The Reaction between Bis(trimethylsilyl)cyclopentadiene and Dichloroketen, and the Diels–Alder Reactions between *N*-Phenylmaleimide and Two Silylated Methylcyclopentadienes †

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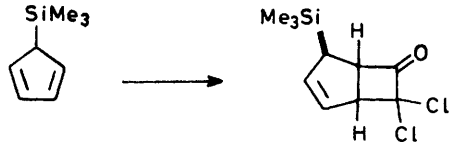
Bis(trimethylsilyl)cyclopentadiene reacts with dichloroketen to give only the adduct (7) derived from the 2,5-disilylated isomer (5). Methyl(trimethylsilyl)cyclopentadiene (18) and trimethylsilylmethylcyclopentadiene (21) give Diels–Alder adducts (19) and (20) and (22) and (23) in which the regioselectivity is unaffected by the presence of the silyl group. Epoxidation of the adduct (22) and acid-catalysed opening of the epoxide lead to formation of the *exo*-methylenenorbornane (26) in a rearrangement controlled by the presence of the silyl group.

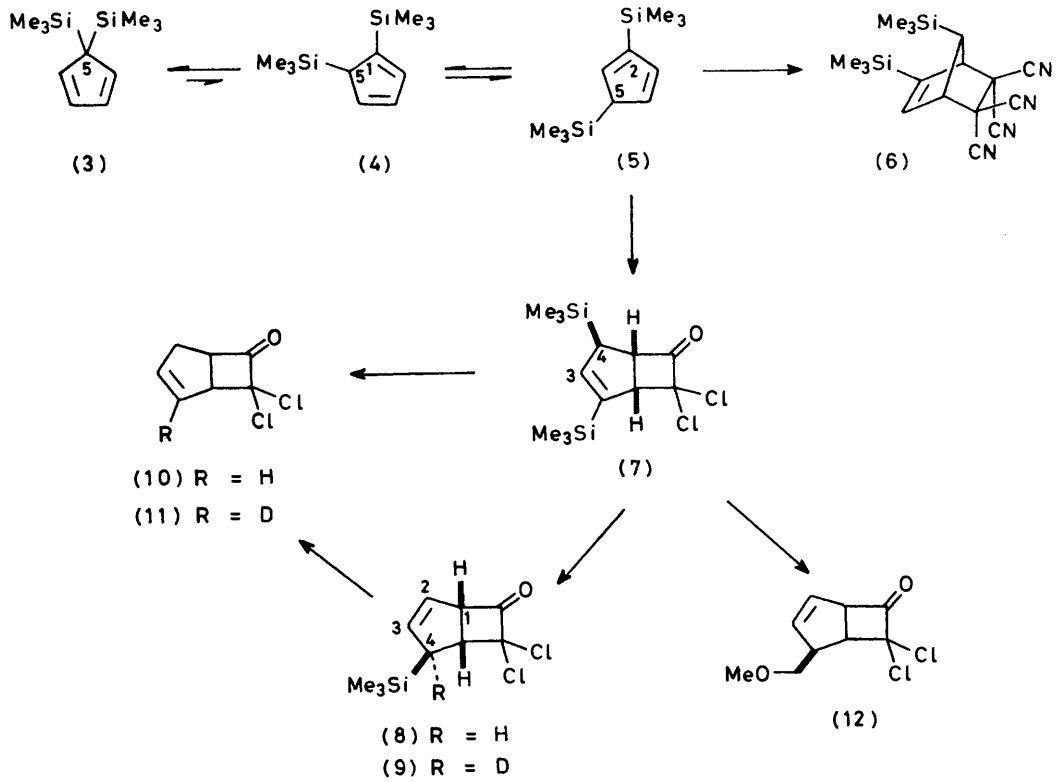
We reported earlier [1] that trimethylsilylcyclopentadiene (1) and dichloroketen react to give the allylsilane (2). We [2] and others [3,4] have reported that Diels–Alder



(1) (2)

reactions of reactive dienophiles with the same diene give 7-silylated norbornenes, but that less reactive dienophiles give more or less of the 2- (and 3-) substituted norbornenes as well. The 2-silylated diene is evidently the most reactive isomer in Diels–Alder reactions but the 5-silylated diene (1), which is the major isomer at equilibrium,[3] often reacts before it rearranges. We were interested in the possibility that a silyl group might modify the reactions of substituted cyclopentadienes, and report here some dichloroketen and Diels–Alder reactions of the three silylated cyclopentadienes (3), (18), and (21).

