynorbornadienes (**1c**) and (**2c**) (*ca.* 1 : 1) in 68% yield upon stirring with *m*-chloroperbenzoic acid at room temperature. Interestingly, the double bonds remain intact under the reaction conditions. Mild oxidation of the alcohol (**1c**) or (**2c**) with Jones' reagent or with dimethyl sulphoxide afforded dimethyl phthalate exclusively.

The reactions described above are not stereospecific, unlike those of early transition metal–alkyl complexes.[6] Like many other Group 8 transition metal-catalysed reactions,[7] in particular those of organonickel compounds,[8] the reactions may proceed *via* a free radical mechanism.

Compound (**3**) was treated with carbon monoxide and methanolic sodium methoxide under refluxing conditions to afford the 7-methoxycarbonyl compound (**1d**) in 31% yield. The reaction is stereospecific and no isomeric compound (**2d**) was isolated. Reduction of (**3**) with an excess of lithium aluminium hydride gave (**4**) in 52% yield.

In summary, we have developed a convenient method for the introduction of various functional groups and for carbon–carbon bond formation at the C-7 position of bicyclo[2.2.1]-heptadienes.

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‡ The proton chemical shifts of the olefinic protons for (**1a**) and (**2a**) are δ 6.15 and 6.85, respectively, for (**1b**) and (**2b**), 6.10 and 6.85, respectively, and for (**1c**) and (**2c**), 6.00 and 6.90, respectively. The isomers can readily be separated by thin layer chromatography.

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