Tetrahedron Vol. 43, No 1, pp. 215 to 224, 1987
Printed in Great Britain

0040-4020/87 \$5.00+.00
Pergamon Journals Ltd.

THE PREPARATION AND DECOMPOSITION OF ALKYL 2-DIAZOPENT-4-ENOATES AND 1-TRIMETHYLSILYL-1-DIAZOBUT-3-ENES

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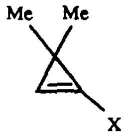
(*Received in UK* 11 *November* 1986)

Abstract - The pyrazolines (12), (18), (21), (26) and (32), prepared by addition of diazomethane to alkyl cyclopropene-1-carboxylates or to 1-trimethylsilylcyclopropenes respectively, rearrange at 20 to 70 °C to diazo-compounds (14), (19), (23), (28) and (36). Pyrazolines (22) and (33) are unchanged under these conditions. Catalytic decomposition of the diazo-compounds is highly dependent on the nature of the substituents and on the catalyst, leading to bicyclobutanes or dienes apparently derived by intramolecular addition, hydrogen shifts or vinyl shifts in intermediate carbenoids. In the case of (36) decomposition in the presence of rhodium acetate leads cleanly to the Z-alkene (37) while in the presence of $PdCl_2(CH_3CN)_2$ the E-isomer (38) is produced.

Diazoalkanes are known to undergo 1,3-dipolar cycloaddition to a number of cyclopropenes under very mild conditions. The reaction can show high regioselectivity, eg., (1, X = CO_2Me or $POPh_2$) leads to (2) with diazopropane.[1,2] In other cases little selectivity is observed;[1,3] thus in the case of a series of 1-(t-butoxycarbonyl)-2-phenylcyclopropenes both (3) and (4) are obtained in ratios of ca. 1:1 to 2:1.[3]



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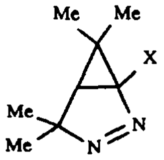

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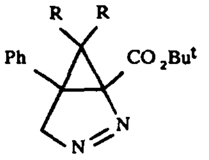

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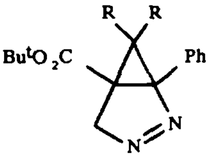

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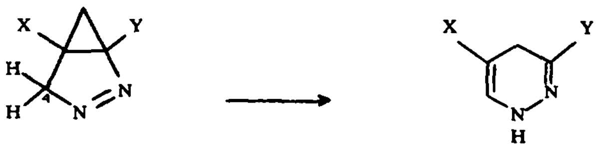
Although the resulting pyrazolines can generally be isolated, a number of examples having a hydrogen on C-4 are reported to rearrange rapidly to dihydropyridazines (5) under the reaction conditions,[4] or on treatment with a trace of acid[1,5] or base:[5,6]



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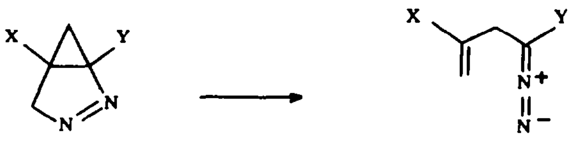
The thermal decomposition of a number of the pyrazolines is also reported. In some cases thermolysis leads to the clean formation of bicyclo(1.1.0)butanes;[5] in other cases, complex products are obtained which are consistent with rearrangement of the pyrazoline to a diazo-compound (6):[7,10]



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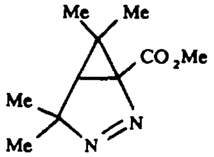
followed by loss of nitrogen to produce a carbene which can undergo a range of intramolecular reactions. The intermediate diazo–compound can sometimes be isolated, and the conditions required for the pyrazoline to diazo–compound rearrangement are strongly dependent on substitutents[7,8,10] and are reported to range from ambient temperature to, eg., refluxing toluene. The conversion of pyrazolines to diazo–compounds may also be brought about by photolysis.[11] Photolysis of the pyrazolines can also lead to nitrogen loss and the production of bicyclobutanes or dienes; the formation of bicyclobutanes has been explained in terms of a diradical intermediate, (7), while the dienes are believed to be derived from the diazo–compound through the corresponding carbene.[9] However, in view of the known conversion of γ,δ–unsaturated α–diazocompounds to bicyclobutanes and dienes, it is not unlikely that both products are carbene derived.[7]

While the diester (9) rearranges with a trace of acid to produce (10), the monoester (8), derived from methyl 3,3–dimethylcyclopropenecarboxylate is reported to be thermally stable; moreover the aryl–analogues (3) and (4) are reported with no comment as to their rearrangement.[1,3]

(7)



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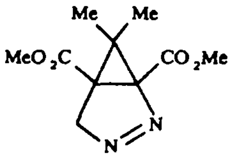

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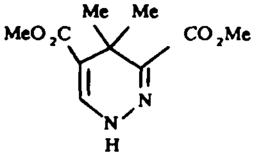

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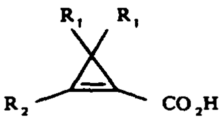
We now describe the isolation of several pyrazolines derived from alkyl cyclopropene carboxylates, their rearrangement to diazo–compounds, in one case at ambient temperature, and the intramolecular trapping of carbenoids derived from these to form bicyclobutanes or dienes. We have also shown that analogous 1–trimethylsilyl–substituted pyrazolines can rearrange to diazo–compounds at ambient temperature and that decomposition of the latter can be strongly dependent on the catalyst.

Cyclopropene–1–carboxylic acids are readily obtained from 1–halo–alkenes by the two step sequence of addition dihalogenocarbene (halogens = bromine or chlorine) followed by treatment with two molecular equivalents of methyl lithium and quenching with carbon dioxide; in the same way quenching with methyl chloroformate or chlorotrimethylsilane leads efficiently to methyl cyclopropene–1–carboxylates and 1–trimethylsilyl–cyclopropenes respectively.[12] Reaction of the acid (11, $R_1 = R_2 =$ Me)[12] with one equivalent of diazomethane at -30 °C led to the corresponding ester. However, with 2.5 mol.equiv. of the reagent a rapid reaction occurred, incorporating a second equivalent of the diazo–compound and leading to (12) in 92% yield after chromatography. N.m.r. analysis showed no evidence for the second regioisomer, (13). When (12) was heated for 48h at 60–70 °C a smooth rearrangement occurred to produce the diazo–compound (14) (85%), the regiochemistry of which was confirmed by the presence of allylic coupling on the low–field methyl group in the ^{1}H n.m.r. and by the i.r. bands at 2085 and 1707 cm^{-1}, typical of α–diazoesters.** Brief reaction of this with a catalytic amount of rhodium acetate in chloroform at 20 °C led to the rapid evolution of nitrogen and the formation of a single product (15) (75% after chromatography). The latter was characterised by four methyl singlets in the ^{1}H n.m.r. at δ 3.63, 1.5, 1.3 and 0.92, together with two doublets (each J 2Hz) at 2.22 and 1.76, and by a ^{13}C spectrum which included four singlets at 21.7, 26.1, 50.8, and 172.6, as well as a double doublet (J ca. 155, 170 Hz) at 36.7 for C_4, showing different couplings to *exo*– and *endo*–hydrogens (see below for (24)).