Bis(trimethylsilyl)cyclopentadiene exists almost exclusively as the 5,5-substituted isomer [5,6] (3), but is known to react in Diels–Alder reactions, even with the most reactive dienophiles, as its 2,5-isomer (5), giving adducts such as (6). There is no product from the 1,5-isomer (4), even though it is almost certainly present as an intermediate between (3) and (5),[7] and even though



(3) (4) (5) (6)

(10) R = H
(11) R = D

(7)

(8) R = H
(9) R = D

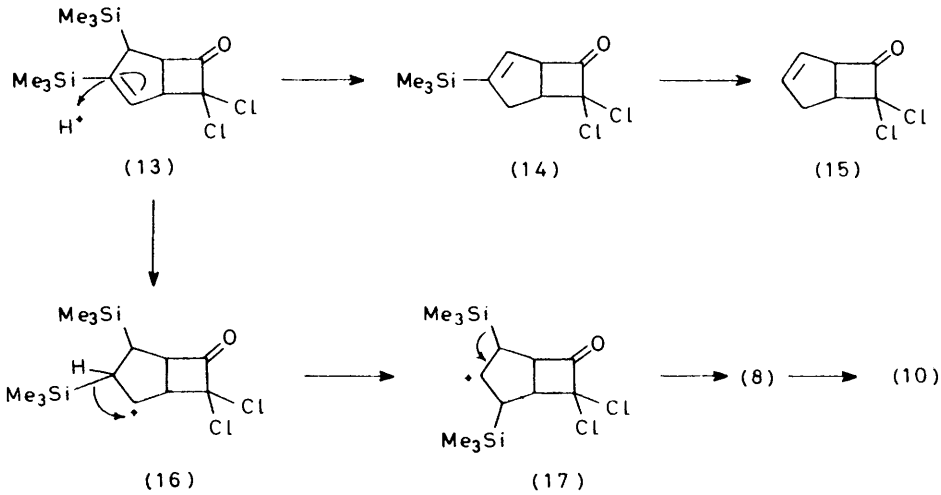
(12)

equilibrating mixtures of 1- and 2-mono-substituted cyclopentadienes usually give Diels–Alder products from both in nearly equal amounts.[8–10] We have now in-

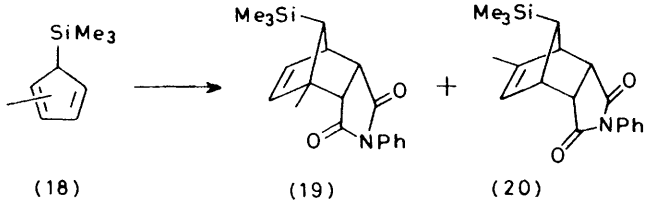
† There are no reprints of this paper.

vestigated the reaction between bis(trimethylsilyl)-cyclopentadiene (3) and dichloroketen, and find that only the adduct (7) is formed, even although equilibrating mixtures of 1- and 2-monosubstituted cyclopentadienes usually [11] give more of the product derived from the 1-substituted isomer. It is not, of course, clear whether the dichloroketen reaction and the Diels–Alder reactions are the result of a low concentration or a low reactivity of the 1,5-disilylcyclopentadiene (4).

