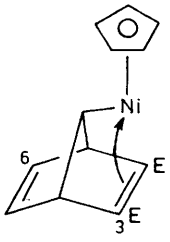
Reactions of the Nickelocene–Dimethyl Acetylenedicarboxylate Adduct: a Route to 7-Substituted Norbornadienes

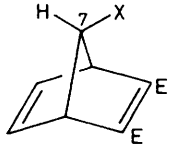
Christine Bleasdale and David W. Jones *
Department of Organic Chemistry, The University, Leeds LS2 9JT

Contrary to an earlier claim, reactions of the complex (**1**) with *m*-chloroperbenzoic acid, *N*-bromosuccinimide, and *N*-chlorosuccinimide give the diester (**15**) and the *syn*-norbornadienes (**2**), (**4**), and (**6**), respectively; reactions of (**1**) with lead tetra-acetate and iodine also proceed with retention of C-7 stereochemistry but with bromine and chlorine inversion at C-7 is increasingly dominant.

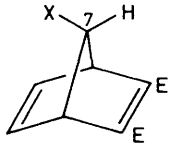
The complex (**1**), readily prepared by addition of dimethyl acetylenedicarboxylate to nickelocene,[1] was recently claimed to be a useful source of 7-substituted norbornadienes.[2] The *syn* and *anti* norbornadienols (**2**) and (**3**) were said to be formed (68% yield, 1:1 ratio) upon reaction of (**1**) with *m*-chloroperbenzoic acid, and reaction of (**1**) with *N*-bromosuccinimide was claimed to give a 1:4 mixture of the bromides (**4**) and (**5**) (61% yield); with *N*-chlorosuccinimide (**1**) apparently gave a 47% yield of (**6**) and (**7**) (ratio 1:1).[2] We describe a reinvestigation of these reactions with conclusions that differ from those previously reported. We also describe the reactions of (**1**) with lead tetra-acetate, iodine, bromine, and chlorine which reaffirm the utility of (**1**) as a precursor of 7-substituted norbornadienes. An increasing degree of inversion accompanies cleavage of the carbon–nickel bond as the electronegativity of the halogen increases.



(**1**)



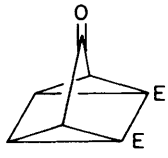
(**2**) X = OH
(**4**) X = Br
(**6**) X = Cl
(**11**) X = OAc
(**14**) X = $OCOC_6H_4Cl$-*m*
(**16**) X = I



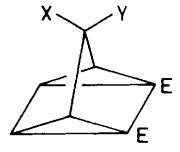
(**3**) X = OH
(**5**) X = Br
(**7**) X = Cl
(**12**) X = OAc

E = CO_2Me

The alleged *syn* and *anti* isomers (**2**) and (**3**) were said to show olefinic resonances at very different shifts (δ 6.00 and 6.90, respectively). Similarly different shifts were reported for the olefinic protons in (**4**) and (**5**) (Δδ 0.7) and (**6**) and (**7**) (Δδ 0.7).[2] Since the olefinic protons in *syn* and *anti* norbornenes show Δδ values[3] of only *ca.* 0.1 p.p.m. and the olefinic protons in norbornadienes usually[3] resonate at δ > 6.5 the assignment of resonances at *ca.* δ 6.0 to the *syn* norbornadienes (**2**), (**4**), and (**6**) was surprising. Accordingly we attempted the preparation of the norbornadienols (**2**) and (**3**) by an alternative route. Reduction of the known[4] quadricyclanone (**8**) ($NaBH_4$, EtOH) gave a *ca.* 1:1 mixture of the quadricyclanols (**9**) and (**10**) from which the individual epimers were obtained by a combination of crystallization from ether and silica chromatography. Ring opening of the quadricyclanol (**9**) with a trace of $Pd(OAc)_2$ in $CDCl_3$ led to a clean conversion into the norbornadienol (**2**), δ($CDCl_3$) 6.73 (2 H, t, *J* 2 Hz, olefinic), 4.02 (1 H, m, 7-H), 3.85 (2 H, m, obscured), 3.80 (6 H, s, 2 × OMe), which however decomposed upon attempted chromatography over both silica and alumina (*cf.* ref. 2). Isomer (**2**) was therefore further characterised as its acetate (**11**) formed by the acetylation (Ac_2O–pyridine) of the crude product of quadricyclane ring opening, δ($CDCl_3$) 6.84 (2 H, dd, *J* 2 and 2.5 Hz, olefinic), 4.68 (1 H, t, *J* 1.75 Hz, 7-H), 3.98 (2 H, ddd, *J* 2, 2.5, and 1.75 Hz, bridgehead), 3.81 (6 H, s, 2 × OMe), and 2.01 (3 H, s, OCOMe). Ring-opening of the quadricyclanol (**10**) proceeded less cleanly and was best carried out by stirring compound (**10**)