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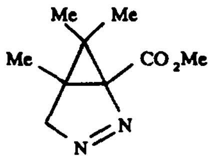

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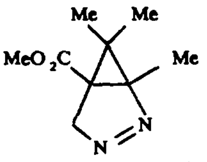

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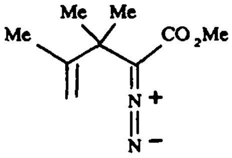

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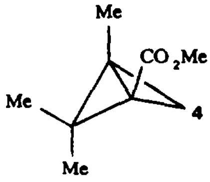

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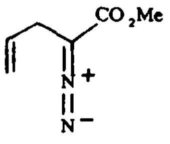
Apparently the rhodium carbenoid derived from (14) undergoes a relatively clean addition to the alkene bond in preference to alternative carbenic reactions such as 1,2-alkyl or alkenyl shifts. This is in contrast to the corresponding reaction of methyl 2-diazopent-4-enoate (16) which leds to an ca. 2:1 mixture of methyl *cis*-penta-2,4-dienoate and the corresponding bicyclobutane in the presence of rhodium acetate;[13] the greater chemoselectivity in the present system presumably reflects the more electron rich nature of the double bond and/or the slower 1,2-shift of alkyl and alkenyl groups rather than of hydrogen. It is interesting to note also that the carbenes (17, X = H or CO_2Et), derived from a variety of routes, undergo both a 1,2-methyl shift and insertion into the C-H bonds of the methyl groups.[14]

Reaction of the dimethylcyclopropene (11, R_1 = Me, R_2 = H) with diazomethane followed a slightly different course, in that with one mol.equivalent of the reagent a mixture of the cyclopropene ester and the pyrazoline (18) was observed. However with, 2.5 mol.equiv., complete transformation to (18) occurred (76%). The pyrazoline showed the expected three methyl singlets in its ^{1}H n.m.r., together with three double doublets at 4.6 (J 18, 7Hz), 4.2 (J 18, 2Hz) and 2.1 (J 7, 2Hz), and the ^{13}C spectrum was again consistent with this structure. This pyrazoline also underwent a clean rearrangement to the corresponding diazo-compound (19) (66%), in this case on heating for 5 days at 70 °C. This is an apparent contrast to the pyrazoline (8) which is reported to be thermally stable.[1] Compound (19) decomposed rapidly on treatment with a catalytic quantity of rhodium acetate, leading to a single major product, (20), which showed spectroscopic properties identical to an authentic sample,[15] together with two minor products (ca. 10% total) which could not be obtained pure. Compound (20) is apparently derived by a 1,2-vinyl shift in the carbenoid derived from (19); the preference for vinyl rather than alkyl migration is not unexpected,[16] and the failure to observe any intramolecular addition, as seen for (16),[13] may reflect conformational changes caused by the presence of the geminal methyl groups; thus the transition state for bicyclobutane formation may be expected to lead to eclipsing of the ester group with the *exo*-methyl.



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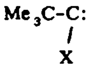

$Me_3C\text{-}\underset{X}{\underset{/}{C}}\!:$

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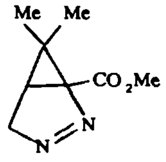

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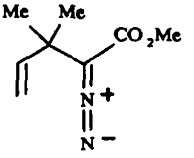

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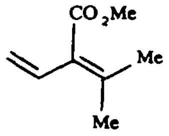
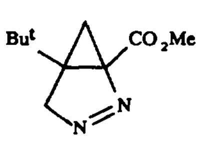


(20)

In the case of the acid (11, R_1 = H, R_2 = t-Bu), reaction with 2.5 mol.equiv. of diazomethane led to an ca. 8:1 mixture of (21) and the regioisomer (22). On standing for 20h at 20 °C the major isomer rearranged in high yield to the diazo-compound (23) which again showed an i.r. band at 2083 cm^{-1}. The minor isomer remained unchanged and could be separated from the diazo-compound by column chromatography. Treatment of (23) with a catalytic amount of rhodium acetate again led to a single product, (24), in essentially quantitative yield (92% after distillation). The bicyclobutane showed just four singlets in its ^1H n.m.r. spectrum including two two-hydrogen singlets at δ 2.2 and 0.9 for the ring hydrogens. The geminal coupling in bicyclobutanes is often small,[17] and indeed in some cases is not observed.[18] The ^{13}C spectrum was interesting in that the carbons of the CH_2-groups appeared as a double double double doublet in the gated decoupled spectrum, with coupling to each of the ring hydrogens (Fig. 1). By analogy with related systems the largest coupling (169.4 Hz) may be assigned as the one-bond coupling to the endo-hydrogen, while the coupling of 155.4Hz is caused by one bond coupling to the exo-hydrogen.[17] The three bond couplings to exo- and endo-hydrogens could be assigned as 13.6 and 5.0 Hz respectively.[17] The formation of (24) in high yield suggests that the carbenoids derived from α-diazoesters may add cleanly to disubstituted γ,δ-alkenes even in the presence of hydrogens at the β-position. The greater selectivity for addition compared to (16) could be caused simply by the electron releasing effect of the t-butyl group, but once again conformational effects in the intermediate carbenoid may play a part; thus the preferred conformation about the C_2-C_3 bond may be expected to orient the t-butyl group away from the rhodium carbenoid, and therefore to direct the vinyl group towards the carbene centre.



