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GENERATION AND REACTIVITY OF STERICALLY HINDERED BICYCLO[3.1.0]HEX-1-ENES

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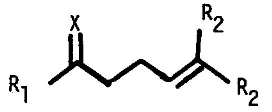
Abstract: 2-t-Butylbicyclo[3.1.0]hex-1-ene dimerizes primarily by a [σ + π] way, whereas 2,5-di-t-butylbicyclo[3.1.0]hex-1-ene undergoes an unusual hydrogen shift reaction to 1,3-di-*t*-butyl-2-methylcyclopentadiene.

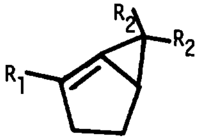
The presence of bulky substituents on or near the strained double bond of a bicyclo[3.1.0]hex-1-ene (1) should decrease the olefin's reactivity in [π + π][1,2] and [σ + π][2] dimerization and ultimately might permit the preparation of a persistent member of the class. In pursuit of this goal we have examined three *t*-butyl-substituted systems and report here the novel behavior of two of them[3].

The previous method[2,4] for generation of the carbenoid intermediates 4a and 4b involved α-elimination from the dibromomethylene derivatives 3a and 3b,



2: X = O; 3: X = CBr$_2$

4: X = C



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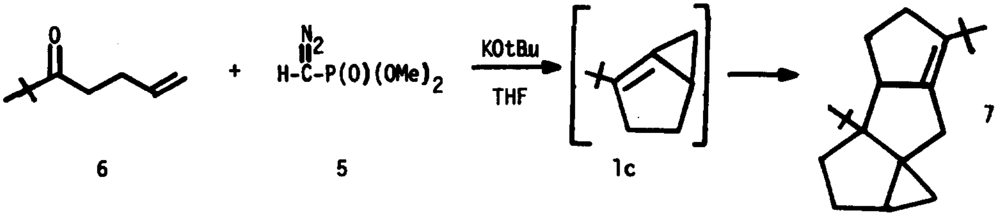
a: R$_1$ = CH$_3$, R$_2$ = H
b: R$_1$ = R$_2$ = CH$_3$
c: R$_1$ = *t*-Bu, R$_2$ = H

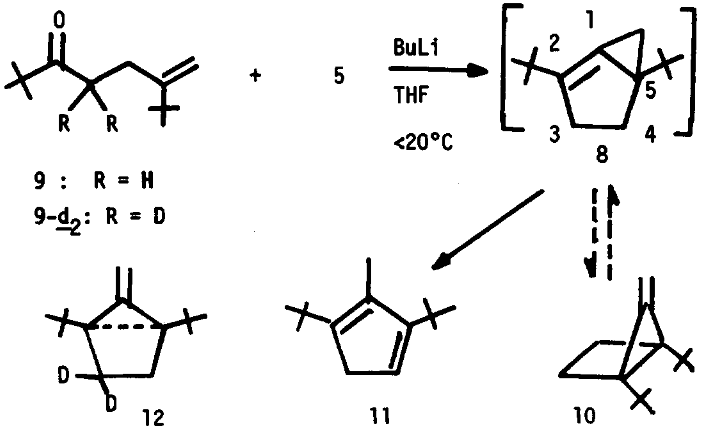
which in turn were prepared by the action of CBr$_4$ and Ph$_3$P[5] on the corresponding ketones 2a and 2b. However, the latter reaction has been reported to fail with sterically hindered ketones[5b], and we find similar results with the *t*-butyl ketone 2c, which does not give useful amounts of 3c by this route.

A solution to this difficulty emerges from the work of Gilbert and his collaborators[6,7], who succeeded in generating 1-methyl-1-*t*-butyl vinylidene from methyl-*t*-butyl ketone and dimethyl diazomethylphosphonate[8] (5). The vinylidene was efficiently trapped by cyclohexene[6]. In an intramolecular variant of this reaction, we find that allyl pinacolone 6[9], 5, and KO*t*-Bu react to give a mixture, the volatile portion of which consists of 45% recovered 6, 45% of a dimeric hydrocarbon, C$_{20}$H$_{32}$, assigned the [σ + π] structure 7[3,10], 7% of an isomeric dimer[11], and traces of other products. The single *t*-butyl group at C$_2$ thus does not suffice to suppress dimerization of the bicyclo[3.1.0]hex-1-ene.



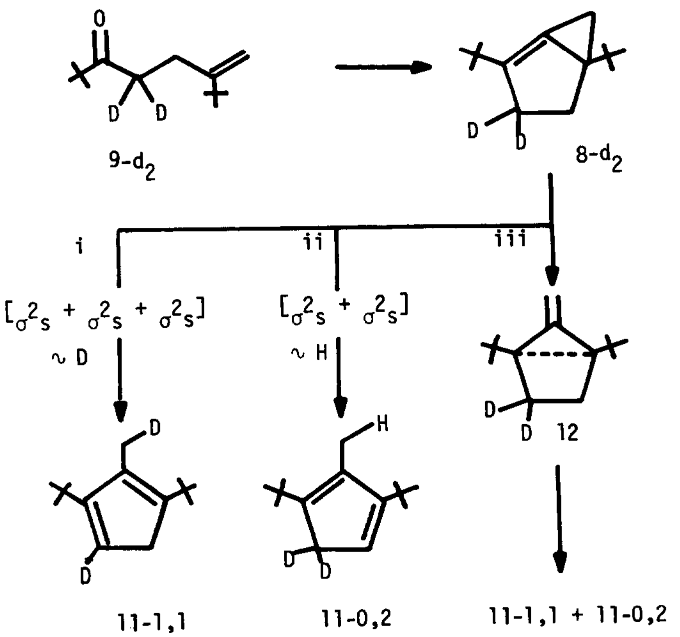
The incorporation of a second *t*-butyl group, as in the 2,5-di-*t*-butyl derivative 8, would be expected to decrease the dimerization rate sharply, because now both sites of the $[\sigma + \pi]$ reaction are sterically encumbered. Moreover, although thermal rearrangement of the bicyclo[3.1.0]hex-1-ene to the methylenebicyclo [2.1.0]pentane system 10 is a potential unimolecular escape route[2c,3] the substitution pattern should make this process much less favorable than usual because the rearranged product 10 embodies the severely destabilizing[12] eclipsed vicinal di-*t*-butyl interaction.