(**8**)

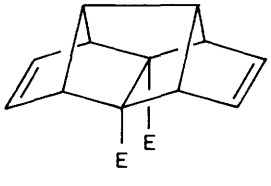


(**9**) X = H, Y = OH
(**10**) X = OH, Y = H
(**13**) X = OAc, Y = H

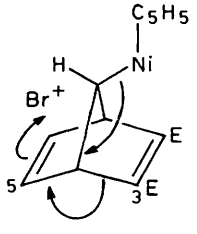
E = CO_2Me

with palladised charcoal in ethyl acetate[5] at 20 °C. This gave a mixture of starting material, unidentified products, and compound (**3**). The ^1H n.m.r. spectrum of the crude product showed a well defined resonance at 6.78 (2 H, m) assigned to the olefinic protons of compound (**3**). Acetylation of this product (Ac_2O–pyridine) followed by silica chromatography gave the *anti*-norbornadienyl acetate (**12**) (38%), δ($CDCl_3$) 6.72 (2 H, td, *J* 2 and *ca.* 0.6 Hz, olefinic), 4.81 (1 H, m, 7-H), 4.02 (2 H, td, *J* 2 and 1.85 Hz, bridgehead), 3.80 (6 H, s, 2 × OMe), and 1.99 (3 H, s, OCOMe). The acetate (**12**) was more efficiently prepared (85%) by ring-opening (Pd–C–$MeCO_2Et$, reflux) of the acetate (**13**). The olefinic resonance in (**11**) is a well defined double

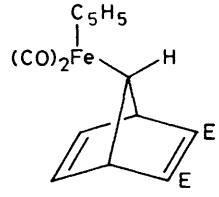
doublet unaffected by irradiation of the C-7 proton whereas the olefinic protons in (**12**) appear as a triplet of doublets owing to coupling to the C-7 proton (*J ca.* 0.6 Hz). The well established stereospecificity of this long-range coupling[6] allows firm assignment of stereochemistry to the epimeric norbornadienes.* The norbornadienols (**2**) and (**3**) prepared as above differ from the oxidation products of compound (**1**) in being unstable to chromatography, and in the chemical shifts of their olefinic protons. Repetition of the reaction of (**1**) with *m*-chloroperbenzoic acid gave a complex product mixture the ^{1}H n.m.r. spectrum of which showed olefinic triplets at δ 6.73, 6.90, and 6.05 (ratio *ca.* 4:4:1). Extraction of the crude product with aqueous sodium hydrogen carbonate removed the signal at δ 6.73,† and acetylation of the crude product (Ac_2O–pyridine) left the signals at δ 6.90 and 6.05 unchanged but shifted that at δ 6.73 to 6.84. Chromatography of the acetylated product gave the acetate (**11**) (9%) (δ 6.84), the *m*-chlorobenzoate (**14**), m.p. 68—71 °C (14%) (δ 6.90), and the known[7] compound (**15**) (3%) (δ 6.05). Compound (**15**) was also obtained (10%) together with (**4**) (16%) from the reaction of complex (**1**) with *N*-bromosuccinimide as well as from several other reactions of (**1**) (see below); it had properties identical with those reported[7] and gave a satisfactory mass spectrum. Thus the allegedly different products obtained from (**1**) and assigned structures (**2**), (**4**), and (**6**) are, in fact, the same diester (**15**) presumably derived from (**1**) by oxidative removal of nickel with coupling of the cyclopentadienyl and norbornadienyl moieties followed by an intramolecular Diels–Alder reaction. Moreover, the products claimed to be (**3**), (**5**), and (**7**) are, in fact, their epimers (**2**), (**4**), and (**6**). The reactions of compound (**1**) with *m*-chloroperbenzoic acid, *N*-bromosuccinimide, and *N*-chlorosuccinimide are, contrary to the earlier claim, quite stereoselective but proceed in poor yield.