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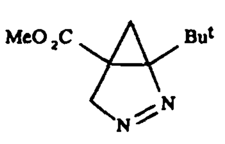

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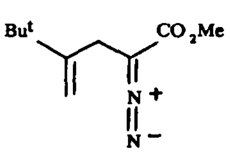

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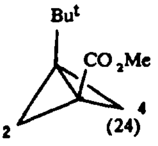
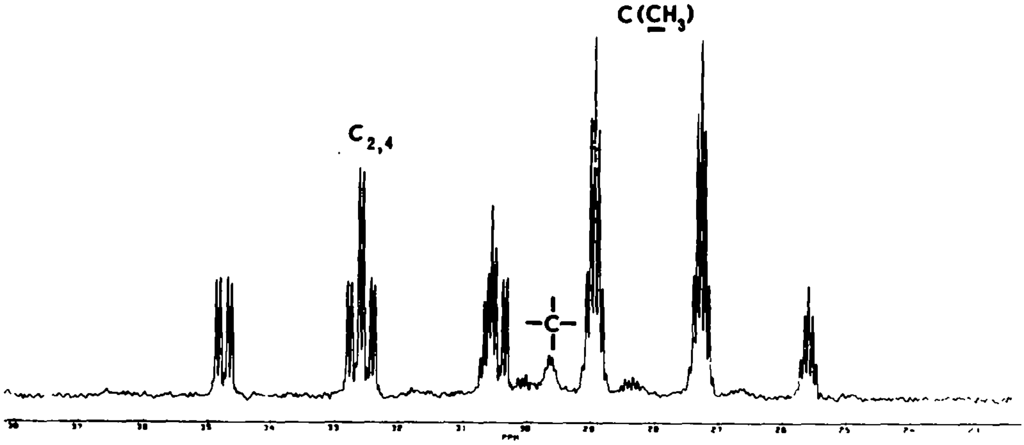


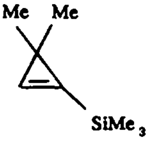
(24)

Fig. 1. Gated Decoupled ^{13}C Spectrum of Compound (24)
(Showing 25 – 35 ppm region only)

75.47 MHz



Addition of diazomethane to the silane (25) also occurred in a regioselective manner, to produce (26). This compound proved to be sensitive to base, rearranging to the crystalline dihydropyridazine (27); indeed if the solution of diazomethane in ether had been dried over solid potassium hydroxide before use, the dihydropyridazine was obtained directly in good yield. In the absence of base the pyrazoline (26) underwent an alternative rearrangement to the diazosilane (28); this process was easily carried out by refluxing for 1h in benzene (93%). Compound (28) was relatively stable to heat, remaining unchanged after refluxing for a further 2h. Surprisingly it was also unchanged by treatment with a catalytic amount of rhodium acetate or cuprous cyanide in refluxing benzene. However, when the catalyst was changed to cuprous iodide, loss of nitrogen did occur in 30m at 80° in benzene. The only major product was the bicyclobutane (29) (71%) which was identical to a sample prepared by reaction of (30) with methyl lithium.[21] The same product was obtained when the cuprous iodide catalyst was replaced by $Pd(MeCN)_2Cl_2$, and apparently arises by addition of the corresponding carbene or a related carbenoid to the double bond. It is interesting to note that while the two reactions of (28) and the reaction of (30) with methyl lithium follow a common pattern of carbene (carbenoid) addition to the double bond, there is a sharp contrast with the reaction of (19) with rhodium acetate, which leads to migration of the vinyl-group in the intermediate carbenoid rather than addition to the relatively unactivated alkene.



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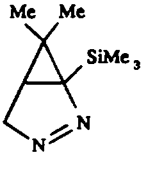

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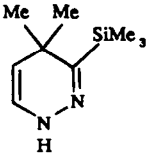

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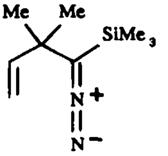

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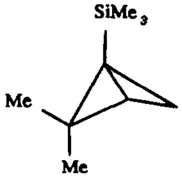

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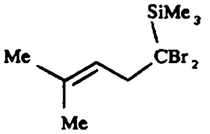
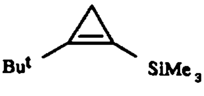


(30)

Addition of diazomethane to the t-butyl system (31) was less selective and led to an ca. 2:1 mixture of (32) and (33). Like the dimethyl-derivative above these compounds both rearranged in the presence of a trace of base to the corresponding dihydropyridazines, (34) and (35) respectively. In addition, (32) rearranged on standing at 20° for 24h to produce the diazosilane (36), which showed a diazo-band at 2039 cm^{-1} in the infra-red, a position very close to that in the diazosilane (28). This could be separated from unreacted (33) by column chromatography. Treatment of compound (36) with a catalytic amount of rhodium acetate led to the Z-diene (37) by 1,2-migration of hydrogen in the intermediate rhodium carbenoid; this could be distinguished from the regioisomaric product in which the positions of Bu^t- and Me_3Si- groups are interchanged on the basis of the presence of ^{29}Si- side bands on the ^{13}C-signal for C_A.[20] The formation of Z-alkenes in rhodium catalysed reactions has already been reported,[13] and in the present case no signals for the E-isomer were seen in the ^{1}H n.m.r.# What was perhaps more surprising, in view of the formation of (24) from (23), was the absence of any bicyclo(1.1.0)butane (39, R = Bu^t) in the product. When the decomposition of (36) was carried out in the presence of $Pd(MeCN)_2Cl_2$ as catalyst, a different stereoselectivity was observed, and the E-diene (38) was obtained in reasonable yield; the ^{1}H n.m.r. of the crude product in this case showed only the signals given by (38), and none for (37). Once again, the regiochemistry of the diene was proved by the presence of ^{29}Si- side bands, in this case on the ^{1}H-signal for H_A.[20]



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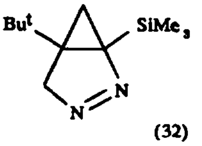

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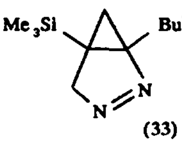

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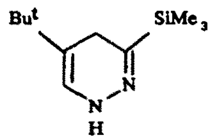

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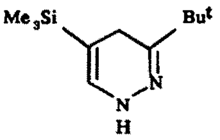

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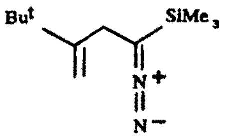

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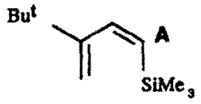

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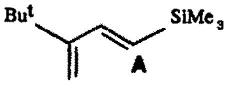

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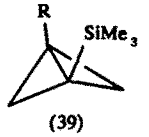
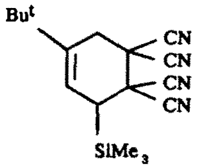
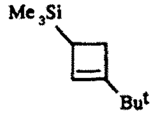


(39)

