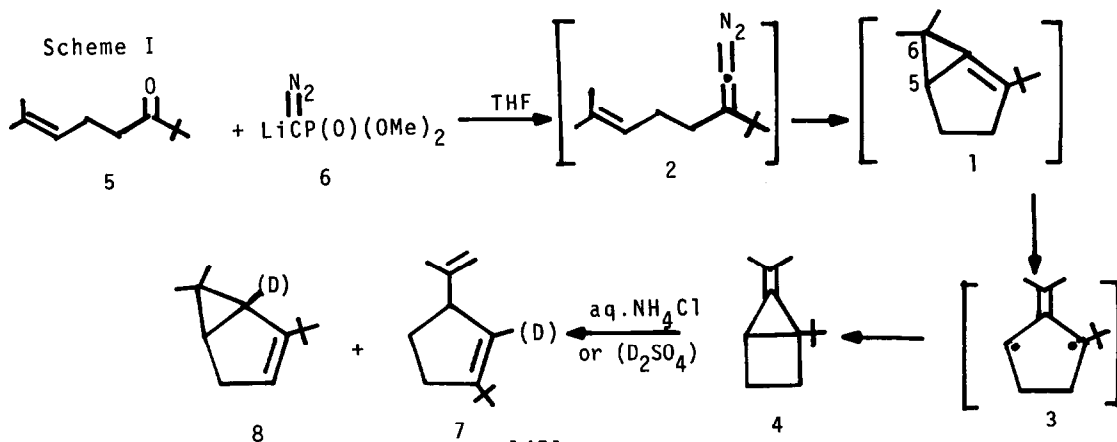# 1-t-BUTYL-5-ISOPROPYLIDENEBICYCLO[2.1.0]PENTANE

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Abstract: The title compound, synthesized by a carbenoid cyclization-rearrange-
ment route, is the most stable member of the bicyclo[2.1.0]pentane series yet
prepared.

The substitution pattern in 2-t-butyl-6,6-dimethylbicyclo[3.1.0]hex-1-ene
(1) should be unfavorable to the known[1-4] modes of dimerization of the bicyclo
[3.1.0]hex-1-enes because both the weak σ-bond (C_5-C_6) and the twisted π-bond
(C_1-C_2) are sterically shielded. Cleavage of the C_5-C_6 bond in 1, however,
should be more facile than in its relative lacking the 6,6-dimethyl substitu-
ents[2,3,4a]. We anticipated, therefore, that the ultimate products of reaction
leading to the very unstable 1 might well be derived from the trimethylenemethane
(TMM) biradical 3. The triplet state of this species might dimerize, like other
2-alkylidenecyclopentane-1,3-diyl triplets[5,6], whereas the singlet TMM might cy-
clize[3,7] to 1-t-butyl-5-isopropylidenebicyclo[2.1.0]pentane 4.

Scheme I shows the result of generating the bicyclo[3.1.0]hex-1-ene 1 by
a modification[4] of the Köbrich[1] vinylidene cyclization. Treatment of ketone 5[8]
with the lithium derivative of dimethyl diazomethylphosphonate 6 at −30° for 30h
in tetrahydrofuran (THF) followed by quenching with degassed aqueous NH_4Cl gives
no hydrocarbon products with mass 328, corresponding to $C_{24}H_{20}$, the dimers of 3.
Instead, the volatile fraction consists of 20% of recovered ketone 5 and 70% of
a 2:1 mixture of monomeric hydrocarbons 7 and 8, to which structures are assigned
on the basis of elemental composition, spectroscopic data, and in the case of
the major product 7, independent synthesis[9-11].
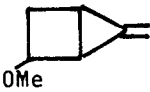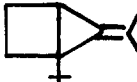

Scheme I

If the cyclization of Scheme I is repeated but the acidic work-up is omitted in favor of direct distillation of the products (25°C, 1 Torr), 1-t-butyl-5-isopropylidenebicyclo[2.1.0]pentane (4) can be isolated in 63% yield[13]. It reacts rapidly with 5% D_2SO_4 to give a 2:1 mixture of 7 and 8. Compound 7 incorporates the deuterium at the ring double bond position, a result that is explicable with a mechanism initiated by deuteration of the exocyclic double bond, cyclopropylcarbinyl → cyclopropylcarbinyl rearrangement[14], and fragmentation[15].

Compound 4 is extremely sensitive to atmospheric O_2, but in degassed benzene-d_6 solution it has remarkable thermal stability, remaining unchanged at room temperature for many hours. Even at 75°C, it decomposes only slowly, 15% of it surviving this temperature for 18 h. In contrast to the other 5-alkylidenebicyclo[2.1.0]pentanes[7,16], which decompose thermally to dimers by unimolecular rate-determining formation of a triplet TMM biradical, 4 gives the monomeric diene 7 as the principal product (75% yield, NMR analysis). Neither compound 8 nor dimeric products are observed in this reaction.