The proof of structure for the adduct (7) was not trivial, since the ^{1}H n.m.r. spectrum, although showing only one olefinic hydrogen, was ambiguous. The coupling between the protons on C-4 and C-3, although not unambiguously identifiable in the narrow multiplets observed, was not more than *ca.* 3 Hz, a low enough value to be allylic coupling between the protons on C-4 and C-2 in the alternative structure (13). The first telling piece of evidence was that complete protodesilylation [12] using sulphuric acid in methanol gave the well known [13] alkene (10). This was the expected, though not inevitable, product from successive protodesilylations of the allylsilanes (7) and (8). We expected that the adduct with the alternative structure (13) would have given a different, and also known,[1] alkene (15), by successive protodesilylations of the allyl and vinyl-silane functions (13) ⟶ (14) ⟶ (15), either in this or in reverse order. However, there is a plausible mechanism by which the adduct (13) could have given the same final product (10). This mechanism, (13) ⟶ (16) ⟶ (17) ⟶ (8) ⟶ (10), involves a 1,2-shift of a silyl group, which is both precedented [14] and reasonable, since overcrowding in (13) would be relieved when the silyl groups move apart. Furthermore, methoxymethylation of the adduct gave, in poor yield (26%), as the only identifiable product, the known [1] cyclopentene (12), which is more simply derived from an adduct of structure (13). Again, there are reasonable mechanisms for the formation of this derivative from the adduct of structure (7), but they are more roundabout. By careful protodesilylation of the adduct (7) using toluene-*p*-sulphonic acid in benzene we were able to isolate the allylsilane (8) in low yield (18%). This intermediate is on the pathway between either structure (7) or (13) and the final product (10) of protodesilylation, but proof of structure was now possible using deuteriated acid. This gave the allylsilane (9) (10%) in which the ^{1}H n.m.r. signal of the hydrogen on C-4 was essentially absent, and the intensity of the signal from the hydrogen on C-3 was unaffected. Furthermore, the signal from the hydrogen on C-5 changed from a double doublet to a doublet. The alternative adduct (13), following the pathway (13) ⟶ (16) ⟶ (17) ⟶ (8), would have placed the deuterium atom on C-3. Protodesilylation of the allylsilane (9) gave the cyclopentene (11), in which one of the olefinic hydrogen signals was missing, thus enabling us to assign the olefinic signals in this compound; the upfield multiplet is from the proton on C-2, and the downfield multiplet is from the proton on C-3. The only puzzle in these reactions is the stereochemistry of the allylsilane (8) and the methoxymethylcyclopentene (12), in both of which the substituent on the cyclopentene ring is *exo*- implying, at some stage, *endo*-protonation.

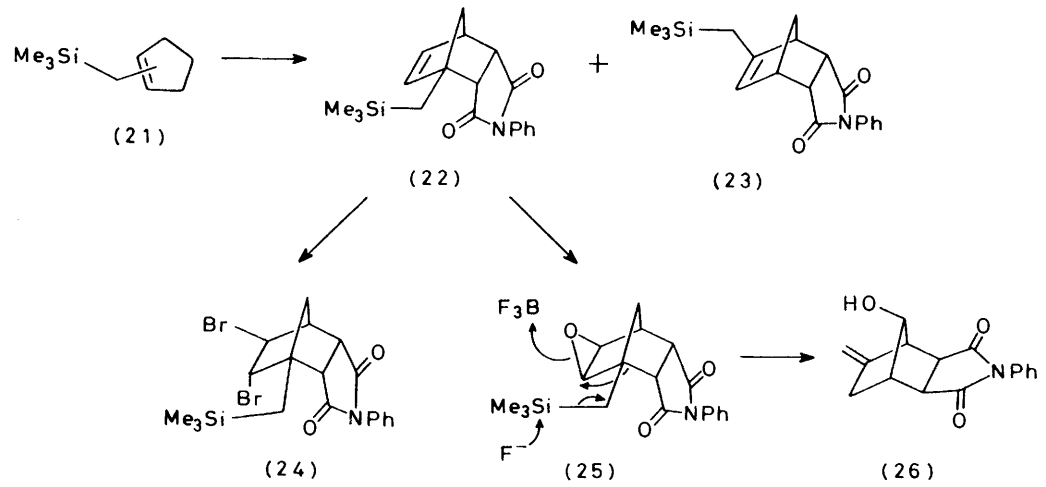


The second disubstituted cyclopentadiene we looked at was the mixture of methyltrimethylsilylcyclopentadienes (18) obtained by methylating the anion of trimethylsilylcyclopentadiene. Without the silyl group, the methylcyclopentadienes are known [8,10] to react in Diels–Alder reactions to give 1- and 2(or 3)-methylnorbornenes in comparable anounts (although Lewis-acid catalysis [10] can change the ratio substantially). Since bistrimethylsilylcyclopentadiene showed such a reluctance to react in any other form than as the 2,5-isomer



(5), there was a real possibility that methyltrimethylsilylcyclopentadiene (18) would react exclusively as the 2-methyl-5-silyl isomer, and give, therefore, a single adduct. The extra trimethylsilyl group, having controlled the Diels–Alder reaction, might then be disposed of, or used, at a later stage in a synthesis.

