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9-*tert*-Butyl-9-azabicyclo[3.3.1]nonan-3-one

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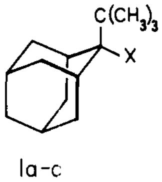
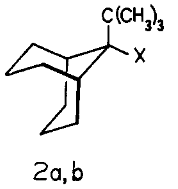
The title compound **7** has been synthesized by reaction of *tert*-butylamine with cycloocta-2,7-dienone. ^{13}C NMR and pK_a measurements of **7** show that the nitrogen atom of **7** is either a flattened pyramid or planar.

Six-membered cyclic compounds in chair conformations bearing axial *tert*-butyl groups are rare, as would be anticipated based upon the severe 1,3-diaxial steric interactions inherent in such conformations.[1] For instance, in order to avoid having an axial *tert*-butyl group, twist boat conformations are preferred for *trans*-1,3-di-*tert*-butylcyclohexane,[2a–c] *cis*-1,4-di-*tert*-butylcyclohexane,[2c,d] and *cis,trans*-1,3,5-tri-*tert*-butylcyclohexane;[2e] however, for both *cis*- and *trans*-1,2-di-*tert*-butylcyclohexane chair conformations with axial *tert*-butyl groups have been found to be important.[2f,g] Other carbocyclic examples are 2-*tert*-butyladamantane (**1c**),[3a] 2-*tert*-butyladamantan-2-ol (**1a**),[3b] and 9-*tert*-butylbicyclo[3.3.1]nonan-9-ol (**2a**).[3c] The corresponding *p*-nitrobenzoates **1b** and **2b** exhibit extraordinarily high solvolytic reactivities due to relief of strain during ionization.[3b–d]



1a-c

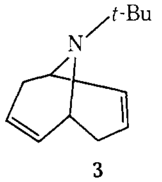


2a, b

a, X = OH
b, X = p-$NO_2C_6H_4CO_2$
c, X = H

Heterocyclic compounds[4,5] such as *cis*-2-alkyl-5-*tert*-butyl-1,3-dioxanes[4a] and 5-*tert*-butyl-1,3,2-dioxaphosphorins[5e] with axially disposed *tert*-butyl groups have also been described. In these molecules the severe 1-*tert*-butyl-3-hydrogen diaxial interactions present in carbocyclic compounds are absent.[6]

Recently Cuthbertson and MacNicol have reported the preparation of 9-*tert*-butyl-9-azabicyclo[3.3.1]nona-2,6-diene (**3**),[7] a compound in which the 1,3-diaxial interactions are diminished by flattening of the carbon bridges. We now report the synthesis and interesting properties of 9-*tert*-butyl-9-azabicyclo[3.3.1]nonan-3-one (**7**). For comparison we have also prepared the *N*-methyl, *N*-ethyl, and *N*-isopropyl analogues **4–6**. We were intrigued with the possibility of detecting a flattening of the nitrogen pyramid to relieve some of the steric



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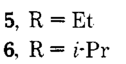
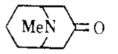
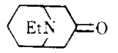
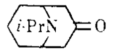
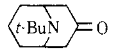


4, R = Me
5, R = Et
6, R = *i*-Pr
7, R = *t*-Bu

Table I. Carbon-13 Chemical Shifts of *N*-Alkylnorpseudopelletierines[a]

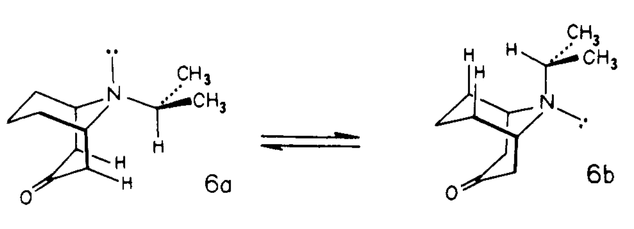
Registry no.	Compd	C-1	C-2	C-3	C-6	C-7	NCC	NCC
552-70-5	4 	55.8	41.8	210.0	29.7	16.1	41.1	
27092-59-7	5 	53.6	42.4	210.1	30.0	16.8	46.4	13.7
56258-85-6	6 	50.6	42.7	211.3	30.3	16.6	47.5	21.9
56258-86-7	7 	48.4	47.0	212.7	32.3	17.2	54.1	30.0

[a] $CDCl_3$ solution, downfield from internal Me_4Si.

