Adamantanone: Stereochemistry of its Homoenolization as shown by ^{2}H Nuclear Magnetic Resonance

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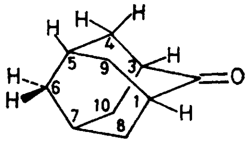
Summary With ^{2}H n.m.r. spectroscopy, it is established that adamantanone undergoes homoenolization with predominant *exo* β-proton exchange under conditions comparable to those required for a variety of polycyclic ketones.

SINCE Nickon and Lambert's initial discovery[1] that a ketonic carbonyl group can activate proton abstraction from carbon atoms more remote than the α-carbon through the formation of homoenolate anions, several examples of homoenolization in polycyclic systems have been described.[2] Somewhat surprisingly, however, under 'homoenolization conditions,' adamantanone (**1**) showed no exchange,[3] although the separation of β-carbon atoms from the carbonyl group is not greatly different in (**1**) from that in a variety of bicyclo[2,2,1]heptanone derivatives known to exhibit β-proton exchange. We report a re-examination of the homoenolization of (**1**) which establishes that (a) both α- and β-hydrogens undergo exchange and (b) the latter process involves the *exo*-hydrogens predominantly. The utility of ^{2}H n.m.r. spectroscopy for such studies is also illustrated.



(1)

To a solution of KOBu^t in Bu^{t}OD (99% deuteriated [H$_2$O] $< 0{\cdot}005$M) prepared by dissolving potassium metal in the alcohol, was added (**1**) to produce a solution 0·2M in ketone and 0·7M in base. Aliquot portions were sealed in glass tubes under nitrogen and heated for various times at 185°. After recovery of (**1**) by pentane extraction (90% yields), the recovered material was examined by mass spectrometry and ^{2}H n.m.r. spectroscopy. The results for four samples are listed in the Table, from which it is apparent that up to five deuterium atoms have been incorporated under these conditions.

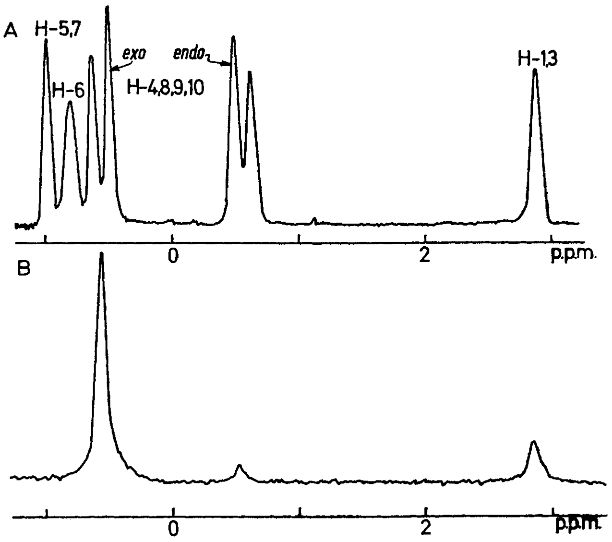


FIGURE. (A) 100 MHz ^{1}H n.m.r. spectrum of (**1**); (B) 15·4 MHz ^{2}H n.m.r. spectrum of [^{2}H$_n$]-(**1**) (213 h sample). Both spectra obtained for CHCl$_3$–C$_6$F$_6$ (4:1) solutions containing 0·17 equiv. of Pr(fod)$_3$; the scale is relative to Me$_4$Si.

Because of its high symmetry, (**1**) has only five types of nonequivalent protons, two of which are at β-positions (C-4, -8, -9, -10), *exo* and *endo* with respect to the carbonyl group. Since the chemical shifts of ^{2}H nuclei are the same as those of the corresponding ^{1}H nuclei, on a p.p.m. scale,[4] the ^{2}H n.m.r. spectra of the deuteriated materials were readily assignable. The spectra are simple with a single line for each nonequivalent deuteron. To obtain precise integrated intensities from the ^{2}H spectra, however, solutions containing Pr(fod)$_3$ as shift reagent were used. Typical spectra of (**1**) and [^{2}H$_n$]-(**1**) are shown in the Figure, from which it can be seen that the *endo*-β-protons were readily distinguished from the *exo*-β-protons by their greater upfield shift in the presence of Pr(fod)$_3$. Exchange preferentially involved the *exo*-β-hydrogens while smaller, but significant, deuterium incorporation occurred at the *endo*-β positions as well as at the bridgehead (C-1, -3). Integration of the spectra of the deuteriated samples by line-shape fitting, together with the total ^{2}H content measured by mass spectrometry, allowed the relative extents of ^{2}H incorporation to be calculated for these three sites of exchange (Table).

TABLE. Deuterium incorporation in (**1**)

(185°; Bu^{t}O$^-$–Bu^{t}OD).

		% ^{2}H by mass spectrometry[a]					% ^{2}H by ^{2}H n.m.r.[b]		
						Atoms D/ molecule	C-1(3)	C-4(8,9,10)	
Time/h	$^2H_1$	$^2H_2$	$^2H_3$	$^2H_4$	$^2H_5$			*endo*	*exo*
127	$26{\cdot}6_8$	$3{\cdot}8_0$	$0{\cdot}4_3$	—	—	0·356	5·0	1·6	29·0
213	$37{\cdot}2_5$	$10{\cdot}4_7$	$1{\cdot}4_7$	—	—	0·626	10·3	2·8	49·4
318	$39{\cdot}0_2$	$13{\cdot}0_0$	$1{\cdot}8_9$	$0{\cdot}1_4$	—	0·713	11·8	3·8	55·7
407	$39{\cdot}7_9$	$16{\cdot}3_0$	$3{\cdot}3_1$	$0{\cdot}7_3$	$0{\cdot}4_8$	0·876	16·9	4·0	66·7

[a] Using a Varian M-66 spectrometer at 30 eV ionization voltage. [b] Spectra obtained in the Fourier transform mode with a Varian XL-100-15 system operating at 15·4 MHz with noise decoupling at 100 MHz. Samples were examined as 15% solutions in $CHCl_3$–C_6F_6 (4:1).

generally applicable[6] and that the stereoselectivity is readily determined. This information is not provided by ^{13}C spectra which otherwise serve as useful monitors for ^{2}H incorporation.[2b,7] A further advantage of ^{2}H spectroscopy is the fact that low enrichment levels are readily measured.

A comparison of the rate of deuterium incorporation at the *exo*-β-positions in (**1**) with that for homoenolization of (**2**) indicates that the former process is *ca.* 10^2 times slower.

During our homoenolization studies it has become apparent that the rates are remarkably sensitive to the water content

From these data it was found that *exo*-β-hydrogen exchange occurs *ca.* 15 times faster than *endo*-β exchange and approximately twice as fast as bridgehead exchange. The stereoselectivity of homoenolization (*i.e.* β-exchange) in this system, therefore, is the same as that deduced for camphenilone (**2**) from the homoketonization of 1-acetoxynortricyclene.[5] With ^{2}H n.m.r. spectroscopy, however, this stereochemical information is directly available for the ketone undergoing exchange. We have employed this approach with a variety of systems to show that it is

of the alcohol used. The rate-depressing effect of water for Bu^{t}O$^-$–Bu^{t}OH has been discussed by Cram *et al.*[8] Each batch of [O-$^2H_1$]alcohol was therefore tested by Karl Fisher titration before use. We prepared KOBu^t *in situ* to avoid the complications attendant on its use.[9]

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