In the event, the silyl group had little effect; the dienes (18) reacted with *N*-phenylmaleimide to give the adducts (19) and (20) in a 9 : 11 ratio, identical to that which we find for methylcyclopentadiene itself. Lewis-acid catalysis had little effect on the ratio.



Our third cyclopentadiene was trimethylsilylmethylcyclopentadiene (21). As expected, this too gave a mixture of adducts (22) and (23) in a 9 : 11 ratio. The former had some potential for a silicon-controlled carbonium ion rearrangement,[2] and we were able to demonstrate this with the reaction of its epoxide (25) with acid, which gave an *exo*-methylenenorbornane (26). A somewhat similar reaction is known in the tin series.[15] A curious reaction of the adduct (22) deserves some final comment. With bromine it gave a single adduct (24) (98%), in which the epibromonium ion intermediate has opened with the incoming bromine appearing on the more hindered side, adjacent to the bridgehead trimethylsilylmethyl group. Although we saw no rearrangement in this reaction (nor could we induce rearrangement in the product), the regioselectivity in the opening of the epibromonium ion may reflect the incipient development of more cationic character at C-2 than at C-3. Alternatively, it is tempting to invoke a hypervalent-silicon intermediate, in which the incoming bromide ion is delivered intramolecularly from the nearby silicon atom.

EXPERIMENTAL

7,7-Dichloro-2,4-exo-bis(trimethylsilyl)bicyclo[3.2.0]hept-2-en-6-one (7).—A solution of triethylamine (2.7 g, 27 mmol) in dry hexane (30 ml) was added dropwise over 2 h to a stirred mixture of 5,5-bis(trimethylsilyl)cyclopentadiene (25) [6] (3.4 g, 16 mmol) and dichloroacetyl chloride (4.0 g, 27 mmol) in dry hexane (100 ml) with cooling in ice under nitrogen. After stirring at 0—5 °C for a further 12 h, the mixture was poured into water (200 ml). The hexane layer was separated, washed with water, dried ($MgSO_4$), and evaporated. The solid residue was crystallised from aqueous methanol to give the *adduct* as needles (3.7 g, 72%), m.p. 55 °C (Found: C, 48.3; H, 6.9; Cl, 21.8. $C_{13}H_{22}Cl_2OSi_2$ requires C, 48.6; H, 6.9; Cl, 22.1%), $\nu_{max.}$ (KBr) 1 800s and 1 565m cm^{-1}, δ (CCl_4) 0.10 and 0.27 (each 9 H, s, $SiMe_3$), 2.63 (1 H, m, $W_{\frac{1}{2}}$ 6 Hz, Me_3SiCH), 4.10 (2 H, dm, $W_{\frac{1}{2}}$ 5 Hz, bridgehead H's) and 6.22 (1 H, dm, $W_{\frac{1}{2}}$ 4 Hz, C=CH).

Reaction of Methoxymethyl Chloride with 7,7-Dichloro-2,4-exo-bis(trimethylsilyl)bicyclo[3.2.0]hept-2-en-6-one (7).—Methoxymethyl chloride (0.1 ml) and the bis-silane (7) (0.311 g) were dissolved in dry dichloromethane (2 ml), and stannic chloride (1 ml) was added with stirring under nitrogen. The mixture was kept at room temperature for 3 days. After the usual work-up the ketone (12) was isolated as an oil (0.057 g, 26%), identical with authentic material [1] (i.r., n.m.r., t.l.c.).

Reaction of an Excess of Protic Acid with 7,7-Dichloro-2,4-exo-bis(trimethylsilyl)bicyclo[3.2.0]hept-2-en-6-one (7).—The bis-silane (7) (0.311 g) in methanol (5 ml) and concentrated sulphuric acid (5 ml) was kept at room temperature for 18 h. It was poured into water (150 ml), extracted with dichloromethane (4 × 20 ml), dried ($MgSO_4$), and evaporated *in vacuo*. The resulting oil was purified by preparative t.l.c. (CH_2Cl_2 on silica) to give the known [13] 7,7-dichlorobicyclo[3.2.0]hept-2-en-6-one (10) as an oil (0.064 g, 37%).