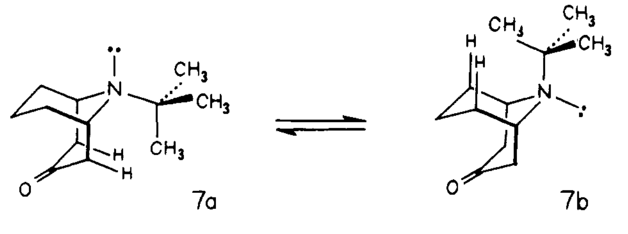
interactions of the axial *tert*-butyl group. Amine rehybridization as a consequence of geometric factors has been observed previously.[8]

The approach chosen for the synthesis of norpseudopelletierine derivatives **4–7** was the double Michael addition[9,10] of the appropriate primary amine to cycloocta-2,7-dienone[11] according to the procedures of Kashman and Cherkez.[10b] The reactions with methylamine, ethylamine, and isopropylamine gave high yields of amino ketones **4–6.** The reaction with *tert*-butylamine proceeded more slowly but gave mainly **7** with four or five minor products which were not investigated. The yield of **7,** after purification by preparative VPC, was 32%.

To evaluate the consequences of steric interaction in compounds **4–7,** we have relied on carbon-13 nuclear magnetic resonance spectroscopy[12] and pK_a measurements. Table I collects the chemical shifts for the various carbon atoms; shielding assignments were made on the basis of relative signal intensities and with the aid of coupled spectra.[13] Particularly revealing are the chemical shifts of the carbons 2(4) and 6(8), which endure only small (nominally 0.3 ppm) downfield shifts as two of the methyl hydrogens of pseudopelletierine (**4**) are sesquentially exchanged for methyl groups. Upon substitution of the final hydrogen by methyl to provide the *tert*-butyl derivative **7,** these carbons experience substantial downfield shifts (4.3 and 2.0 ppm). The origin of the observed shifts is certainly steric in nature, and the direction (downfield) and magnitudes of the shifts are in agreement with Stothers' results for δ steric effects.[14] The *N*-ethyl and *N*-isopropyl amino ketones **5** and **6** can adopt preferred conformations in which the methyl groups lie away from the axial hydrogens at carbons 2, 4, 6, and 8, as illustrated in **6a** and **6b.** When the last methyl group is added to give **7,** interaction of one of the methyl groups with the axial hydrogens becomes obligatory. To relieve the severity of this steric interaction, the *tert*-butyl group must be tilted away from a purely axial orientation, and the nitrogen pyramid must be flattened toward planarity. Probably the nitrogen atom is not completely planar (sp^2 hybridization) because of the repulsion of the nitrogen lone pair for the carbon ligands.[15] We draw attention to the fact that the shift increments per methyl group are greater, especially for *tert*-butyl amino ketone **7,** at carbons 2 and 4 than at carbons 6 and 8. Assuming that the deshielding effects (δ effect) of the methyl groups are approximately the same for the two types of conformations, this indicates that conformations with the *N*-alkyl groups axial to the piperidone rings are preferred to conformations with the *N*-alkyl group axial to the piperidine rings. This preference is probably the result of the presence of the trigonal carbon atom in the ketonic bridge, permitting greater flattening of that bridge and concomitant movement of the axial hydrogens at C-2 and C-4 away from the axial *N*-alkyl group.[15]



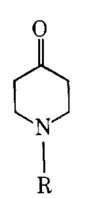
6a 6b



7a 7b

With each additional methyl group the likelihood of a γ-steric interaction between the bridgehead carbons and the methyl carbons also is enhanced. Such γ-steric effects[17] result in the signals of the bridgehead carbon atoms being shifted progressively upfield by approximately 2.5 ppm for each additional methyl group. This finding is in accord with the results reported by Grant and Cheney,[18] who have advanced a steric polarization mechanism to account for such γ upfield shifts. Additional support for this interpretation is available from the ^1H NMR data (see Experimental Section) for the bridgehead positions which undergo increasing deshielding as the number of methyl groups increases.[19]