(**15**)



(**17**)



(**18**)

E = CO_2Me

We have found that reaction of (**1**) with lead tetra-acetate (CH_2Cl_2, 20 °C) also proceeds with retention of C-7 stereochemistry to give the *syn*-acetate (**11**) (37%) and (**15**) (6%). Likewise, with iodine in dichloromethane (−78 °C—20 °C) compound (**1**) gives the *syn*-iodide (**16**) (51%) and the diester (**15**) (28%). With bromine (CH_2Cl_2, −78 °C), however, the carbon–nickel bond is cleaved with predominant inversion of stereochemistry, a 1:2.6 mixture of the epimers (**4**) and (**5**) being formed (53% yield). This trend continues in the reaction of (**1**) with chlorine (CH_2Cl_2, −78 °C) which gave (**6**) and (**7**) (62% yield, ratio *ca.* 1:10). An increasingly important oxidation-induced S_N2 reaction,[8] competing with an oxidative addition–reductive elimination process at the metal[9] may explain these results. Alternatively, the product of apparent inversion at C-7 may arise by electrophilic attack at C-6 followed by migration of C-3 to C-5 and loss of the metal (**17**; arrows). In contrast to the reaction with bromine, reaction of compound (**1**) with phenyltrimethylammonium perbromide gives mainly (61%) the *syn*-bromide (**4**). 7-Halogeno-2,3-bis(methoxycarbonyl)norbornadienes are also available from cyclopentadienylthallium by reaction with *N*-bromo- or *N*-chloro-succinimide in dimethyl acetylenedicarboxylate.[10] This procedure gives mainly the 7-*anti*-compounds. These may also be available by the reaction of electrophiles with the complex (**18**).[11]

Experimental

M.p.s were determined with a Kofler hot-stage apparatus. Unless otherwise stated i.r. spectra of solids refer to Nujol mulls and i.r. spectra of oils to liquid films. ^{1}H N.m.r. spectra refer to solutions in deuteriochloroform measured with a Perkin-Elmer R32 or a JEOL FX90Q spectrometer. Low resolution mass spectra were obtained with a Kratos MS 25 instrument and accurate mass measurements were made using a Kratos MS 950 instrument. Where accurate mass measurement was used to establish molecular formulae, the purity of the sample was checked by t.l.c. in more than one solvent system as well as by n.m.r. measurements and for crystalline samples by crystallisation to constant m.p. Chromatography on silica refers to short-column chromatography over Kieselgel G (Merck).[12] Ether refers to diethyl ether and light petroleum to the fraction b.p. 60—80 °C.

syn- *and* anti-1,5-*Bis(methoxycarbonyl)quadricyclan*-3-*ol*.—Sodium borohydride (0.35 g, 9 mmol) was added to 1,5-bis(methoxycarbonyl)quadricyclan-3-one‡ (2.0 g, 9 mmol) in dry ethanol (60 ml) at −5 °C. The mixture was stirred for 25 min prior to dilution with sulphuric acid (0.2M; 40 ml) and was then allowed to warm to 20 °C. The aqueous layer was saturated with sodium chloride and extracted with dichloromethane. The combined extracts were washed with saturated aqueous sodium hydrogen carbonate, dried ($MgSO_4$), and evaporated. Chromatography on silica in benzene–ether (1:1) gave a mixture of epimeric alcohols (1.62 g, 80%). Crystallisation from ether gave syn-1,5-*bis(methoxycarbonyl)quadricyclan*-3-*ol* (0.58 g, 29%), m.p. 75—77.5 °C (from benzene–light petroleum) (Found: C, 58.9; H, 5.25. $C_{11}H_{12}O_5$ requires C, 58.9; H, 5.4%), $\nu_{max.}$ 3 450, 3 440, 1 725, and 1 690 cm^{-1}; δ 4.98 (1 H, br d, *J* 9 Hz, 3-H), 3.69 (6 H, s, 2 × CO_2Me), 2.94 (1 H, br d, *J* 9 Hz, exch. D_2O, OH), 2.47 (2 H, d, *J* 5 Hz, 6-H and 7-H), and 2.34 (2 H, d, *J* 5 Hz with further coupling, 2-H and 4-H); δ_C 170.0 (CO), 76.7 (C-3), 51.7 (Me), 40.3 (C-2 and C-4), 29.6 (C-1 and C-5), and 26.4 (C-6 and C-7); *m/z* 164, 163, 134, 133, 105, and 59 (10.8, 100.0, 3.9, 16.8, 8.2, and 3.8%). Chromatography of a portion 200 mg) of the mother liquors on silica (80 g) in dichloromethane–ether (4:1) gave first anti-1,5-*bis(methoxycarbonyl)quadricyclan*-3-*ol* (110 mg), m.p. 44—47 °C (from benzene–light petroleum) (Found: M^+, 224.069. $C_{11}H_{12}O_5$ requires *M*,