6,6-Dichloro-4-exo-trimethylsilylbicyclo[3.2.0]hept-2-en-7-one (8).—The water of crystallisation of toluene-*p*-sulphonic acid monohydrate (0.114 6 g) was removed by azeotropic distillation with dry benzene (15 ml) until 5 ml of solvent remained. The bis-silane (7) (0.2 g) was added and the mixture heated under reflux with stirring for 120 h. It was taken up in dichloromethane (25 ml), filtered, washed with saturated sodium hydrogencarbonate (25 ml) and water (2 × 25 ml), dried ($MgSO_4$), and evaporated *in vacuo*. The resulting oil was purified by t.l.c. (hexane–benzene, 1 : 1 v/v, on silica) to give the *allylsilane* (8) as an oil (0.028 g, 18.5%) (R_F 0.4), $\nu_{max.}$ (CCl_4) 1 805 (4-membered-ring C=O), 1 250 (SiMe) cm^{-1}, δ (CCl_4) 5.85 and 5.50 (each 1 H, m, =C–H), 4.47 (1 H, dm, *J* 8 Hz, CH–C=O), 3.26 (1 H, dd, *J* 8 Hz and 1.8 Hz, $CHCCl_2$), 2.64 (1 H, dm, *J* 1.8 Hz, Me_3SiCH), and 0.4 (9 H, s, Me_3Si) (Found: M^+, 250.016 0. $C_{10}H_{14}O$-

$^{35}Cl^{37}ClSi$ requires *M*, 250.016 0. Found: M^+, 248.020 4. $C_{10}H_{14}O^{35}Cl_2Si$ requires *M*, 248.019 0) *m/z* 248 (21.5%), 220 (9, *M* − CO), 213 (10.7, *M* − Cl), and 73 (100, Me_3Si^+).

6,6-*Dichloro*-4-exo-*trimethylsilyl*[4-endo-^{2}H]*bicyclo*[3.2.0]-*hept*-2-*en*-7-*one* (9).—The water of crystallisation of toluene-*p*-sulphonic acid monohydrate (0.28 g) was removed by azeotropic distillation with dry cyclohexane. Deuterium oxide (1 g) was added, the mixture was stirred for 5 min, and the deuterium oxide was removed by azeotropic distillation with dry cyclohexane. Deuterium oxide (1 g) was again added and the mixture was stirred and azeotroped until 10 ml of solvent remained. The bis-silane (7) (0.642 g) was added to this suspension and the mixture was heated under reflux for 1 week. The mixture was worked up as before to give the *deuterioallylsilane* (9) as an oil (0.052 g, 10.5%), identical with the sample above, except that the ^{1}H n.m.r. signal at δ 2.64 was greatly reduced in intensity, the signal at δ 3.26 had collapsed to a doublet (*J* 8 Hz), and the molecular ion was now at *m/z* 249.

7,7-*Dichloro*[2-^{2}H]*bicyclo*[3.2.0]*hept*-2-*en*-6-*one* (11).—A solution of the deuterioallylsilane (9) (0.030 2 g) in methanol–sulphuric acid (1 : 1 v/v) (6 ml) was kept at room temperature for 24 h. It was poured into water (150 ml), extracted with dichloromethane (4 × 20 ml), dried ($MgSO_4$), and evaporated *in vacuo* to give the crude *ketone* (11), identical with authentic non-deuteriated material. The ^{1}H n.m.r. signal at δ 5.78 (the higher-field olefinic signal) was much reduced in intensity.