The basicity data (Table II) for these bicyclic amines are also quite interesting. Usually the basicity of amines is enhanced by increasing β substitution. For example, the conjugate acids of trimethylamine, dimethylethylamine, dimethylisopropylamine, and dimethyl-*tert*-butylamine have pK_a values of 9.81, 10.16, 10.47, and 10.69, respectively.[21a] Recently measured pK_a values for the conjugate acids of 4-piperidone (**8a**), *N*-methyl-4-piperidone (**8b**), *N*-ethyl-4-piperidone (**8c**), and *N*-*tert*-butyl-4-piperidone (**8d**) are 8.6, 8.1, and 8.3, and 9.0, respectively.[21b]



8a, R = H
b, R = Me
c, R = Et
d, R = *t*-Bu

The pK_a values for the conjugate acids of amino ketones **4–7** measured in 35:64 (v/v) ethanol–water are near 7. Amino ketones **4–6** show the normal trend of increased basicity paralleling increased β substitution. However, *tert*-butyl amino ketone **7** is *less* basic than **5** and **6.** Such a decrease in basicity would be expected to accompany a change in nitrogen hybridization toward sp^2. Flattening of the nitrogen pyramid to

Table II. Basicity and UV Absorption Data for *N*-Alkylnorpseudopelletierines

Compd	pK_a'[a]	λ_{max} (ϵ)[b]	λ_{max} (ϵ)[b]
4	6.90	206 (1400)	246 (770)
5	7.24	208 (1780)	242 (825)
6	7.46	201 (2190)	246 (1020)
7	7.05	202 (1690)	230 (1580)[c]

[a] pK_a' of the conjugate acid determined in 36:64 (v/v) ethanol-water at 25.0 °C. [b] Pentane solution. [c] There is also a shoulder at ca. 265 nm.

relieve the interactions of the *tert*-butyl group with the axial hydrogens at carbons 2, 4, 6, and 8 would impart greater p character to the lone pair orbital. Protonation of the nitrogen lone pair would localize the lone pair to one side of the nitrogen atom and would require more s character in the N–H bond than in the original lone pair orbital, thus imparting more p character to the three N–C bonds. Because the protonated *tert*-butyl amino ketone experiences greater steric interactions than the free amine its pK_a is lowered.

The ultraviolet absorption spectra of compounds **4**–**6** are also of interest (Table II). The observed short wavelength maxima (ca. 205 nm) are typical of tertiary amines,[8b] and the long wavelength maxima (ca. 245 nm) are consistent with those found for other β-amino ketones in which σ-coupled charge transfer transitions give rise to similar values.[22] The *tert*-butyl derivative **7** behaves somewhat anomalously since it displays a maximum at 230 nm. Perhaps this indicates that on account of rehybridization at the nitrogen atom the lone pair of electrons is geometrically less suitable for through-bond coupling with the carbonyl group. Palacek[23] and Hudec[22b] have demonstrated that σ coupling is quite dependent upon the orientation of the lone pair of electrons relative to the carbonyl group.[23]

We are continuing active investigation of this and other hindered amines and hope to determine the precise geometry about the nitrogen atoms of sterically crowded amines.

Experimental Section

Melting points (taken on a Thomas-Hoover capillary apparatus) and boiling points are uncorrected. pK_a' determinations were carried out according to the procedure of Thomson[24] using an Instrument Laboratory Model 265 Electrometer. Ultraviolet spectra were recorded with a Cary Model 14 spectrophotometer. Infrared spectra were obtained on a Perkin-Elmer Model 457 spectrophotometer. Proton magnetic resonance spectra were obtained with a Varian Associates T-60 instrument. ^{13}C NMR spectra were measured with a JEOL JNM PS-100 spectrometer interfaced with a Digilab Nova 1200 computer. Vapor phase chromatographic analyses and collections were performed with a Varian Aerograph Model 90-P instrument employing a 0.25 in. diameter by 6 ft column packed with 5% SE-30 on Chromosorb G. Mass spectra were obtained on an Associated Electrical Industries MS-902 spectrometer. Elemental analyses were carried out by Spang Microanalytical Laboratory, Ann Arbor, Mich.