The observations place an upper limit of ∿2.9 X $10^{-5}s^{-1}$ at 75°C for any thermal unimolecular reaction of 4. This substance thus is by far the most stable member of the 5-alkylidenebicyclo[2.1.0]pentane family yet prepared. Table I shows the known[7,16] and estimated activation parameters for this series. If it is assumed that the hypothetical TMM dimer formation from 4 would have the same low Arrhenius pre-exponential term observed[7,16] for the other members of the group, the activation energy for unimolecular decomposition of 4 is at least 9.4 kcal/mol greater than that for the analog lacking the t-butyl group (entry 2). Since an alkyl substituent normally decreases the activation energy for C-C bond cleavage by about 2.5 kcal/mol[17], the t-butyl group actually may be said to strengthen the bridge bond of 5-isopropylidenebicyclo[2.1.0]pentane by at least 11.9 kcal/mol.

Table I. Thermal dimerization of 5-alkylidenebicyclo[2.1.0]pentanes.

Entry	Cpd	Ref.	Ea kcal/mol	log A A in s^{-1}	Threshold Temp, °C
1		16	12.6[b]	9.7[a]	−65
2		7,16	13.6	9.5	−40
3	OMe	16	16.9	9.8	+5
4		this work	>23[b]	9.7[a]	>+75

[a]Assumed by analogy to the average of A in entries 2 and 3.
[b]Calculated from the observed rate constant and assumed A-factor.

It seems likely that the origin of this effect is the destabilization of the triplet biradical **3** and its immediately preceding transition state. Formation of the triplet TMM **3**, a potential precursor of dimeric product, is made difficult by the severe steric clash between the t-butyl substituent and the syn methyl group in the planar configuration[18].

3
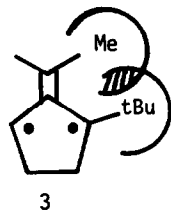
In the singlet manifold, stereomutation by torsion about the exocyclic bond is a well-known property of TMM biradicals derived by thermal cleavage of the bridge bond of 5-alkylidenebicyclo[2.1.0]pentanes[3,19]. For the 2 methoxy-5-syn-6-d derivative, $\Delta G^{\ddagger} \sim 17$ kcal/mol. A search for syn-anti interconversion of the allylic methyl groups on the NMR time scale in the case of the t-butyl compound **4** is negative. The minimum coalescence temperature of 348 K and an approximate equation[20] lead to $\Delta G^{\ddagger}$ for this process >18.6 kcal/mol.

These results suggest that achievement of the planar configuration of singlet biradical **3** may be difficult. Since the planar TMM seems to be responsible for the singlet cycloaddition chemistry of 5-isopropylidenebicyclo[2.1.0]pentane[7,21], markedly different chemical behavior of the 1-t-butyl-5-isopropylidene-derivative **4** is to be anticipated.

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9. Compound 8: Retention time on OV-17 5' X 1/4" column at 80°C 22.5m. MS m/e: 164 (parent), 149, 107 (base), 91, 57. MS M_r 164.1563. Calcd. for $C_{12}H_{20}$: 164.1565; NMR (CCl_4/benzene-d_6, 270 MHz) $\delta 4.97$ (s, 1H), 2.25 (AB q, $J = 8.5$, 2H), 1.58 (m, 1H), 1.17 (m, 1H), 0.99 (s, 9H), 0.97 (s, 3H), 0.73 (s, 3H).

10. Compound 7: Retention time 31.3m. MS m/e: 164 (parent), 149, 107 (base), 93, 91, 79. MS M_r 164.1563. Calc. for $C_{12}H_{20}$: 164.1565; NMR (CCl_4/benzene-d_6, 270 MHz) $\delta 5.17$ (m, 1H), 4.64 (s, 1H), 4.57 (s, 1H), 3.17 (br s, 1H), 2.23-1.95 (m, 3H), 1.58 (s, 3H), 1.53 (m, 1H), 0.99 (s, 9H).

11. Synthesis of 7: Reaction of 6,6-dimethylbicyclo[3.1.0]hexan-2-one[12] and t-butyl lithium followed by distillation of the product from oxalic acid.

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13. Compound 4: MS m/e: 164 (parent), 149, 107, 71, 57, 42 (base); MS M_r 164.1565. Calcd. for $C_{12}H_{20}$: 164.1565. ^{1}HNMR (benzene-d_6, 270 MHz): $\delta 2.30-1.97$ (m, 3H), 1.88 (s, 3H), 1.82 (s, 3H), 1.75-1.60 (m, 2H), 0.91 (s, 9H); ^{13}CNMR (benzene-d_6, 67.88 MHz) $\delta 128.9$ (obscured by solvent peaks), 116.0, 31.5, 27.7, 27.0, 23.9, 23.1, 22.6, 21.5, 20.6.

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15. Scheme I predicts that C_1 of 8 should bear deuterium, a feature of the mechanism that awaits the complete assignment of the HNMR spectrum.

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