Methyl(*trimethylsilyl*)*cyclopentadiene* (18).—5-Trimethylsilylcyclopenta-1,3-diene [16] (1.38 g) in dry tetrahydrofuran (THF) (4 ml) was gradually added to a suspension of sodium hydride (0.24 g) in dry THF (15 ml) with stirring at room temperature under nitrogen. The mixture was warmed to initiate the reaction, and then kept at room temperature for 1 h. Methyl iodide (0.66 ml) was added dropwise and the mixture was kept at room temperature for 1 h. It was poured into water (50 ml), extracted with ether (2 × 25 ml), dried ($MgSO_4$), and evaporated *in vacuo*. The resulting oil was distilled (bulb-to-bulb) to give the dienes [17] (10.7 g, 70.5%) δ (CCl_4) 6.40—5.90 (3 H, m, olefinic), 3.30—2.70 (1 H, m, Me_3SiCH), 2.03 and 1.97 (3 H, s, Me) and −0.02 and −0.04 (9 H, s, Me_3Si) (Found: M^+, 152.102 1. $C_9H_{16}Si$ requires *M*, 152.102 1), *m/z* 152 (13%), 137 (5, *M* − Me), and 73 (100, Me_3Si).

Reaction of Methyl(*trimethylsilyl*)*cyclopentadiene* (18) *with* N-*Phenylmaleimide*.—The diene (0.152 g) and *N*-phenylmaleimide (0.173 g) were kept in ether (3 ml) at room temperature for 1 h. The ether was evaporated off *in vacuo* to give a mixture of mainly 1- and 5-methyl-7-trimethylsilyl-substituted norborn-5-enes [9 : 11 respectively (n.m.r.)]; δ ($CDCl_3$) [1-methyl isomer (19)] 7.50—6.92 (5 H, m, Ph), 6.29 (1 H, dd, *J* 6 and 2 Hz, 5-H), 5.95 (1 H, d, *J* 6 Hz, 6-H), 3.55—2.97 (3 H, m, bridgehead + CH–C=O), 1.63 (3 H, s, MeC), 1.20 (1 H, m, Me_3SiCH), and −0.03 (9 H, s, Me_3Si); δ ($CDCl_3$) [5-methyl isomer (20)] 7.50—6.92 (5 H, m, Ph), 5.67 (1 H, m, =CH), 3.55—2.97 (4 H, m, bridgehead + CH–C=O), 1.77 (3 H, d, *J* 1.8 Hz, MeC), 1.20 (1 H, m, Me_3SiCH), and −0.03 (9 H, s, Me_3Si) (For isomeric mixture: Found: M^+, 325.149 3. $C_{19}H_{23}NO_2Si$ requires *M*, 325.149 8).

Reaction of Methylcyclopentadiene with N-*Phenylmaleimide*.—*N*-Phenylmaleimide (1.73 g) and methylcyclopentadiene (1.0 g) were kept at room temperature in ether (12 ml) for 0.5 h. The 1- and 2-methylnorbornenes were present in the ratio 9 : 11, respectively (n.m.r.). Both these adducts are known,[9] but had been prepared before separately from isolated 1- and 2-methylcyclopentadienes.

Trimethylsilylmethylcyclopentadiene (21).—Cyclopentadiene (1.32 g) in THF (5 ml) was added to sodium hydride (0.24 g) in THF (10 ml) at 0 °C under nitrogen and the mixture kept at 0 °C for 0.5 h. Trimethylsilylmethyl iodide (2.14 g) in dry THF (5 ml) was added dropwise and the mixture was heated under reflux for 1 h. Aqueous work-up and distillation (bulb-to-bulb; 75 °C at 15 mmHg) gave a mixture of the isomeric 1- and 2-substituted *dienes* (21) as an oil (0.905 g, 60%) $\nu_{max.}$ (liquid film) 3 060 (=C–H), 1 640 and 1 610 (conjugated C=C), and 1 252 ($SiMe_3$) cm^{-1}, δ (CCl_4) 6.80—6.00 (3 H, m, =CH), 3.20 and 3.05 (2 H, m, $=CCH_2$), 2.20 and 2.12 (2 H, each d, *J* allylic 1.5 Hz, Me_3Si-CH_2), and 0.04 and 0.03 (9 H, each s, Me_3Si) (Found: M^+, 152.102 8. $C_9H_{16}Si$ requires *M*, 152.102 0), *m/z* 152 (45.5%), 137 (3.6, *M* − Me), and 73 (100, $^+SiMe_3$).