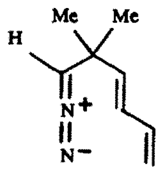
Although there are a number of routes to the synthetically useful 1−trimethylsilylbuta−1,3−dienes,[22] the ability to obtain E− or Z−isomers by choice of catalyst is noteworthy.$^+$ Considerable catalyst dependence has been reported in the decomposition of a number of diazocompounds, but the change in stereoselectivity in the above reactions of (36) is remarkably sharp.[19] Moreover, in the presence of cuprous iodide, the decomposition of (36) followed yet a different course, and an ca. 3:2 mixture of (38) and the bicyclobutane (39, R = t−Bu) was observed. The latter was obtained pure by treatment of the mixture with tetracyanoethylene, when (38) was converted to the [4+2]−cycloadduct (40); flash distillation then produced pure (39, R = t−Bu). The bicyclobutane could be characterised by comparison of its spectra with those of (39, R = Me), obtained by reaction of 1,1−dibromo−1−trimethylsilyl−3−methylbut−3−ene with methyl lithium.[21] Moreover, on standing for 3 days in deuterochloroform solution it underwent a clean rearrangement to the cyclobutene (41). This showed a complex n.m.r. spectrum for the four ring hydrogens (Fig. 2a) with coupling constants of J_{ab} 0.7, J_{ac} 0.55, J_{ad} 1.0, J_{bc} 13.4, J_{bd} 4.6, J_{cd} 1.7 Hz. Double irradiation at the frequency of Ha led to the AMX pattern shown in Fig. 2b. Similar rearrangements have been reported for a number of other bicyclobutanes, and the coupling constants are very simiar to those reported.[18,21]



(40)



(41)



(42)

We wish to thank The Arabian Gulf University for supporting H.H.H.

EXPERIMENTAL

Cyclopropenes were prepared as previously described.[12]

Unless otherwise stated all new compounds were homogeneous by t.l.c. and/or g.l.c.; n.m.r. spectra were run in $CDCl_3$ solution and recorded for ^1H at 200 or 300MHz on Bruker Spectrospin instruments, and ^{13}C spectra were recorded at the corresponding frequency on the same instruments. Infra−red spectra were obtained on a Nicolet F.T. instrument, while mass spectra were measured on an AEI MS9 or a Kratos MS80 using the E.I. method. Melting points are uncorrected.

1−Carbomethoxy−6,6−dimethyl−2,3−diazabicyclo(3.1.0)hex−2−ene (18)

Diazomethane in ether (9.6ml, 1.4M, 2.5 mol.equiv.) was added at 0 °C to 3,3−dimethylcyclopropenecarboxylic acid (0.6 g) in ether (10 ml). The mixture was allowed to reach 20° and after 10 min the excess of diazomethane and the ether were removed at 14 mmHg to give a yellow oil which was one spot on t.l.c. Column chromatography over silica eluting with petrol (b.p. 40−60°) and ether gave 1−carbomethoxy−6,6−dimethyl−2,3−diazabicyclo(3.1.0)hex−2−ene (18) (0.68 g, 76%) (Found M^+: 168.0891. $C_8H_{12}N_2O_2$ requires M: 168.0899) which showed δ_H 4.65 (1H, dd, J 18, 7 Hz), 4.22 (1H, dd, J 18, 2Hz), 3.88 (3H, s), 2.12 (1H, dd, J 7, 2 Hz), 1.38 (3H, s), 0.62 (3H, s); δ_C 168.1s, 86.9s, 76.2t, 52.4q, 32.6d, 32.5s, 20.4q, 13.7q; ν_{max} 1732, 1438, 1303, 1212, 1110 cm^{-1}.

1−Carbomethoxy−5,6,6−trimethyl−2,3−diazabicyclo(3.1.0)hex−2−ene (12)

A solution of diazomethane in ether (6.4ml, 1.4M, 2.5 mol.eqiv.) was added to 2,3,3−trimethylcyclopropenecarboxylic acid (0.45 g) in ether (10 ml) at −30° and the products were allowed to reach 20 °C. After 10min the products were worked up as before and the residue was purified by column chromatography over silica eluting with 6:4 petrol (b.p. 40-60°) and ether to give 1-carbomethoxy-5,6,6-trimethyl-2,3-diazabicyclo(3.1.0)hex-2-ene (0.6 g, 92%) (Found M^+: 182.1053. $C_9H_{14}N_2O_2$ requires M: 182.1055) which showed δ_H 4.43 (1H, d, J 19Hz), 4.39 (1H, d, J 19Hz), 3.88 (3H, s), 1.42 (3H, s), 1.38 (3H, s), 0.66 (3H, s); δ_C 167.5s, 83.8s, 82.3t, 51.5q, 37.5s, 34.9s, 16.0q, 14.9q, 11.1q; ν_{max} 1727, 1436, 1276, 1094 cm^{-1}.

Reaction of 2-t-Butylcyclopropene-1-carboxylic acid with Diazomethane

A solution of diazomethane in ether (102ml, 0.4molar, 2.5mol.equiv.) was added to 2-t-butylcyclopropene-1-carboxylic acid (2.29g) in ether (30ml) at 0 °C. The products were allowed to reach 20° and after 20min were worked up as above. The residue was a mixture of two components. The major product was obtained pure by fractional crystallisation from acetone and characterised as 1-carbomethoxy-5-t-butyl-2,3-diaza-bicyclo(3.1.0)hex-2-ene (2.23g, 70%) (Found: C, 61.3, H 8.2, N 14.35, M^+ 196.1193. $C_{10}H_{16}N_2O_2$ requires: C, 61.2, H 8.2, N 14.3, M 196.1212) which showed δ_H 4.86 (1H, d, J 20Hz), 4.36 (1H, d, J 20Hz), 3.90 (3H, s), 2.28 (1H, d, J 7Hz), 0.96 (9H, s), 0.39 (1H, d, J 7 Hz); δ_C (D_8-acetone, −40 °C) 169.3s, 82.9t, 75.6s, 53.2q, 48.7s, 31.6s, 28.2q, 25.0t; ν_{max} 2963, 1730, 1241, 1130 cm^{-1}.

The minor component was obtained pure by rapid chromatography of the mixture over silica eluting with 8:2 petrol and ether. This also gave the major component, but contaminated with a little of the rearranged diazo-compound (see below). A more efficient way to obtain the minor component was to allow complete rearrangement of the major one, and then to separate using column chromatography. The minor product was characterised as 1-carbomethoxy-5-t-butyl-3,4-diazabicyclo(3.1.0)hex-3-ene (0.3g, 9%), m.p. 68-70 °C (Found: C, 61.1, H 8.3, N 14.2) which showed δ_H 5.18 (1H, d, J 19Hz), 4.50 (1H, d, J 19Hz), 3.69 (3H, s), 2.06 (1H, d, J 6Hz), 1.11 (9H, s), 0.17 (1H, d, J 6 Hz); δ_C 169.7s, 92.5s, 83.0t, 52.3q, 33.0s, 32.6s, 27.9q, 20.0t; ν_{max} 1742, 1439, 1153, 915 cm^{-1}.

