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ADDITION OF ACETIC ACID TO BICYCLO[2.2.1]HEPTA-2,5-DIENE CATALYZED BY PLATINUM COMPLEXES

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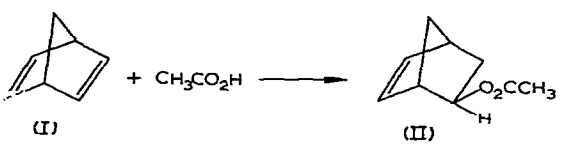
SUMMARY

Selected platinum complexes catalyze the stereoselective addition of acetic acid to bicyclo[2.2.1]hepta-2,5-diene to form *exo*-5-acetoxybicyclo[2.2.1]hept-2-ene. Experiments with acetic acid-O-d_1 have shown that the reaction involves a highly stereoselective skeletal rearrangement of the substrate to produce *syn*-7-deuterio-*exo*-5-acetoxybicyclo[2.2.1]hept-2-ene. A possible mechanism is presented.

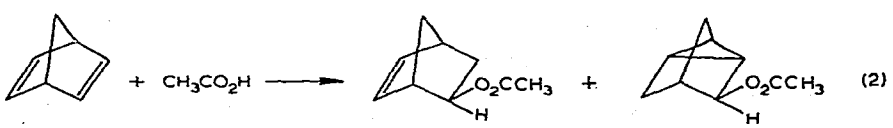
RESULTS AND DISCUSSION

We have discovered that selected platinum complexes catalyze the stereoselective addition of acetic acid to bicyclo[2.2.1]hepta-2,5-diene (I) to form *exo*-5-acetoxybicyclo[2.2.1]hept-2-ene (II) (eqn. 1).



(I) (II) (1)

It is well known that acetic acid will add readily to (I) in the presence of an added strong protonic acid[1,2] or slowly when heated in the absence of any catalyst[3] to form (II) and the nortricyclyl acetate (III) (eqn. 2).



(I) (II) (III) (2)

However, experiments with acetic acid-O-d_1 have shown the platinum-catalyzed reaction to be unique. Unlike the acid-catalyzed or uncatalyzed reactions, it involves a highly stereoselective skeletal rearrangement to *syn*-7-deuterio-*exo*-5-acetoxybicy-

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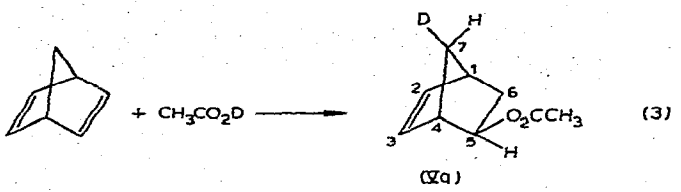
clo[2.2.1]hept-2-ene (double-bond and deuterium are *syn*) (eqn. 3).



(3)

(Xa)

Before discussing the mechanistic implications of the deuterium labeling experiments, a general description of the reaction seems in order, since it is a new example of homogeneous metal catalysis. In the absence of a catalyst, equimolar amounts (250 mmoles) of acetic acid and (I) in 20 ml of benzene underwent only a 1.2% conversion at 120° in 17 hours. The olefinic ester, (II), was the main product along with a trace of (III). On the other hand, under the same conditions with 0.5 mmole of tris-(triphenylphosphine)platinum(0)[4] present, the conversion of (I) increased to 46% and (II) was formed in 95% yield* along with a 5% yield of unidentified dimers ($C_{14}H_{16}$) of (I); (III) was not detected. Other platinum catalysts gave somewhat reduced conversions of (I) but with similar yields (Table 1). The conversion of (I) was higher, 66%, with $(Ph_3P)_3Pt$ as the catalyst in the absence of benzene. Total conversion of (I) was achieved by increasing the reaction time, which indicates that the catalysts remain active over extended periods.