* All assignments of *syn-anti*-stereochemistry made herein are based on this long range coupling which was clearly observed using a Jeol FX90Q spectrometer and 8-fold enhanced digital resolution; the highly resolved multiplets observed in expanded spectra were appropriately simplified in double irradiation experiments.

† The decomposition of this norbornadienol with sodium hydrogen carbonate may explain the failure of the original authors to observe this product.

‡ Quadricyclane = tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane.

224.069), $\nu_{max.}$ 3 600, 3 315br, and 1 760 cm^{-1}; δ 5.02 (1 H, br m, 3-H), 3.67 (6 H, s, 2 × CO_2Me), 2.7 (2 H, d, *J* 5 Hz, 6-H and 7-H), 2.33 (2 H, d, *J* 5 Hz with further coupling, 2-H and 4-H), and 1.85 (1 H, br s, exch. D_2O, OH); *m/z* 194, 192, 164, 163, 134, and 105 (3.5, 5.7, 10.3, 100.0, 4.2, and 9.3%). Continued elution of the column gave a mixture of *syn*- and *anti*-isomers (50 mg), δ_C *syn*-isomer as above, *anti*-isomer 169.6 (CO), 76.0 (C-3), 51.7 (Me), 38.7 (C-2 and C-4), 28.5 (C-1 and C-5), and 27.1 (C-6 and C-7). Further elution of the column gave the pure *syn*-isomer (45 mg).

anti-3-*Acetoxy*-1,5-*bis*(*methoxycarbonyl*)*quadricyclane*.—A mixture of the foregoing *anti*-quadricyclanol (25 mg, 0.11 mmol), acetic anhydride (0.5 ml), and pyridine (20 mg) was stirred (14.5 h) and then quenched with crushed ice (10 g) and extracted into ether. The water-washed ether extract was dried ($MgSO_4$), evaporated, and the product chromatographed on silica (15 g) in benzene–ether (17:3) to give anti-3-*acetoxy*-1,5-*bis*(*methoxycarbonyl*)*quadricyclane* (22 mg, 75%) as an oil (Found: M^+, 266.078. $C_{13}H_{14}O_6$ requires *M*, 266.079); $\nu_{max.}$ 1 760 cm^{-1}; $\lambda_{max.}$(EtOH) 270 nm (ε 1 200); δ 5.65 (1 H, t, *J* 2 Hz, 3-H), 3.66 (6 H, s, 2 × CO_2Me), 2.69 (2 H, d, *J* 6 Hz, 6-H and 7-H), 2.46 (2 H, d, *J* 6 Hz with further coupling, 2-H and 4-H) and 2.10 (3 H, s, COMe); *m/z* 195, 164, 163, 77, and 43 (7.4, 10.2, 100.0, 6.8, and 43.8%).