Methyl 2-Diazo-3,3-dimethylpent-4-enoate (19)

1-Carbomethoxy-6,6-dimethyl-2,3-diazabicyclo(3.1.0)hex-2-ene (0.3g) was heated at 70° for 5 days in a sealed tube. T.l.c. then showed no starting material and column chromatography over silica eluting with petrol (b.p. 40-60°) and ether (9:1) gave a single product, methyl 2-diazo-3,3-dimethylpent-4-enoate (0.2g, 66%) as a yellow oil (Found M^+: 168.0886. $C_8H_{12}N_2O_2$ requires M: 168.0887) which showed δ_H 5.94 (1H, dd, J 18, 9 Hz), 5.14 (1H, br.d, J 18Hz), 5.10 (1H, br.d, J 9Hz), 3.69 (3H, s), 1.34 (6H, s); δ_C 166.6s, 143.9d, 112.4t, 62.6s, 51.4q, 35.4s, 26.2q; ν_{max} 2082s, 1704s, 1302s, 1083s cm^{-1}.

Methyl 2-Diazo-3,3,4-trimethylpent-4-enoate (14)

1-Carbomethoxy-5,6,6-trimethyl-2,3-diazabicyclo(3.1.0)hex-2-ene (0.2g) was heated in a sealed tube for 2 days at 60-70 °C. T.l.c. showed complete reaction of the starting material and the formation of a single product which was separated by column chromatography over silica, eluting with 9:1 petrol (b.p. 40-60°) and ether and characterised as methyl 2-diazo-3,3,4-trimethylpent-4-enoate (0.17g, 85%) (Found M^+: 182.1101. $C_9H_{14}N_2O_2$ requires M: 182.1196) which showed δ_H 4.88 (2H, br.s), 3.70 (3H, s), 1.77 (3H, br.s), 1.38 (6H, s); δ_C 166.6s, 149.1s, 111.0t, 63.0s, 51.4q, 38.3s, 26.2q, 19.7q; ν_{max} 2974, 2085, 1707, 1305, 1081 cm^{-1}.

Methyl 2-Diazo-5,5-dimethyl-4-methylenehexanoate (23)

(a) A solution of 1-carbomethoxy-5-t-butyl-2,3-diazabicyclo(3.1.0)hex-2-ene (1.31g) in chloroform (20 ml) was allowed to stand at 20 °C, and the progress of the reaction was monitored by n.m.r. After 2 days complete reaction of the starting material had occurred and a single product had formed. This was obtained pure by column chromatography on silica, eluting with 8:2 petrol and ether and characterised as methyl 2-diazo-5,5-dimethyl-4-methylenehexanoate (1.19g, 91%) (Found M^+: 196.1209. $C_{10}H_{16}N_2O_2$ requires M: 196.1212) which showed δ_H 4.98 (1H, br.s), 4.75 (1H, br.s), 3.72 (3H, s), 3.06 (2H, br.s), 1.08 (9H, s); δ_C 167.6s, 152.4s, 109.7t, 55.9br.s, 51.9q, 35.7s, 29.1q, 26.1t (further split into narrow dd, in agreement with allylic coupling); ν_{max} 2963, 2083, 1699, 1438, 1204, 1107 cm^{-1}.

(b) The starting material was allowed to stand without solvent for 3 days at 20 °C. Complete rearrangement to the diazo-compound was observed by ^{1}H n.m.r.

Methyl 2,3,3-Trimethylbicyclo(1.1.0)butane-1-carboxylate (15)

A solution of methyl 2-diazo-3,3,4-trimethylpent-4-enoate (80mg) in chloroform was treated with rhodium acetate (8mg). A rapid evolution of nitrogen occurred and after 10 min t.l.c. showed complete consumption of the starting material. The products were worked up as above to give an oil which was purified by column chromatoraphy over silica eluting with 9:1 petrol and ether and was characterised as methyl-2,3,3-trimethyl- bicyclo(1.1.0)butane-1-carboxylate (53mg, 75%) (Found M^+: 154.1050. $C_9H_{14}O_2$ requires M: 154.1045) which showed δ_H 3.62 (3H, s), 2.22 (1H, d, J 2Hz), 1.76 (1H, d, J 2Hz), 1.50 (3H, s), 1.30 (3H, s), 0.92 (3H, s); δ_C 172.6s, 51.2q, 50.8s, 36.7dd, 26.1s, 21.7s, 19.4q, 16.1q, 10.0q; ν_{max} 1713, 1439, 1293, 1135, 1101 cm^{-1}.

Methyl 3-t-Butylbicyclo(1.1.0)butane-1-carboxylate (24)

A solution of methyl 2-diazo-5,5-dimethyl-4-methylenehexanoate (110mg) in chloroform (2ml) was treated with rhodium acetate (6mg) at 20 °C. A rapid evolution of gas occurred and after 2 min the solution became colourless. The product showed only one spot on t.l.c. and the ^{1}H n.m.r. showed only one set of signals. The solvent was removed at 14mmHg and the residue was flash distilled at 20 ° and 0.01 mmHg to give methyl 3-t-butylbicyclo(1.1.0)butane-1-carboxylate (87mg, 92%) (Found M^+: 168.1152. $C_{10}H_{12}O_2$ requires M: 168.1150) which showed δ_H 3.64 (3H, s), 2.19 (2H, s), 1.02 (9H, s), 0.92 (2H, s); δ_C 172.8s, 51.7q, 39.7s, 32.6dddd (J 169.4, 155.4, 13.6, 5.0 Hz), 29.7s, 28.2 q.septets (J 125.5, 4.7Hz), 14.4s; ν_{max} 2966, 1714, 1322, 1146, 770 cm^{-1}.

