Homo-Diels–Alder Route to Homoiceane (Tetracyclo[6.3.1.1^{2,7}.0^{4,10}]tridecane)

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Homo-Diels–Alder reaction of tricyclo[5.3.1.0^{4,9}]undeca-2,5-diene (**1**) results in a one-step construction of the didehydrohomoiceane skeleton, from which homoiceane (**10**) and further cyclised derivatives may be synthesized.

The [2 + 2 + 2] cycloaddition of a 1,4-diene with a dienophile, the homo-Diels–Alder reaction, is a potentially useful synthetic reaction, producing two C–C bonds and a cyclopropane ring in one step.[1] The use of 1,4-dienes, however, has been limited mainly to bridged cyclohexa-1,4-dienes; studies have been restricted almost exclusively to norbornadiene, which is the most reactive of such 1,4-diene systems. Recently we have found that tricyclo[5.3.1.0^{4,9}]undeca-2,5-diene (**1**)[2] reacts with tetracyanoethene faster than norbornadiene to give the homo-Diels–Alder adduct,[3] providing the first example of a cyclo-octa-1,4-diene system participating as a diene partner in the homo-Diels–Alder reaction. In addition to its mechanistic interest, the resulting adduct (homoiceane) is a homologue of iceane.[4] This communication describes the first synthesis of homoiceane (**10**) and further cyclised derivatives by using this highly efficient one-step framework construction.

When a 2 : 3 mixture of (**1**) and maleic anhydride (MA) in *o*-dichlorobenzene was heated under reflux for 12 h, the single homo-Diels–Alder adduct (**2**), m.p. 153—155 °C,† was obtained (81%). The ^{13}C n.m.r. spectrum of (**2**) [δ 174.7 (s), 44.1 (d), 32.6 (t), 31.9 (t), 31.0 (d), 28.4 (d), 18.4 (d), 15.4 (d), and 5.5 (d)] clearly indicated C_s symmetry. Basic hydrolysis of (**2**) followed by treatment with CH_2N_2 gave the *exo*-dimethyl ester (**4**). Cycloaddition of (**1**) with dimethyl acetylenedicarboxylate (DMAD) afforded the adduct (**5**), m.p. 63—64 °C, but in low yield (22%). However, addition of a catalytic amount of $Ni(CN)_2(PPh_3)_2$[5] (2 mol%) increased the yield to 45%. Hydrogenation of (**5**) over Pd black took place from the *exo*-side, probably owing to steric hindrance by 10-H, to give the *endo*-dimethyl ester (**6**) which is an isomer of (**4**).

The stereochemical assignments to (**4**) and (**6**) were further supported by a steric compression effect observed in their ^{13}C n.m.r. spectra. The C-3 (C-4) signal appears at higher field (δ 6.3) in (**4**) than in (**6**) (δ 10.6), whereas the C-10 signal is at lower field (δ 32.2) in (**4**) than in (**6**) (δ 29.2). Thus, it is

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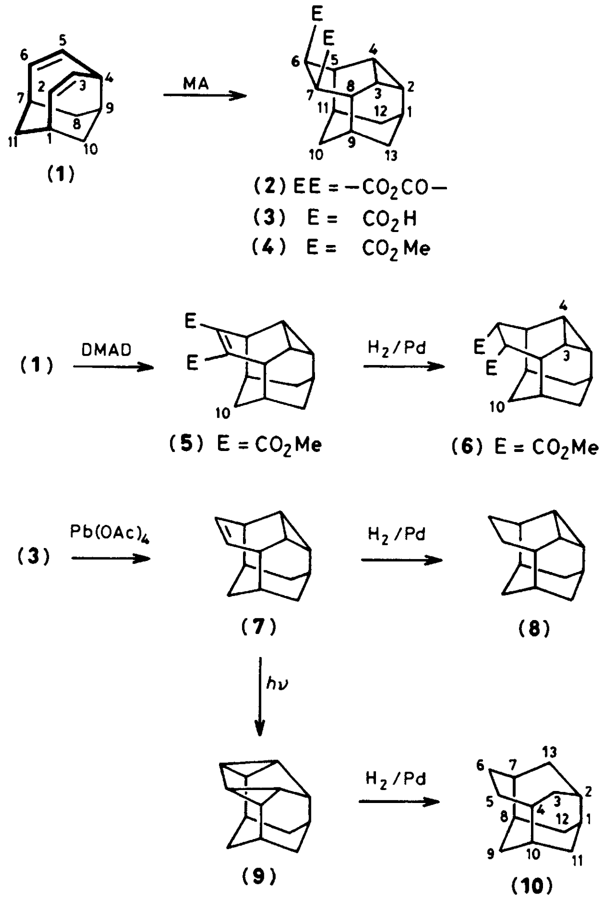
† All new compounds gave satisfactory analytical and spectral data.



(1)

(2) EE = $-CO_2CO-$
(3) E = CO_2H
(4) E = CO_2Me

(5) E = CO_2Me

(6) E = CO_2Me

(7)

(8)

(9)

(10)

noteworthy that the present homo-Diels–Alder reaction proceeds exclusively in an *endo*-selective fashion.‡

Oxidative decarboxylation of the dicarboxylic acid (**3**) by $Pb(OAc)_4$ in pyridine[7] gave the 3,13-cyclo compound (**7**) (65%), hydrogenation (Pd black; MeOH) of which gave the saturated compound (**8**) (97%).§ Irradiation of (**7**) in ether by a medium-pressure mercury lamp through a quartz filter induced a $[_{\pi}2 + {}_{\sigma}2]$ cycloaddition to give compound (**9**) (64%), along with a small amount of unchanged (**7**).¶ The ^1H n.m.r. spectrum of (**9**) showed no olefinic protons and its ^{13}C n.m.r. spectrum [δ 35.6 (d), 35.5 (t), 33.8 (d), 33.3 (d), 32.4 (t), 27.1 (d), 26.7 (d), and 22.5 (d)] clearly indicated C_s symmetry. This highly strained hydrocarbon (**9**) is expected to be reactive in the presence of transition metals, and, when treated with Pd black under H_2 in MeOH, hydrogenation of the two cyclopropane rings took place simultaneously to afford a 1 : 1 mixture of homoiceane (**10**) and (**8**) (91%), along with a small amount of an unidentified product. The ^{13}C n.m.r. spectrum of (**10**) [δ 35.0 (t), 34.2 (t and d), 32.8 (t), 31.7 (d), 30.7 (t), 30.2 (d), and 26.4 (d)] clearly indicated C_s symmetry.

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‡ In the reaction of norbornadiene with maleic anhydride, 67—79% *endo*-selectivity was observed.[6] The steric hindrance due to the C-11 methylene bridge of (**1**) may cause the *endo*-selectivity in the present example.

§ Further hydrogenation of (**8**) under more drastic conditions gave an unwanted product rather than (**10**).

¶ The ratio of (**9**) to (**7**) was 2.7 : 1 after 12 h irradiation; further irradiation did not change this ratio.