anti-7-*Acetoxy*-2,3-*bis*(*methoxycarbonyl*)*norbornadiene*.—A mixture of 10% palladium-on-charcoal (20 mg), *anti*-3-acetoxy-1,5-bis(methoxycarbonyl)quadricyclane (20 mg), and ethyl acetate (5 ml) was stirred under reflux for 15 h. Evaporation of the filtered product and chromatography on silica (15 g) in benzene–ether (19:1) gave anti-7-*acetoxy*-2,3-*bis*(*methoxycarbonyl*)*norbornadiene* (17 mg, 85%), m.p. 84—85 °C (from ether–pentane) (Found: C, 58.75; H, 5.2. $C_{13}H_{14}O_6$ requires C, 58.65; H, 5.3%); $\nu_{max.}$ 1 740, 1 730, 1 710, and 1 630 cm^{-1}; $\lambda_{max.}$(EtOH) 227 and 268sh nm (ε 4 100 and 1 600); δ 6.72 (2 H, td, *J* 2 and *ca.* 0.6 Hz, 5-H and 6-H), 4.81 (1 H, m, 7-H), 4.02 (2 H, td, *J* 2 and 1.85 Hz, 1-H and 4-H), 3.80 (6 H, s, 2 × CO_2Me), and 1.99 (3 H, s, COMe); *m/z* 195, 164, 163, 133, 77, 44, and 43 (9.8, 9.1, 100.0, 7.4, 13.4, 12.0, and 50.5%).

anti-7-*Acetoxy*-2,3-*bis*(*methoxycarbonyl*)*norbornadiene*.—*anti*-1,5-Bis(methoxycarbonyl)quadricyclan-3-ol (9 mg), 10% palladium-on-charcoal (9 mg), and ethyl acetate (0.5 ml) were stirred at 20 °C (7 h). Evaporation of the filtered product and treatment with acetic anhydride (0.3 ml) and pyridine (20 mg) (12 h) gave, after aqueous work-up and chromatography on silica in benzene–ether (19:1), *anti*-7-acetoxy-2,3-bis(methoxycarbonyl)norbornadiene (4 mg, 38%) identical (^1H n.m.r. and t.l.c.) with the sample previously prepared. Chromatography also gave recovered starting material (4 mg, 38%).

syn-7-*Acetoxy*-2,3-*bis*(*methoxycarbonyl*)*norbornadiene*.—*syn*-1,5-Bis(methoxycarbonyl)quadricyclan-3-ol (40 mg) in deuteriochloroform (0.5 ml) was treated with palladium acetate (0.4 mg) in deuteriochloroform (0.5 ml) in an n.m.r. tube. After 27 h at 20 °C the ^1H n.m.r. spectrum was consistent with complete conversion into *syn*-2,3-bis(methoxycarbonyl)norbornadien-7-ol; δ 6.75 (2 H, t, *J* 2.5 Hz, 5-H and 6-H), 4.03 (1 H, m, 7-H), 3.85 (2 H, m, 1-H and 4-H, partly hidden), and 3.80 (6 H, s, 2 × OMe). The solution was evaporated and a portion of the product (17 mg) treated with acetic anhydride (0.5 ml) and pyridine (20 mg) at 20 °C (14 h). The product was diluted with ice-cold water (10 ml), extracted into ether, washed with water, and the ether layer dried ($MgSO_4$). Chromatography of the evaporated product on silica (8 g) in benzene–ether (49:1) gave syn-7-*acetoxy*-2,3-*bis*(*methoxycarbonyl*)*norbornadiene* (20 mg, 99%) as an oil (Found: M^+, 266.079. $C_{13}H_{14}O_6$ requires *M*, 266.079); $\nu_{max.}$ 1 735, 1 710, and 1 630 cm^{-1}; $\lambda_{max.}$ 230 and 267 nm (ε 4 700 and 3 700); δ 6.84 (2 H, dd, *J* 2 and 2.4 Hz, 5-H and 6-H), 4.68 (1 H, t, *J* 1.7 Hz, 7-H), 3.98 (2 H, ddd, *J* 2.5, 2.0, and 1.7 Hz, 1-H and 4-H), 3.81 (6 H, s, 2 × CO_2Me), and 2.01 (3 H, s, COMe); *m/z* 224, 164, 163, 133, and 77 (4.9, 10.3, 70.0, 4.5, and 16.6%).