Methyl 3-methyl-2-vinylbut-2-enoate (20)

Methyl 2-diazo-3,3-dimethylpent-4-enoate (160mg) in chloroform (3ml) was treated with rhodium acetate (2mg) at 20 °C. A vigorous evolution of nitrogen occurred and after 5m a colourless solution was obtained which showed no signals due to starting material in the ^{1}H n.m.r. The products were filtered and the solvent was removed at 14mmHg to give an oil (110mg, 83% crude yield) which showed one major component by g.l.c., and two minor components (ca. 10%) very close together. The major product was collected and characterised as methyl 3-methyl-2-vinylbut-2-enoate (Found M^+: 140.0823. Calculated for $C_8H_{12}O_2$ M: 140.0837) which showed δ_H 6.55 (1H, dd, J 16, 11 Hz), 4.85 – 5.2 (2H, complex), 3.78 (3H, s), 1.83 (6H, s); ν_{max} 3093, 1731, 1219 cm^{-1}. The ^{1}H n.m.r. and i.r. spectra were identical to those of an authentic sample.[15]

6,6-Dimethyl-1-trimethylsilyl-2,3-diazabicyclo(3.1.0)hex-2-ene (26)

A solution of diazomethane in ether (20ml, 0.4Molar) was added at 0° to 3,3-dimethyl-1-trimethylsilylcyclopropene (850mg) in ether (20ml) and the mixture was allowed to stand for 2h at 20 °C. Excess diazomethane and the solvent were removed at 14mmHg. N.m.r. of the residue showed the presence of a single major product which was purified by column chromatography over silica, eluting with 7:3 petrol and ether and characterised as 6,6-dimethyl-1-trimethylsilyl-2,3-diazabicyclo(3.1.0)hex-2-ene (870mg, 79%) (Found M^+: 182.1840. $C_9H_{18}N_2Si$ requires: 182.1238) which showed δ_H, (C_6D_6) 4.21 (1H, dd, J 7.0, 18.8 Hz), 4.01 (1H, dd, J 1.9, 18.8 Hz), 1.17 (1H, dd, 1.9, 7.0 Hz), 1.13 (3H, s), 0.54 (3H, s), 0.33 (9H, s); δ_C (C_6D_6) 80.1s, 76.2t, 31.3d, 27.1s, 24.3q, 14.7q, 0.0q; ν_{max} 2955, 1251, 840 cm^{-1}. This material rearranged to the corresponding diazo-compound (see below) on standing at 20° either neat or in benzene for 3-5 days.

1,2-Diaza-3-trimethylsilyl-4,4-dimethylcyclohexa-2,5-diene (27)

Diazomethane in ether (22.5ml, 0.4 Molar; dried over solid potassium hydroxide) was added to 1-trimethylsilyl-3,3-dimethylcyclopropene (0.84g) in ether (10ml) at 0 °C and the products were allowed to stand for 1h at 20°. Excess diazomethane and solvent were removed at 14mmHg and the residue was recrystallised from ether to give 1,2-diaza-3-trimethylsilyl-4,4-dimethylcyclohexa-2,5-diene (0.99g, 91%), m.p. 71-73° (Found M^+: 182.1236, $C_9H_{18}N_2Si$ requires M: 182.1239) which showed δ_H (C_6D_6) 7.1 (1H, br.s), 5.76 (1H, dd, J 8, 5Hz), 4.27 (1H, dd, J 8, 3Hz), 1.08 (6H, s), 0.35 (9H, s) (the 5 and 3Hz couplings on the signals at 5.76 and 4.27 respectively disappeared when the signal at 7.1 was irradiated); δ_C (C_6D_6) 154.5s, 126.6d, 104.2d, 32.7s, 27.3q, 0.7q; ν_{max} 3293, 2965, 1458, 1247, 756 cm^{-1}. This compound decomposed on standing for 3-5 days at 20 °C.

1-Diazo-2,2-dimethyl-1-trimethylsilylbut-3-ene (28)

6,6-Dimethyl-1-trimethylsilyl-2,3-diazabicyclo(3.1.0)hex-2-ene (950mg) was refluxed in benzene (10ml) for 60m, when n.m.r. showed no starting material remained. The solvent was removed at 14mmHg and the residue was identified as 1-diazo-2,2-dimethyl-1-trimethylsilylbut-3-ene (879mg, 93%) (Found M^+: 182.1247. $C_9H_{18}N_2Si$ requires M 182.1239) which showed δ_H 5.68 (1H, dd, J 18, 9 Hz), 5.1-4.6 (complex, 2H), 1.07 (6H, s), 0.8 (9H, s); δ_C (C_6D_6) 146.5d, 111.5t, 41.5s, 37.9s, 27.5q, 0.8q; ν_{max} 2035, 1254, 840 cm^{-1}. The compound was stable to heating for a further 2h under the same conditions but decomposed rapidly on attempted chromatography over silica; however the n.m.r. of the crude product showed no other components were present.

1-Trimethylsilyl-2,2-dimethylbicyclo(1.1.0)butane (29)

(a) 1-Diazo-2,2-dimethyl-1-trimethylsilylbut-3-ene (200mg) in benzene (3ml) was treated with cuprous iodide (10mg). No evolution of gas occurred, but after heating at 80 °C for 30m complete reaction had occurred. The products were worked up as before and distilled at 20 °C and 0.5mmHg to give 1-trimethylsilyl-2,2-dimethylbicyclo(1.1.0)butane (120mg, 71%) as a colourless oil (Found M^+: 154.1192. $C_9H_{18}Si$ requires M: 154.1178) which showed δ_H 1.66 (1H, d, J 2.6 Hz), 1.43 (1H, d, J 2.6 Hz), 1.40 (1H, s), 1.19 (3H, s), 1.06 (3H, s), 0.26 (9H, s); very minor signals (equivalent to ca. 5% of the product) were also observed in the olefinic region. This compound was identical by ^{1}H n.m.r. to a sample prepared by reaction of 5,5-dibromo-5-trimethylsilyl-2-methylpent-2-ene with methyl lithium.[21]

(b) The diazo-compound was treated with a catalytic quantity of $Pd(MeCN)_2Cl_2$ in benzene for 30m at 80 °C. N.m.r. showed complete reaction and the formation of the above bicyclobutane (29) as the only major product.

(c) The diazo-compound was treated with a catalytic quantity of cuprous cyanide in benzene for 3h at 80 °C. N.m.r. showed only starting material.

(d) The diazo-compound was treated with a catalytic quantity of rhodium acetate in benzene for 30m at 80 °C. N.m.r. showed only starting material.