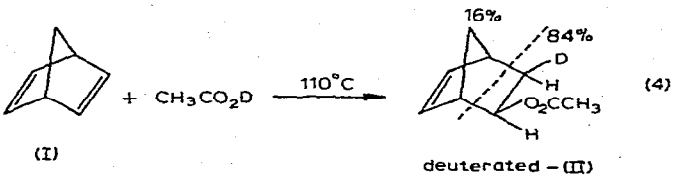
TABLE 1

Catalyst	*Conversion of (I) (%)*
None	1.2
$(Ph_3P)_3Pt$	46
$(Ph_3P)_2Pt(O_2CCH_3)_2$[5]	14
$(Ph_3P)_2Pt(O_2CCF_3)_2$[5]	29
$(Ph_3P)_2PtO_2$[6]	11

When the uncatalyzed reaction was carried out at 175° rather than 120°, the conversion of (I) increased from 1.2% to 44% with the accompanying formation of appreciable amounts (7–9%) of the nortricyclyl ester (III). However, with $(Ph_3P)_3Pt$ present at 175°, only a trace of (III) was formed and the by-product (8%) consisted of dimers of (I): conversion of (I) to mainly (II) was total.

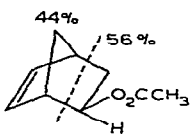
Platinum complexes appear to be the best catalyst systems. $(Ph_3P)_2Ni(CO)_2$, $(Ph_2PCH_2CH_2PPh_2)Ni(CO)_2$, $(Ph_3P)_4Ni$, $(cyclooctene)_2Ir(CO)Cl$ and $Fe_3(CO)_{12}$ were also tested but found to be inactive. $(Ph_3P)_3RhCl$ gave mainly dimers of (I). $(Ph_3P)_4Pd$ appeared to polymerize (I) although low yields of (II) were produced. It was previously shown that the uncatalyzed addition of acetic acid-O-d_1 to (I) produces, in low yield, largely deuterated-(II) with most (84%) of the deuterium in the *exo*-6-position *cis* to the *exo*-5-acetate group (eqn. 4)[3]. Some scrambling (16%)

* Yields based on converted (I).



occurred, placing the deuterium in the segment of the molecule on the left of the dotted line in eqn. (4). The location and stereochemical configuration of the deuterium in (II) were determined via mass spectrometric[7,8] and NMR[7] analyses, respectively. We have obtained roughly similar results, Table 2, for the uncatalyzed addition of the acetic acid-O-d_1 to (I) under the conditions described above for the platinum-catalyzed reaction. A *cis* 1,2-addition appears to predominate for the uncatalyzed reaction.

When the addition of acetic acid-O-d_1 is catalyzed by sulfuric or perchloric acids, the product is predominantly the nortricyclyl ester (III): the ratio of (II)/(III) typically is 19/81. Extensive deuterium scrambling occurs so that (II) has a deuterium distribution in the indicated segments roughly as follows:



(4a)

The deuterium in the 6-position is mainly *cis* to the acetate moiety.

In contrast to the above acid-catalyzed or uncatalyzed reactions, the $(Ph_3P)_3$-Pt- or $(Ph_3P)_2Pt(O_2CCH_3)_2$-catalyzed addition of acetic acid-O-d_1 to (I) selectively

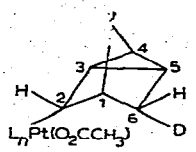
TABLE 2

ADDITION OF ACETIC ACID-O-d_1 TO BICYCLO[2.2.1]HEPTA-2,5-DIENE

Catalyst (mmoles)	*Temp. (°C)*	*Reaction time (h)*	*Conv. (%)*	*Selectivity*[a]			*Deuterium content*[b]	
				(II)	*(III)*	$C_{14}H_{16}$, *dimers*[b] *of (I)*	*(II), total for all positions*[c]	*(II), for 1,2,3,4 and 7 positions*[d]
$(Ph_3P)_3Pt$ (0.5)	120	17	31	95		5	11% d_0 88% d_1 1% d_2	15% d_0 85% d_1 Trace d_2
$(Ph_3P)_2Pt$-$(O_2CCH_3)_2$ (0.5)	120	17	14	96	Trace	4	9% d_0 91% d_1 0% d_2	16% d_0 84% d_1 0% d_2
None	150	17	21	87	9	4	33% d_0 67% d_1 0% d_2	95% d_0 5% d_1 0% d_2