Reactions of the Complex (**1**).—(*a*) *m*-Chloroperbenzoic acid (80%, 216 mg), the complex (**1**) (331 mg), and dichloromethane (5 ml) were stirred at 20 °C (2 days). After further addition of *m*-chloroperbenzoic acid (216 mg) reaction was complete in a few minutes. After dilution of the product with dichloromethane it was washed with aqueous sodium hydrogen sulphite, washed *once* with aqueous sodium hydrogen carbonate, dried ($MgSO_4$), and evaporated. The ^1H n.m.r. spectrum showed olefinic triplets at δ 6.73, 6.90, and 6.05 (ratio *ca.* 4:4:1) attributed to (**2**), (**14**), and (**15**) respectively. In view of the instability of (**2**) the total product was acetylated in acetic anhydride (2 ml) containing pyridine (3 drops) (16 h). Aqueous work-up and isolation in dichloromethane followed by chromatography on silica in benzene–ether (19:1) gave first an oily fraction not further examined, followed by the impure *m*-chlorobenzoate (**14**) (49 mg). Rechromatography of this product on silica (45 g) in benzene–ether (50:1) removed a slightly less polar impurity to give syn-7-(3-*chlorobenzoyloxy*)-2,3-*bis*(*methoxycarbonyl*)*norbornadiene* (**14**) (44 mg) m.p. 68—71 °C (from light petroleum) (Found: C, 60.15; H, 4.3; Cl, 9.9. $C_{18}H_{15}ClO_6$ requires C, 59.6; H, 4.1; Cl, 9.8%) (Found: M^+, 362.055 and 364.053. $C_{18}H_{15}{}^{35}ClO_6$ requires 362.056, $C_{18}H_{15}{}^{37}ClO_6$ requires 364.053); δ 3.81 (6 H, s, 2 × CO_2Me), 4.10 (2 H, dt, *J* 2.62 and 1.83 Hz, 1-H and 4-H), 4.93 (1 H, t, *J ca.* 1.83 Hz, 7-H), 6.89 (2 H, dd, *J* 2.62 and 1.83 Hz, 5-H and 6-H), and 7.3—7.8 (m, 4 H, ArH). Irradiation of 7-H (δ 4.93) left the signal of 5-H and 6-H (δ 6.89) unchanged; *m/z* 50, 77, 92, 111 (chlorophenyl cation), 139 (3-chlorophenyl cation), 163 (methylated phthalic anhydride cation), 192, and 344 (2.1, 5.6, 1.3, 19.7, 100, 14.2, 1.3, and 1.6%).

Continued elution of the column gave the compound (**15**) (7 mg), m.p. 59—61 °C (from light petroleum) (lit.,[7] m.p. 62—62.5 °C), δ 2.54 (2 H, m), 3.35 (4 H, m), 3.61 (6 H, s), 6.05 (4 H, t, *J ca.* 2 Hz); (Found: M^+, 272.105. $C_{16}H_{16}O_4$ requires *M*, 272.105); *m/z* 240, 213, 212, 208, 207, 181, 153, 152, 105, 91, 77, and 59 (12.3, 16.6, 3.6, 5.0, 4.7, 4.1, 10.6, 30.2, 15.1, 2.7, 6.7, 5.7, and 3.5%).

Continued elution of the column gave the *syn*-acetate (**11**) (24 mg) identical (^1H n.m.r.) with the sample prepared previously.

When oxidation of compound (**1**) was conducted in benzene or dichloromethane with 3-chloroperbenzoic acid (2 equiv.) added in one portion, the ^1H n.m.r. spectrum of the crude product indicated the same products in the same proportions. When the crude oxidation product in dichloromethane was washed repeatedly (4 ×) with saturated aqueous sodium hydrogen carbonate the ^1H n.m.r. spectrum of the product showed a reduction of the signal at δ 6.73 due to compound (**2**) and the appearance of a new signal at δ 7.0; the signals at δ 6.90 due to compound (**14**) and at δ 6.05 due to compound (**15**) remained unchanged.