Reaction of 1-trimethylsilyl-2-t-butylcyclopropene with diazomethane

A solution of 1-trimethylsilyl-2-t-butylcyclopropene (1.5g) in ether (15ml) was treated with diazomethane (24.5ml, 0.4M, 1.1 mol.equiv.) at 0 °C and the solution was allowed to warm to 20 °C. After 6h the excess of diazomethane and the solvent were removed at 14mmHg to give an oil (1.5g, 81%) which showed two spots very close together on t.l.c. The mixture (250mg) was refluxed for 20m in benzene (4ml) when n.m.r. showed complete reaction of the major component and t.l.c. showed two spots. The solvent was removed at 14mmHg and the residue was subjected to rapid chromatography through a short column of silica, eluting with 8:2 petrol and ether. The first component was characterised as 5-diazo-3-methylene-5-trimethylsilyl-2,2-dimethylpentane (36) (115mg, 46%) (Found M^+: 210.1544. $C_{11}H_{22}N_2Si$ requires M: 210.1552) which showed δ_H 4.90 (1H, br.s), 4.77 (1H, br.s), 2.66 (2H, br.s), 1.05 (9H, s), 0.15 (9H, s); δ_C (D_6-acetone) (−40 °C) 154.9s, 109.4t, 36.4s, 29.7q 28.5t (further split into narrow dd), −1.5q; ν_{max} 2961, 2039, 1251, 841 cm^{-1}. The second component was 5-trimethylsilyl-1-t-butyl-2,3-diazabicyclo(3.1.0)hex-2-ene (33) (65mg, 26%) (Found M^+: 210.1544. $C_{11}H_{22}N_2Si$ requires M: 210.1552) which showed δ_H 4.44 (1H, d, J 19Hz), 4.32 (1H, d, J 19Hz), 1.11 (9H, s), 1.03 (1H, d, J 6Hz), 0.08 (9H, s), −0.36 (1H, d, J 6Hz); δ_C 90.2s, 85.3t, 32.1s, 28.7q, 20.0t, 18.6s, −0.56q; ν_{max} 2958, 1363, 1253, 840 cm^{-1}. The spectra of the first component of the original diazomethane reaction could be determined by subtraction of the spectra of (33) from those of the crude reaction mixture; on this basis it was identified as 5-t-butyl-1-trimethylsilyl-2,3-diazabicyclo(3.1.0)hex-2-ene (32) which showed δ_H 4.4 (1H, d, J 18Hz), 4.7 (1H, d J 18Hz), 1.0 (9H, s), 0.35 (9H, s), 1.4 (1H, d, J 5Hz), −0.05 (1H, d, J 5 Hz); δ_C (D_6-acetone, −40 °C) 82.6t, 69.5s, 45.4s, 31.2s, 29.3q, 24.3t, 0.49q.

t–Butyl–trimethylsilyl–1,2–diazacyclohexa–2,5–dienes (34) and (35)

(a) A solution of 1–trimethylsilyl–2–t–butycyclopropene (31) (1.0g) in ether (10ml) was treated with diazomethane in ether (17.8ml, 0.4M) (dried over KOH) for 18h at 20 °C. Work up as before gave a solid (1.1g, 94% crude yield) which was an ca. 2:1 mixture of two components. These were separated by column chromatography over silica, eluting with 8:2 petrol and ether. The first product to be eluted was *5–t–butyl–3–trimethylsilyl–1,2–diazacyclohexa–2,5–diene* (34) (0.65g, 52%), m.p. 78–80 °C (Found M^+: 210.1555. $C_{11}H_{22}N_2Si$ requires M: 210.1552) which showed δ_H 7.5 (1H, br.s), 6.1 (1H, d, J 5 Hz), 2.5 (2H, s), 1.1 (9H, s), 0.2 (9H, s); ν_{max} 3291, 2960, 1248, 838 cm^{-1} This compound decomposed on standing at 20 °C. The minor component decomposed rapidly on the column and was not fully characterised. However, on the basis of n.m.r. signals at δ_H 7.2 (1H, b.s), 6.3 (1H, d, J 5Hz), 2.43 (2H, s), 1.05 (9H, s), and 0.03 (9H, s) it was provisionally characterised as 3–t–butyl–5–trimethylsilyl–1,2–diaza–cyclohexa–2,5–diene (35).

(b) The cyclopropene (31) was allowed to stand for 5h at 20 °C with diazomethane in ether (2.5 mol.equiv., dried over KOH) as above. The products were worked up as before to give a solid which was a 2:1 mixture of the pyrazolines (32) and (33) (ratio 2:1) and the dihydropyridazines (34) and (35) (ratio 2:1) by ^1H n.m.r. The mixture was allowed to stand for 18h at 20 °C in ether over solid potassium hydroxide. N.m.r. then showed no pyrazoline to be present, and instead indicated a 2:1 mixture of the dihydropyridazines (34) and (35).

Z–4–trimethylsilyl–2–t–butylbuta–1,3–diene (37)

5–Diazo–5–trimethylsilyl–2,2–dimethyl–3–methylenepentane (36) (80mg) in chloroform (3ml) was treated with rhodium acetate (2mg) at 20 °C. After 10m evolution of gas was complete and the solution had become colouress. Examination of the n.m.r. showed that a single product had been formed. The products were filtered and the solvent was removed from the filtrate at 14mmHg and the residue was flash distilled at 0.5mmHg and 50 °C to give a colourless oil, *Z–4–trimethylsilyl–2–t–butylbuta–1,3–diene* (63mg, 91%) (Found M^+: 182.1495. $C_{11}H_{22}Si$ requires M: 182.1491) which showed δ_H 6.9 (1H, d, J 14 Hz), 5.5 (1H, d, J 14 Hz), 4.86 (2H, s), 1.1 (9H, s), 0.1 (9H, s); δ_C 158.0s, 147.2d, 131.2d (showing side bands (ca. 5%) at J ca. 75 Hz), 109.9t, 29.6q, 35.2s, 0.8q,; ν_{max} 2959, 1247, 838, 737 cm^{-1}. The ^1H n.m.r. showed no signals for the E–isomer (38) (see below).