Pseudopelletierine (4). Method C of Kashman[10b] was followed. To a stirred solution of 2.92 g (0.0433 mol) of methylamine hydrochloride in 45 ml of absolute methanol at room temperature was added 4.6 g of anhydrous sodium carbonate, followed by 5.28 g (0.0433 mol) of cycloocta-2,7-dienone.[11] After 22 h VPC, NMR, and IR indicated that the reaction was 95% complete. Workup consisted of filtering the yellow mixture and concentrating to a semisolid, which was taken up in methylene chloride and filtered. The filtrate was extracted with 6 M aqueous HCl solution; the combined extracts were basicified, extracted with methylene chloride, and dried (Na_2SO_4), and the bulk of the solvent removed by atmospheric distillation using a 16-in. Vigreux column. The remainder of the solvent was removed on a rotary evaporator to provide 5.79 g of a yellow, waxy solid which was sublimed (52–54 °C, 0.25 Torr) to give 4.57 g (69%) of slightly yellow solid, mp 46–55 °C (lit.[10a] 62–64 °C). Analysis by VPC showed a single peak.

***N*-Ethylnorpseudopelletierine (5).** Method A of Kashman[10b] was used. To stirred solution of 1.22 g (0.0100 mol) of cycloocta-2,7-dienone[11] in 2 ml of methanol at room temperature was added through a serum cap by means of a syringe 0.5 g (0.73 ml, 0.0110 mol) of ethylamine. When an NMR spectrum of an aliquot indicated the absence of cyclooctadienone, the solution was concentrated on a rotary evaporator, and the liquid residue distilled (bp 62 °C, 0.07 Torr; lit.[23] 90–95 °C, 0.1 Torr) to afford 1.43 g (85%) of **5**. VPC analysis showed only one peak.

***N*-Isopropylnorpseudopelletierine (6).** The procedure used for the preparation of **5** was employed, except that 0.841 g (0.0069 mol) of cycloocta-2,7-dienone and 0.455 g (0.5 ml, 0.0076 mol) of isopropylamine were used to give 1.14 g (91%) of crude **6** which on VPC analysis showed only one peak. Samples for spectra, pK_a' determination, and analysis were obtained by preparative VPC: mp 57.5–59.5 °C; NMR ($CDCl_3$) 3.67 br, 2 H, 1.17 d (J = 6 Hz), 6 H; IR ($CHCl_3$) 1691 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 181 (45), 166 (100), 138 (53), 124 (61), 123 (23), 122 (26), 96 (36), 82 (30), 80 (46), 79 (28), 70 (26), 55 (28), 52 (25), 50 (26), 44 (31), 43 (40), 42 (38), 41 (77).

Anal. Calcd for $C_{11}H_{19}NO$: C, 72.88; H, 10.56; N, 7.73. Found: C, 72.90; H, 10.51; N, 7.82.

***N*-*tert*-Butylnorpseudopelletierine (7).** The procedure used for **5** was followed, substituting 0.85 g (1.22 ml, 0.0110 mol) of *tert*-butylamine for ethylamine. Preparative VPC afforded 0.620 g (32%) of liquid **7**: NMR ($CDCl_3$) 3.82 br, 2 H, 1.23 s, 9 H; IR (neat) 1700 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 195 (22), 180 (100), 96 (31), 82 (31), 43 (31), 41 (25).

Anal. Calcd for $C_{12}H_{21}NO$: C, 73.80; H, 10.84; N, 7.17. Found: C, 73.83; H, 10.88; N, 7.09.

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Registry No.—Cycloocta-2,7-dienone, 1073-76-3; isopropylamine, 75-31-0; *tert*-butylamine, 75-64-9.

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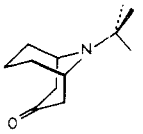
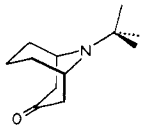
(15) The experimental data do not exclude the possibility that the nitrogen atom in **7** is planar. For example, the NMR spectrum can be explained on the

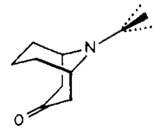
basis of an equilibrium of N-planar conformations **7c**, **7d** (and **7e**) with **7c** predominating over **7d**. Carbons 2 and 4 would be deshielded by the δ effect in **7c** and carbons 6 and 8 would be deshielded in **7d**. An attempt to resolve the question by low temperature ^{1}H NMR was unsuccessful. While some changes were evident, the spectra were not sharp enough to permit any rigorous conclusions.[16]