(*b*) *N*-Bromosuccinimide (180 mg), the complex (**1**) (331 mg), and carbon tetrachloride (5 ml) were boiled under reflux (6 h) in the presence of a few crystals of azoisobutyronitrile. The product was cooled to 0—5 °C, filtered, and evaporated and the product chromatographed on silica in benzene–ether (19:1) to give first an unidentified product (20 mg) and then the bromo compound (**4**) (45 mg), m.p. 54—55 °C (from light petroleum) (Found: Br, 26.9. $C_{11}H_{11}BrO_4$ requires Br, 27.9%) (Found: M^+, 285.984 and 287.982. $C_{11}H_{11}{}^{79}BrO_4$ requires 285.984, $C_{11}H_{11}{}^{81}BrO_4$ requires 287.982); *m/z* 288, 286, 257, 255, 229, 227, 207, 179, 148, 133, 119, 105, 89, 77, and 63 (2.2, 2.4, 1.9, 1.9, 1.4, 1.5, 67.4, 4.3, 3.6, 4.3, 4.7, 7.7, 10.7, 6.9, and 7.7%); δ 3.83 (6 H, s), 4.10 (2 H, m, 1-H and 4-H), 4.37 (1 H, t, *J* 1.5 Hz, 7-H), and 6.9

(2 H, dd, *J* 2.56 and 2.0 Hz). The signal at δ 6.9 was unchanged upon irradiation at the position of 7-H (δ 4.37). Continued elution of the column gave compound (**15**) 27 mg) identical (^{1}H n.m.r.) with the sample previously obtained.

(*c*) *N*-Chlorosuccinimide (438 mg), the complex (**1**) (270 mg), carbon tetrachloride (12 ml), and a few crystals of azoisobutyronitrile were boiled under reflux (16 h). The cooled mixture was filtered, evaporated, and the residue chromatographed on silica in benzene–ether (19:1) to give syn-7-*chloro*-2,3-*bis*(*methoxycarbonyl*)*norbornadiene* (**6**) (37 mg) as an oil (Found: M^+, 242.035 and 244.032. $C_{11}H_{11}{}^{35}ClO_4$ requires *M*, 242.035, $C_{11}H_{11}{}^{37}ClO_4$ requires *M*, 244.032); $\nu_{max.}$ 1 630 and 1 720 br cm^{-1}; δ 3.84 (6 H, s), 4.05 (2 H, m, 1-H and 4-H), 4.26 (1 H, t, *J ca.* 1 Hz, 7-H), and 6.91 (2 H, dd, *J ca.* 2.5 and 2.0 Hz, 5-H and 6-H); *m/z* 244, 242, 211, 207, 183, 163, 152, 125, 105, 89, 77, and 59 (6.6, 18.4, 28.5, 100, 86.3, 25.5, 26.0, 18.8, 19.7, 32.5, 21.7, and 21.2%). Continued elution of the column gave the compound (**15**) (10 mg) in impure form (^{1}H n.m.r. spectrum).

(*d*) Lead tetra-acetate (575 mg) was added to a stirred solution of the complex (**1**) (165 mg) in dichloromethane (5 ml) and stirring continued at 20 °C (90 min). After the addition of glycerol and continued stirring (10 min) the mixture was diluted with dichloromethane and washed with water (3 ×). Evaporation of the dried ($MgSO_4$) organic layer and chromatography of the residue on silica in benzene–ether (39:1) gave after an unidentified product (17 mg), *syn*-7-acetoxy-2,3-bis(methoxycarbonyl)norbornadiene (**11**) (49 mg) identical (^{1}H n.m.r.) with a sample prepared earlier. Continued elution of the column gave compound (**15**) (8 mg) identical (^{1}H n.m.r.) with the samples isolated earlier.

(*e*) Iodine (160 mg), benzene (4 ml), and the complex (**1**) (90 mg) were boiled gently (1 min). Chromatography of the product on silica in benzene–ether (19:1) gave first syn-7-*iodo*-2,3-*bis*(*methoxycarbonyl*)*norbornadiene* (46 mg), m.p. 73—74 °C (from light petroleum) (Found: C, 39.75; H, 3.35; I, 37.8. $C_{11}H_{11}IO_4$ requires C, 39.5; H, 3.29; I, 38.0%); $\nu_{max.}$ 1 705, 1 725, and 1 630 cm^{-1}; δ 3.83 (6 H, s), 4.15 (2 H, dt, *J* 2.7 and 1.5 Hz, 1-H and 4-H), 4.48 (1 H, t, *J* 1.5 Hz, 7-H), and 6.87 (2 H, dd, *J* 2.7 and 2.30 Hz). Irradiation of the signal due to 7-H (4.48 δ) failed to simplify the resonance of 5-H and 6-H (δ 6.87); *m/z* 303, 207, 179, 161, 147, 105, 89, 77, 63, and 51 (0.5, 18.4, 0.8, 0.4, 0.9, 2.4, 2.9, 2.3, 2.3, and 0.9%) (Found: M^+, 333.970. $C_{11}H_{11}IO_4$ requires *M*, 333.970).