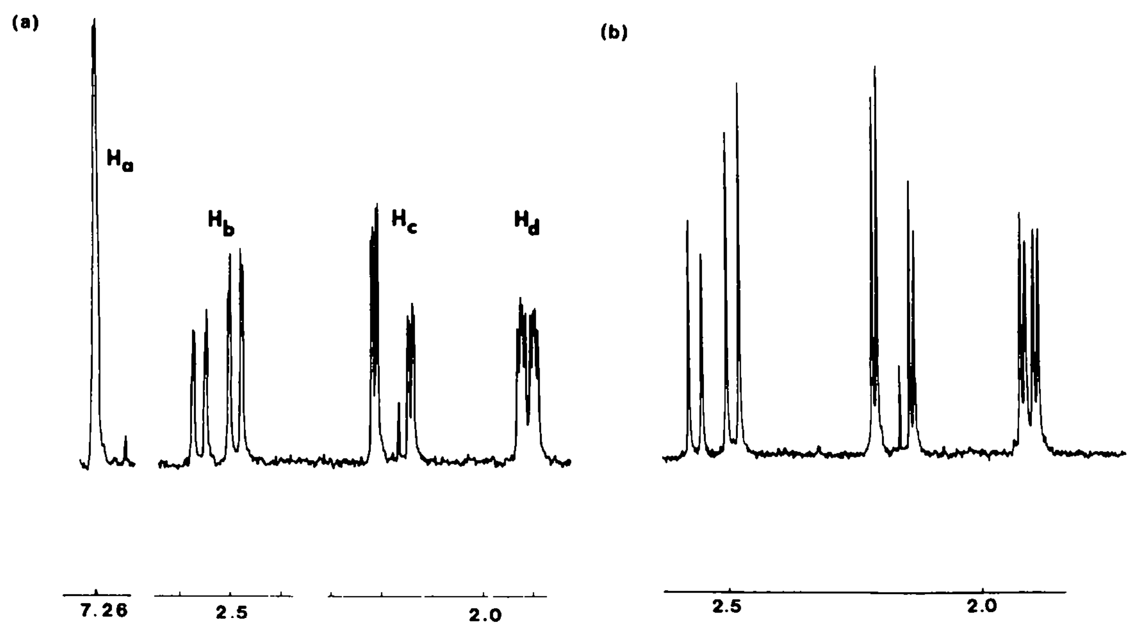
E–4–Trimethylsilyl–2–t–butylbuta–1,3–diene (38)

(a) 5–Diazo–5–trimethylsilyl–2,2–dimethyl–3–methylenepentane (36) (150mg) in chloroform (6 ml) was treated with $PdCl_2(MeCN)_2$ (8mg) for 15m at 60 °C. N.m.r. showed complete reaction of the starting material, and the formation of a single product. Work up as above followed by distillation of the residue at 0.5mmHg and 50 °C gave *E–4–trimethylsilyl–2–t–butylbuta–1,3–diene* (96mg, 74%) as a colourless oil (Found M^+: 182.1491. $C_{11}H_{22}Si$ requires M: 182.1491) which showed δ_H 6.53 (1H, dt, J 19, 0.5,Hz), 5.96 (1H, d, J 19Hz, showing side–bands (ca. 5%) at J 5 Hz), 5.02 (1H, br.dd, J 1,0.5 Hz), 4.72 (1H, dd, J 1, 0.3 Hz), 1.01 (6H, s), 0.95 (3H, s), 0.05 (9H, s); δ_C 158.2s, 144.0d (further split into narrow dd), 130.7d, 107.3t, 35.2s, 29.6q, –1.0q.

Fig. 2. 200 MHz ^1H N.M.R. of Compound (41) Showing the Signals for the Four Ring Hydrogens

(a) Normal spectrum

(b) Spectrum with double irradiation at δ 7.26



(b) 5-Diazo-5-trimethylsilyl-2,2-dimethyl-3-methylenepentane (36) (167mg) in chloroform (3ml) was treated with cuprous iodide (10mg); after 30m at 20 °C, n.m.r. showed only the starting material. The mixture was refluxed for 30m, after which time the yellow colour had disappeared. The products were filtered and the solvent was removed at 14mmHg. The remaining oil was purified by column chromatography over silica, eluting with 8:2 petrol and ether to give an oil (120mg, 83%) which showed a single spot on t.l.c. but was found to contain two components (ratio ca. 3:2) by ^1H n.m.r. The first component was E-4-trimethylsilyl-2-t-butylbuta-1,3-diene which was identical by n.m.r. to that obtained above. This was removed by treating the mixture (43mg) in chloroform (2ml) with tetracyanoethylene (30mg) for 15m at 20 °C, after which n.m.r. showed no signals for the diene. The solvent was removed at 14mmHg and the residue was flash distilled at 1 mmHg and 20 °C to give a distillate (10mg) which was characterised as 1-t-butyl-3-trimethylsilylbicyclo(1.1.0)butane (39, R = Bu^t) (Found M^+: 182.1493, $C_{11}H_{22}Si$ rquires M: 182.1491) which showed δ_H 1.06 (2H, s), 0.99 (9H, s), 0.09 (9H, s), −0.04 (2H, s); δ_C 30.7, 29.0, 28.7; 28.4, −0.35; ν_{max} 2960, 1248, 837 cm^{-1}. The residue was purified by recrystallisation from ether and characterised as 1-t-butyl-4,4,5,5-tetracyano-3-trimethylsilylcyclohexene (40) (29mg) m.p. 139-142 °C (Found M^+: 310.1600. $C_{17}H_{22}N_4Si$ requires M: 310.1614) which showed δ_H 5.51 (1H, br.s), 3.03 (1H, br.s), 2.50 (1H, br.s), 1.10 (9H, s), 0.32 (9H, s); δ_C 138.6s, 115.4d, 112.6s, 112.0s, 110.8s, 110.5s, 40.4s, 40.1s, 35.9s, 32.4d, 32.0t, 28.5q, 2.29q; ν_{max} 2972, 2220 cm^{-1}.

3-Trimethylsilyl-1-t-butylcyclobutene (41)

A solution of 1-t-butyl-3-trimethylsilylbicyclo(1.1.0)butane (39, R = t-Bu) in deuterochloroform was allowed to stand for 3 days at 20 °C. N.m.r. then showed complete reaction of the starting material and its replacement by a single product. This was characterised as 3-trimethylsilyl-1-t-butylcyclobutene (41) (Found M^+: 182.1491. $C_{11}H_{22}Si$ requires M: 182.1491) which showed δ_H 7.26 (1H, br.s), 2.50 (1H, ddd, J 13.4, 4.6, 0.7 Hz), 2.18 (1H, ddd, J 13.4, 1.7, 0.55 Hz), 1.94 (1H, ddd, J 4.6, 1.7, 1.0 Hz) 1.0 (9H, s), −0.05 (9H, s); δ_C 157.1, 124.8, 32.8, 28.7, 28.0, −3.4..

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* Compound (36) decomposes if exposed to silica for extended periods, and some E-diene (38) results; if care is not taken this can be carried through to the reaction of (36) with rhodium acetate, leading to a reduced cis-trans selectivity.

** See eg. Aldrich Library of Infra-red spectra.

† It is possible that (38) is derived by isomerisation of (37); model studies suggested that the Pd-catalyst did indeed bring about this reaction, but the rate appeared to be lower than that of the direct reaction from (32) to (38).