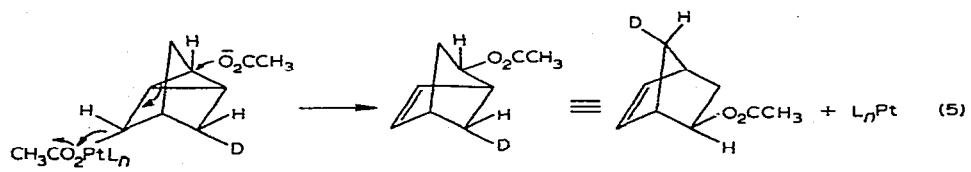
[a] See text for structures of (II) and (III). [b] Determined mass spectrometrically. [c] Deuterium content of the whole molecule in contradistinction to footnote *d*. Throughout the text the specific deuterium-labelled product *syn*-7-deuterio-*exo*-5-acetoxybicyclo[2.2.1]hept-2-ene is noted as compound (Va). [d] These deuterium values are those for the segment of the molecule on the left side of the dotted line as shown in eqn. (4).

produces *syn*-7-deuterio-*exo*-5-acetoxybicyclo[2.2.1]hept-2-ene, [eqn. (3), Table 2]. The details of the structure assignment are given in the Experimental Section. In this particular experiment no benzene solvent was used. The product was 85–90% monodeuterated, with the remaining material being mainly undeuterated. Interpretation of these results is difficult; however, the stereochemical results may be explained by invoking (IV) as a transient intermediate although it has not been isolated. Attack of acetic acid or acetate ion on the 4-position of (IV) would induce a *trans*-displacement



(IV) (4b)

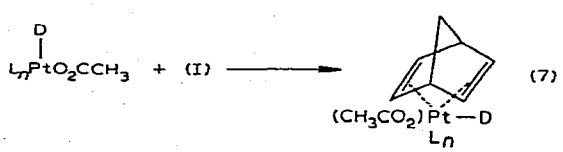
of the platinum moiety to produce *syn*-7-deuterio-*exo*-5-acetoxybicyclo[2.2.1]hept-2-ene and the original catalyst (eqn. 5). A nucleophilic attack at the 5-position would

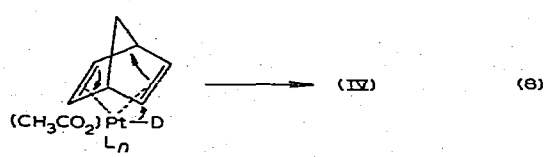


have to result in a *cis*-displacement of the platinum moiety, which is probably less favourable. The latter path would produce the unobserved addition product with deuterium vicinal to the acetate group.

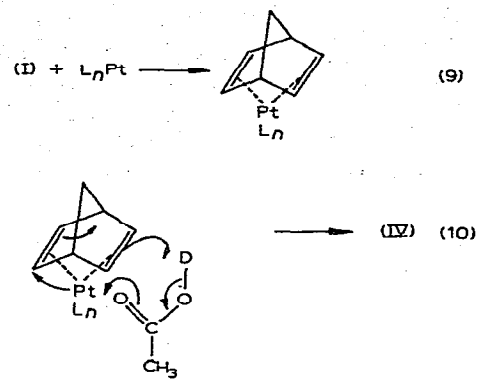
Three possible paths are suggested, without proof, for the formation of the transient intermediate (IV), with $(Ph_3P)_3Pt$ as the catalyst. Path A involves the oxidative addition of acetic acid to $(Ph_3P)_3Pt$ to form a Pt^{II} hydride (eqn. 6), which

Path A

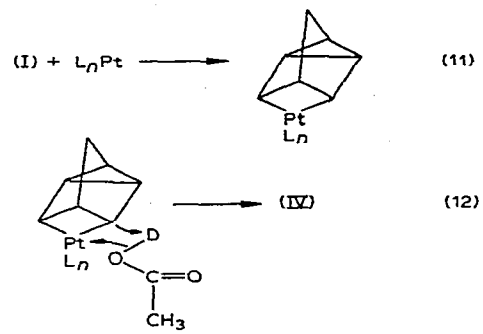




Path B



Path C



in turn coordinates with (I) (eqn. 7) and transfers the hydride atom to the *endo* position of (I) to form (IV) (eqn. 8). We do not favor this path because $(Ph_3P)_3Pt$ in refluxing (118°) acetic acid was not converted to the Pt^{II} hydride in the absence of air the $(Ph_3P)_3Pt$ being recovered unchanged. Path B seems most likely: here the coordinated platinum undergoes oxidation as the hydrogen on the acetic acid is transferred to the *endo* position to form (IV) (eqn. 10). In Path C, (IV) could be formed via acetolysis of a platinum–carbon bond; this possibility cannot be excluded. Similar mechanisms can be written for reactions catalyzed by bis(triphenylphosphine)-platinum(II) acetate.