Reaction of the Diene (21) *with* N-*Phenylmaleimide*.—The diene (21) (0.152 g) in ether (2 ml) was added to *N*-phenylmaleimide (0.173 g) in ether (3 ml) and the mixture was kept at room temperature for 24 h. Evaporation *in vacuo* at room temperature gave quantitatively the isomeric adducts (22) and (23) which were separated by chromatography (the best solvent system was di-isopropyl ether–methanol–acetic acid, 95 : 4 : 1 v/v). N-*Phenyl*-1-*trimethylsilylmethylbicyclo*[2.2.1]*hept*-5-*ene*-2,3-endo-*dicarboximide* (22) gave plates, m.p. 139—140 °C (from hexane) (Found: C, 69.9; H, 7.13; N, 4.1. $C_{19}H_{23}NO_2Si$ requires C, 70.2; H, 7.07; N, 4.3%), $\nu_{max.}$ ($CHCl_3$) 1 770 and 1 710 (–CO–N–CO–) and 1 250 cm^{-1} ($SiMe_3$), δ ($CDCl_3$) 6.20 (5 H, m, Ph), 6.19 (1 H, dd, *J* 6 and 2 Hz, 5-H), 6.03 (1 H, d, *J* 6 Hz, 6-H), 3.49 (2 H, m, HCC=O), 3.10 (1 H, d, *J* 5 Hz, bridgehead H), 1.78 (1 H, d, *J* 15 Hz, $Me_3SiCH_AH_X$), 1.74 (1 H, d, *J* 8 Hz, 7-H_{anti}), 1.58 (1 H, d, *J* 8 Hz, 7-H_{syn}), 1.26 (1 H, d, *J* 15 Hz, $Me_3SiCH_AH_X$), and 0.14 (9 H, s, Me_3Si), *m/z* 310 (8%, *M* − Me), and 73 (100, Me_3Si^+). N-*Phenyl*-5-*trimethylsilylmethylbicyclo*[2.2.1]*hept*-5-ene-2,3-endo-*dicarboximide* (23) gave plates, m.p. 126—127 °C (from hexane) (Found: C, 70.2; H, 7.13; N, 4.40. $C_{19}H_{23}NO_2Si$ requires C, 70.2; H, 7.07; N, 4.3%), $\nu_{max.}$ ($CHCl_3$) 1 780 and 1 710 (–CO–N–CO–) and 1 250 cm^{-1} ($SiMe_3$), δ ($CDCl_3$) 7.20 (5 H, m, Ph), 5.61 (1 H, m, =CH), 3.47 (3 H, m, H–C–C=O, and 1 bridgehead H), 3.27 (1 H, m, remaining bridgehead H), 7.94—7.46 (4 H, m, Me_3SiCH_2 and 7-H_2), and 0.10 (9 H, s, $SiMe_3$), *m/z* 325 (4.5%), 310 (2.5, *M* − Me), and 73 (100, Me_3Si^+).

5-exo,6-endo-*Dibromo*-N-*phenyl*-1-*trimethylsilylmethylbicyclo*[3.2.1]*heptane*-2,3-endo-*dicarboximide* (24).—Bromine (0.025 g) in carbon tetrachloride (0.2 ml) was added to a stirred solution of the 1-trimethylsilylmethylated norbornene (22) (0.05 g) in carbon tetrachloride (1 ml) at room temperature and the mixture was kept for 24 h. The resulting precipitate was taken up into dichloromethane (25 ml), washed with water (25 ml), sodium thiosulphate solution (25 ml), and water (25 ml), dried ($MgSO_4$), and evaporated *in vacuo* to give the *dibromide* (24) (0.073 g, 98%) as plates, m.p. 153—154 °C (from $CHCl_3$–hexane) (Found: C, 46.7; H, 4.85; N, 2.7; Br, 32.7. $C_{19}H_{23}NBr_2O_2Si$ requires C, 47.0; H, 4.75; N, 2.2; Br, 32.9%), $\nu_{max.}$ ($CHCl_3$) 1 775 and 1 715 (OCNCO) and 1 250 cm^{-1} ($SiMe_3$) δ ($CDCl_3$) 7.37 (5 H, m, Ph), 4.45 (2 H, m, H-CBr), 3.50 (1 H, d, *J* 8 Hz, 2-H), 3.40 (1 H, dd, *J* 8 and 4 Hz, 3-H 3.21 (1 H, dt, *J* 4 and 1.8 Hz, bridgehead H), 1.39 (1 H, dd, *J* 11 and 1.8 Hz, 7-H *syn* to Br), 1.79 (1 H, ddd, *J* 11, 1.8, and 1 Hz, 7-H *anti* to Br), 1.61 (1 H, d, J_{AB} 14 Hz, $Me_3Si\ CH_AH_B$), 1.43 (1 H, d, J_{AB} 14 Hz, $Me_3SiCH_AH_B$), and 0.22 (9 H, s, $SiMe_3$), *m/z* 468

