

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.

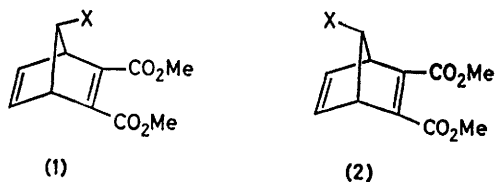
Bicyclo[2.2.1]heptadienes with a substituent at C-7 have long been recognized as being useful synthons for the preparation of various complex molecules of theoretical as well as practical interest.¹ However, a general route for the synthesis of these highly interesting intermediates was lacking.² We 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-dimethoxy-carbonylnorbornane.³ It has been well established that the

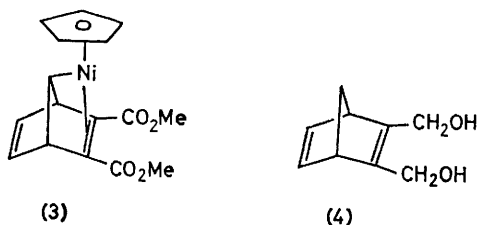
transition metal-alkyl σ -bond can readily be cleaved, which makes them useful in organic synthesis.⁶ Thus, we felt that (3) could be a useful starting material for the preparation of various 7-substituted bicyclo[2.2.1]heptadienes.

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

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



- a; X = Br
 b; X = Cl
 c; X = OH
 d; X = CO₂Me



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-hydroxy-

[‡] 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.

norbornadienes (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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