EXPERIMENTAL SECTION

Materials

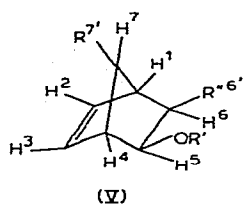
The bicyclo[2.2.1]hepta-2,5-diene (I) purchased from Matheson Coleman and Bell, was distilled before use and stored under nitrogen. Tris(triphenylphosphine)-platinum(0)[4], bis(triphenylphosphine)diacetatoplatinum(II)[5], bis(triphenylphosphine)bis(trifluoroacetato)platinum(II)[5], tris(triphenylphosphine)chlororhodium(I)[9], tetrakis(triphenylphosphine)palladium(0)[10], tetrakis(triphenylphosphine)nickel(0)[11] and chlorocarbonylbis(cyclooctene)iridium(I)[12] were prepared as described in the literature or with minor variations. Dicarbonylbis(triphenylphosphine)nickel(0) and dicarbonyl[1,2-bis(diphenylphosphino)ethane]nickel(0) were used as purchased from Strem Chemicals.

exo-5-Acetoxybicyclo[2.2.1]*hept-2-ene* (*II*). An 85-ml autoclave was flushed with nitrogen and charged with 46 g of bicyclo[2.2.1]heptadiene, 30 g of glacial acetic acid and 1.0 g of tris(triphenylphosphine)platinum(0). The mixture was sealed under a nitrogen atmosphere and stirred and heated at 120° for 64 h. Analysis of the liquid product by GLC showed a nearly 100% conversion to a mixture containing 95% *exo*-5-acetoxybicyclo[2.2.1]hept-2-ene (II) and a small amount (5%) of mixed bicyclo-[2.2.1]heptadiene dimers.

endo-5-Acetoxybicyclo[2.2.1]*hept-2-ene.* This compound was prepared from freshly distilled cyclopentadiene and vinyl acetate as described by Alder and Rickert[13]. Analysis by GLC indicated that there was a 40% yield of *exo*-5-acetoxybicyclo-[2.2.1]hept-2-ene and *endo*-5-acetoxybicyclo[2.2.1]hept-2-ene in a molar ratio of 22/78. Fractional distillation with a spinning-band column produced several cuts of about the same boiling point, 89°/31 mmHg. The major component of the purest (>90%) fraction was 5-*endo*-acetoxybicyclo[2.2.1]hept-2-ene. This structure was confirmed by NMR spectroscopy since the chemical shift of the *exo*-5-proton (5.2 ppm) is downfield from that of the *endo*-5-proton (4.5 ppm)[7]. Comparative GLC emergence times and sample "spiking" experiments* indicated that the isomer in the smallest amount (*exo*-acetoxy) corresponded to that produced in the platinum-complex-catalyzed addition of acetic acid to bicyclo[2.2.1]heptadiene. This, therefore, shows that the product from the platinum-catalyzed addition is the *exo*-acetoxy isomer.

Structure assignment for syn-7-deuterio-exo-5-acetoxybicyclo[2.2.1]*hept-2-ene*

After equimolar amounts (250 mmoles) of acetic acid-O-d_1** and bicyclo[2.2.1]-heptadiene had been heated at 120° for 17 h in the presence of 0.5 mmole tris(triphenylphosphine)platinum(0), GLC analysis of the product showed a 31% conversion of (I) to *exo*-5-acetoxybicyclo[2.2.1]hept-2-ene (95% yield). The liquid product was distilled and a fraction boiling at 86°/30 mmHg was used for mass spectrometric and NMR studies.