Treatment of ketone 9[13] with two equivalents of the lithium derivative of the phosphonate 5 at −30°C for 24h, followed by bulb-to-bulb distillation at 20°C gives a 63% yield of a mixture of monomeric ($C_{14}H_{24}$) hydrocarbons in addition to $\sim$20% of recovered ketone 9. The major component (90%) of the hydrocarbon product is 1,3-di-*t*-butyl-2-methylcyclopenta-1,4-diene (11), identified spectroscopically[14] and by independent synthesis[15].



For the astonishing rearrangement 8 → 11, we consider three mechanisms whose consequences differ when 11-d_2 is generated from the ketone 9-d_2: (i) an allowed D-shift via a $[_{\sigma}2_s + {_{\sigma}2_s} + {_{\sigma}2_s}]$ intramolecular reaction; (ii) an essentially unprecedented, forbidden $[_{\sigma}2_s + {_{\sigma}2_s}]$ 1,3-H-shift; (iii) formation of a symmetrical or effectively symmetrical intermediate (symbolized as 12, which could represent 10, the corresponding trimethylenemethane, or a rapidly equilibrating pair (8-3,3-$d_2 \rightleftharpoons$ 8-4,4-d_2), followed by H- or D- shift. The observed result, as determined by direct ^{2}HNMR on a sample of 11 as obtained from 95% enriched 9-d_2, shows the ratio of methyl to ring deuterium = 0.18. This is consistent with a mixed-mechanism, e.g., if k_i/k_{ii} = 18/82, but an alternative single mechanism is (iii), with k_H/k_D = 2.25.

Scheme IV



$\frac{\text{Me D}}{\text{ring D}}$	1.0	0.0	0.0 if $k_H >> k_D$ 0.33 if $k_H = k_D$

Regardless of which is correct, the hydrogen-shift reaction, occurring at or below 20°C, provides an unprecedented escape route for the bicyclo[3.1.0]hex-1-ene 8. The result suggests that even when dimerization is sterically retarded, these extremely unstable species can make use of normally inaccessible pathways in order to evade a monomeric existence.

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10. Major isomer (*3c* or regioisomer): Retention time on OV-17 GC column 27.5 m. ^{1}NMR (benzene-d_6/CCl$_4$, 270 MHz): δ2.87 (br m, 1H), 2.38 (d, 2H), 1.83-1.19 (m, 9H), 0.98 (s, 9H), 0.88 (m, 1H), 0.80 (s, 9H), 0.70 (m, 1H); ^{13}C NMR (CDCl$_3$, 67.88 MHz) δ144.1(s), 133.7(s), 62.1, 51.6, 38.3, 37.1, 36.4, 34.9, 33.1, 32.3, 31.0, 30.8, 27.8, 27.6, 25.6, 17.4 (pseudo-t). MS: m/e 272 (parent), 215 (base), 159, 145, 57. MS M_r 272.2501. Calcd. for $C_{20}H_{32}$: 272.2504.
11. Minor isomer (*3c* or regioisomer?): Retention time 32.5 m. ^{1}H NMR (benzene-d_6/CCl$_4$, 270 MHz): δ1.14 (s, 9H), 0.80 (s, 9H), 0.56 (m, 1H), 0.39 (m, 1H). Contamination with the major isomer prevented the assignment of other NMR resonances; MS: m/e 272 (parent), 259, 159, 145, 57 (base); MS M_r 272.2501. Calcd. for $C_{20}H_{32}$: 272.2504.
12. The steric strain energy in *cis*-1,3-di-*t*-butylethylene has been estimated by molecular mechanics calculations to be 11.6 kcal/mol: (a)Wiebenaga, E. H.; Bouwhuis, E. *Tetrahedron* 1969, *25*, 453; (b) Ermer, O.; Lifson, S. *ibid.* 1974, *30*, 2425.
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14. NMR (benzene-d_6, 270 MHz): δ5.9 (s, 1H, C_4), 2.75 (m, 2H, CH_2), 2.19 (m, 3H, CH_3), 1.27 (s, 9H), 1.19 (s, 9H); UV: λ_{max}234 (cyclohexane); MS: m/e 192 (M+), 177, 121 (base), 57. MS M_r 192.1882. Calcd. for $C_{14}H_{24}$ 192.1878.
15. From 2-methyl-3-*t*-butylcyclopent-3-en-2-one[16] and *t*-butyl lithium followed by gas chromatography (GC) to give an 80% yield of *11* and its two double bond shift isomers, which also are formed from pure *11* on GC.
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