7c



7d



7e

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(19) It should be pointed out that the methyl groups do not experience shifts corresponding in magnitude to those of the carbons 2(4) or 6(8) and the bridgehead carbons. Such a lack of reciprocity of shifts for sterically interacting carbons is not uncommon.[20] In addition, the opposite directions of the γ and δ steric effects would tend to counteract one another in the case of the methyl groups. The shifts of the methyl groups observed as more methyl groups are added are typical of β substituent effects.[17]

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Terpenes and Related Systems. 16.[1] Fate of Representative Bicyclic Sesquiterpenes in Strong Acid Medium. A General Rearrangement of Hydroazulene Sesquiterpenenes to Decalin Types

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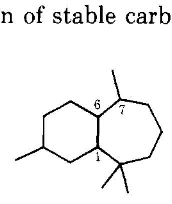
Rearrangement of several naturally occurring bicyclic sesquiterpenes of himachalane (**1**), guaiane (**2**), cadalane (**3**), and eudesmane (**4**) types has been studied in strong acid medium under stable carbocation conditions. The structures of the carbocations (**8** and **40**) formed from α- and β-himachalenes (**5** and **6**) and from selinenes (**38**), respectively, have been deduced from ^{1}H NMR spectral data. Quenching of these cationic solutions provides convenient preparation of conjugated dienes **9**, **10**, and **28**. A novel and general rearrangement of guaiane-type hydroazulenic sesquiterpenes to (+)-10-epizonarene (**22**), a naturally occurring heteroannular diene of the cadalane family, has been discovered. (−)-γ-Murrolene (**33**) has been found to rearrange stereospecifically to another heteroannular diene, (−)-zonarene (**34**), of cadalane type. Probable mechanisms for the rearrangements encountered in the present study are discussed.

Acid-catalyzed rearrangements of polyisoprenoids have been extensively investigated by organic chemists since the dawn of this century.[2] This high level of interest has been sustained by the unraveling of numerous unique rearrangements that are synthetically useful and mechanistically fascinating.[3] Furthermore, the recognition[4a–d] that cationic cyclizations play a key role in the biogenesis of isoprenoids has provided the impetus to mimic[4e,f] many of these rearrangements in the laboratory by generating appropriate carbonium ions. Isoprenoids in particular, as they contain tertiary carbon centers and double bonds, are highly amenable to deep-seated structural changes on creation of an electron-deficient site.[2–4] Over the years, a variety of media have been employed to study the acid-catalyzed rearrangements of terpenoid substrates. The recent advent of carbonium ion stabilizing solvents,[5–7] e.g., H_2SO_4, FSO_3H, etc., has opened new possibilities for deflecting the normal course of terpene rearrangements, under stable carbonium ion conditions.[5,6]

The dichotomy in the behavior of carbonium ions under varying acidity of the medium has been demonstrated in many cases. Perhaps the earliest example[8] in the field of isoprenoids is the conversion of camphor to β-camphorsulfonic acid in sulfuric acid and camphor-π-sulfonic acid in fuming sulfuric acid. Recently, Deno[9] and Sorenson[10] have extensively studied the rearrangements of monoterpenes camphene, fenchol, and borneol in sulfuric acid and fluorosulfonic acid and shown that stable cyclohexenyl cations are formed in this medium, in direct contrast[2,11,12] to their behavior in weakly acidic media. A similar dependence of the mode of rearrangement on the acidity of the reaction medium has been demonstrated by us[13,15,17,18] in the rearrangements of sesquiterpene hydrocarbons humulene[13,14] and longifolene[15,16] as well as abietic-type[17–19] diterpene resin acids. This ability of polyisoprenoids to undergo novel molecular rearrangements[9,10,13,15,17–20] in strong acid medium, under the conditions salubrious to the formation of stable carbocations, has encouraged us to in-



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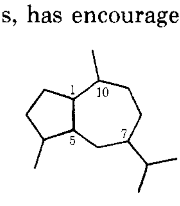

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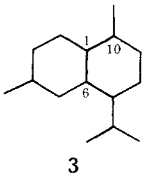

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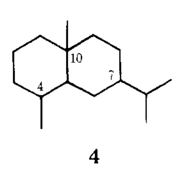

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