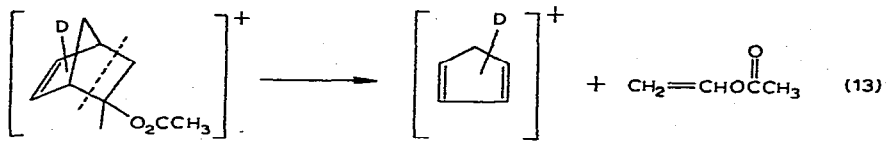
(V)

(Va) R′=CH_3 C(O)–, R7′=D, R″=H
(Vb) R′=H, R7′=D, R″=H
(Vc) R′=H, R7′=H, R″=H
(Vd) R′=CH_3 C(O)–, R7′=H, R″=D
(Ve) R′=H, R7′=H, R″=D

An examination of the mass spectrum of the deuterated *exo*-acetate product showed the deuterium to be essentially all (96.6%) in the cyclopentadiene ion, formed via a retrograde Diels–Alder fragmentation, eqn. (13), which occurs in the mass spectrometer (see Table 2):

* By "spiking" we mean the introduction of some of the authentic material into the product before GLC examination.

** The acetic acid-O-d_1 used was purchased from Bio-Rad Laboratories: the labeled position was 99.2% deuterium according to NMR data.



(13)

This fragmentation pattern has been used previously[7] as a diagnostic tool to locate deuterium in the two segments of the molecule. This evidence eliminates positions 6, 6′ and 5 [see structure (V) above] from consideration as sites for the deuterium; therefore, only positions 1, 2, 3, 4, 7 and 7′ are possibilities.

Because of interference from the methyl-proton resonance in the NMR spectrum, samples of both the deuterated and the undeuterated acetate were hydrolyzed ($NaOH-H_2O/CH_3OH$, room temperature) to the respective alcohols for further analysis. Sublimation afforded the purified white waxy deuterated alcohol, (Vb), and the undeuterated alcohol, (Vc).

The NMR studies were carried out on the above resultant alcohols with a Varian HR-100 spectrometer. Partial confirmation of the mass spectral evidence cited above was found when the NMR spectrum, see Fig. 1, of the deuterated alcohol, (Vb), still contained the signal (3.8 ppm) from the *endo* proton, H^5, α to the oxygen, which appears as a doublet of doublets where the coupling constants are: J_{5-6} 6.3 Hz, $J_{5-6'}$ 2.5 Hz. Protons 6 and 6′ (1.3 and 1.55 ppm), Figs. 1 and 2, appear as an AB quartet as indicated in Fig. 2A, where $J_{6-6'}$ is 11.3 Hz. The lower half of the quartet is split by proton 5 where J is 6.3 Hz and hence is assigned to proton 6. Proton 6′ shows coupling to protons 5 and 1 and when either proton 1, Fig. 2B, or proton 5, Fig. 2C, is

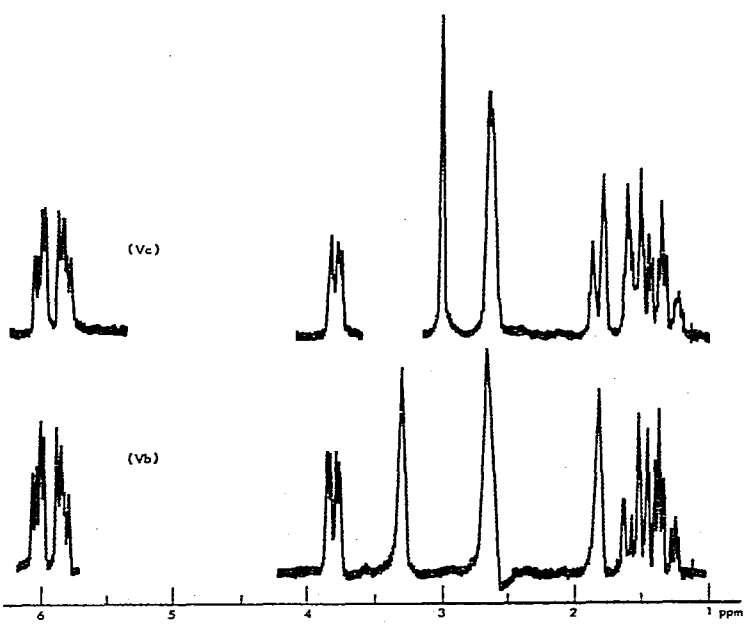


Fig. 1. NMR 100 MHz spectra of *syn*-7-deuterio-*exo*-5-hydroxybicyclo[2.2.1]hept-2-ene, (Vb), and *exo*-5-hydroxybicyclo[2.2.1]hept-2-ene, (Vc), in hexadeuterobenzene.