(19.2%, M − Me), 404 (100, M − Br), and 73 (61.5, Me_3Si^+).

5,6-exo-*Epoxy*-N-*phenyl*-1-*trimethylsilylmethylbicyclo*-[3.2.1]*heptane*-2,3-endo-*dicarboximide* (25).—3-Chloroperbenzoic acid (0.105 g of 85% pure material) was added to the 1-trimethylsilylmethylated norbornene (22) (0.15 g) and disodium hydrogen phosphate (0.225 g) in dichloromethane (5 ml) under nitrogen and the mixture was kept at room temperature for 1 week. It was poured into saturated sodium hydrogen carbonate solution (25 ml) and the mixture was extracted with dichloromethane (25 ml). The extracts were washed with saturated sodium hydrogencarbonate solution (25 ml) and water (25 ml), dried (Na_2SO_4), and evaporated *in vacuo* to give the *epoxide* (25) (0.137 g, 87%) as needles, m.p. 179—180 °C (from $CHCl_3$–hexane) (Found: C, 66.9; H, 6.81; N, 4.1. $C_{19}H_{23}NO_3Si$ requires C, 66.9; H, 6.75; N, 4.1%), $\nu_{max.}$ ($CHCl_3$) 1 775 and 1 710 (OCNCO) and 1 250 cm^{-1} ($SiMe_3$), δ ($CDCl_3$) 7.36 (5 H, m, Ph), 3.49 (1 H, d, J_{AB} 5 Hz, H_A–C–O), 3.40 (1 H, d, J_{AB} 5 Hz, H_B–C–O), 3.10 (3 H, m, CH–C=O + bridgehead H), 1.77 (1 H, dm, J 10 Hz, 7-H), 1.62 (1 H, d, J 15 Hz, $Me_3SiCH_AH_B$), 1.16 (1 H, d, J 15 Hz, $Me_3SiCH_AH_B$), 1.10 (1 H, dm, J 10 Hz, 7-H), and 0.18 (9 H, s, Me_3Si), *m/z* 341 (37.7%), 326 (42.9, M − Me), and 73 (100, Me_3Si).

7-syn-*Hydroxy*-5-exo-*methylene*-N-*phenylbicyclo*[3.2.1]-*heptane*-2,3-*dicarboximide* (26).—Boron trifluoride–ether (0.2 ml) was added to a stirred solution of the epoxide (25) (0.60 g) under nitrogen in dichloromethane (3 ml), and the mixture was heated under reflux for 24 h and poured into water (50 ml). The mixture was extracted with dichloromethane (25 ml) and the extracts were washed with saturated sodium hydrogen carbonate solution (50 ml) and water (50 ml), dried ($MgSO_4$), and evaporated *in vacuo*. The n.m.r. spectrum of the crude product indicated that the *methylene-norbornene* (26) had been formed in approximately 60% yield. The crude mixture was purified by t.l.c. (hexane–acetone 1 : 1 v/v) (with poor recovery), $\nu_{max.}$ ($CHCl_3$) 3 400 (–OH) 1 780 and 1 710 cm^{-1} (OCNCO) δ ($CDCl_3$), 7.30 (5 H, m, Ph), 5.27 and 5.08 (each 1 H, br s, $=CH_2$), 4.10 (1 H, s, O–CH), 3.47 (1 H, s, OH), 3.09—2.61 (4 H, m, bridgehead H + HCC=O), and 1.60 (2 H, m, $=CCH_2$) (Found: M^+, 269.105 0. $C_{16}H_{15}NO_3$ requires M, 269.105 2), *m/z* 269 (100%) and 241 (11, M − CO).

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