Continued elution of the column gave compound (**15**) (21 mg). When the reactants were mixed in dichloromethane at −78 °C and the mixture allowed to warm to 20 °C (2 h) an identical mixture of products was obtained.

(*f*) Trimethylphenylammonium perbromide (205 mg) was added to the complex (**1**) (90 mg) in tetrahydrofuran (4 ml) at 20 °C. The characteristic colour of the complex was immediately discharged. The mixture was diluted with ether, washed with saturated aqueous sodium hydrogen carbonate, washed with water, dried ($MgSO_4$), and evaporated. Chromatography of the residue on silica in benzene–ether (19:1) gave the *syn*-bromide (**4**) (48 mg) identical with the previously obtained material (^{1}H n.m.r.).

(*g*) Chlorine (36 mg) in carbon tetrachloride (0.36 ml) was added to the complex (**1**) (83 mg) in dichloromethane (4 ml) at −78 °C. After warming to 20 °C the mixture was evaporated and the residue chromatographed on silica in benzene–ether (19:1) to give first a mixture of the *syn*- and *anti*-7-chloro-2,3-bis(methoxycarbonyl)norbornadienes (34 mg), ratio *ca.* 1:10 (^{1}H n.m.r.). Crystallisation of the mixture from light petroleum gave pure anti-7-*chloro*-2,3-*bis*(*methoxycarbonyl*)*norbornadiene*, m.p. 57—58 °C (Found: C, 54.7; H, 4.3. $C_{11}H_{11}ClO_4$ requires C, 54.4; H, 4.5%) (Found: M^+, 242.034, 244.032. $C_{11}H_{11}{}^{35}ClO_4$ requires *M*, 242.032. $C_{11}H_{11}{}^{37}ClO_4$ requires *M*, 244.032); *m/z* 244, 242, 207, 185, 183, 152, 124, 105, 89, 77, and 59 (8.4, 27.3, 100, 32.7, 94.9, 44.0, 20.1, 31.5, 63.8, 44.5, and 57.5%); δ 3.80 (6 H, s), 4.04 (2 H, q, *J* 1.8 Hz, 1-H, and 4-H), 4.43 (1 H, br, 7-H), and 6.79 (2 H, td, *J* 1.8 and 0.5 Hz, 5-H and 6-H). Irradiation at the resonance frequency of 7-H reduced the signal due to 5-H and 6-H to a triplet. Further elution of the column gave the complex (**1**) (7 mg).

(*h*) Bromine (87 mg) in dichloromethane (2 ml) was added to the complex (**1**) (90 mg) in dichloromethane (3 ml) at −78 °C. After warming to 20 °C the mixture was evaporated and chromatographed on silica in benzene–ether (19:1) to give a mixture of *syn*- and *anti*-7-bromo-2,3-bis(methoxycarbonyl)-norbornadienes (38 mg), ratio *ca.* 1:2.6. The ^{1}H n.m.r. spectrum of the mixture showed the following signals [in addition to those previously described for the *syn*-isomer (**4**)] δ 3.80 (6 H, s), 4.10 (2 H, m, 1-H and 4-H), 4.57 (1 H, tt, *J* 1.55 and 0.68 Hz, 7-H), 6.82 (2 H, td, *J* 1.63 and 0.63 Hz, 5-H and 6-H); irradiation at the resonance position of 7-H (δ 4.57) reduced the resonance of 5-H and 6-H to a triplet. The mass spectrum of the mixture was very similar to that previously described for the *syn*-isomer (**4**).

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