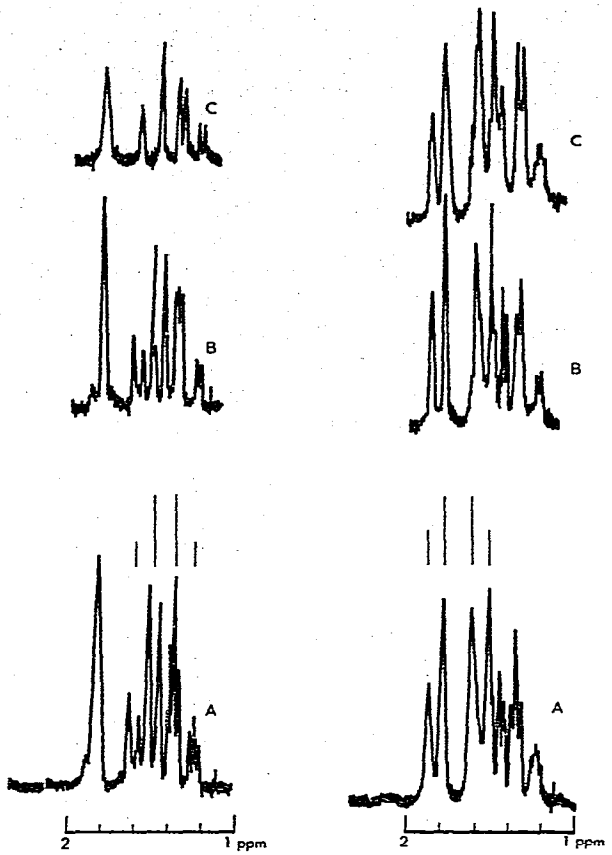


Fig. 2. *syn*-7-Deuterio-*exo*-5-hydroxybicyclo[2.2.1]hept-2-ene, (Vb).

Fig. 3. *exo*-5-Hydroxybicyclo[2.2.1]hept-2-ene, (Vc).

irradiated, simple AB quartets appear from which it is found that again $J_{5-6'}$ is 2.5 Hz and $J_{1-6'}$ is 2.7 Hz. Irradiation of the bridgehead protons 1 and 4 at 2.7 ppm also produces a simple AB quartet for protons 2 and 3 (not shown) where J_{2-3} is 6.5 Hz. The signal at 3.3 ppm, Fig. 1, (Vb), is due to the hydroxyl proton; the position of this signal is concentration dependent and is at 3.0 ppm in Fig. 1, (Vc). The above coupling constants are in agreement with earlier reports see Table 3.

Therefore, all the peaks in the spectrum of the deuterated alcohol, Fig. 1, (Vb), have been accounted for with the exception of the singlet at 1.82 ppm. This, then, is the signal corresponding to a proton at either 7 or 7'. In the undeuterated sample this singlet is half of an AB quartet, $J_{7-7'}$ is 8 Hz, and the other methylene bridge proton is to be found in the upfield multiplet at 1.55 ppm [see Fig. 1, (Vc) or Fig. 3A]. It is known[14] that a proton in the 7' position would be significantly coupled (2–4 Hz) to the *endo* protons 5 and 6. However, the only peak assignable is a singlet, therefore, the deuterium is in the 7' position. This is also consistent with the above assigment for protons 5 and 6. Furthermore, one would expect a proton that is above a double bond, as would be the one at 7', to be shifted upfield and one adjacent to an oxygen atom, as in

TABLE 3

OBSERVED COUPLING CONSTANTS FOR *exo*-5-ACETOXYBICYCLO[2.2.1]HEPT-2-ENE

Coupling constant	*Observed (Hz)*	*Literature (Hz)*	*Ref.*
J_{2-3}	6.5	5.6–5.9	14b
$J_{1-6'}$	2.7	2.9–4.3	14b
$J_{7-7'}$	8.0	8.9–9.7	14b
J_{5-6}	6.3	6.8–7.7	14b, d
$J_{5-6'}$	2.5	2.1	14d
$J_{6-6'}$	11.3	12.0	14e
$J_{1-2}=J_{3-4}$	3.0	3.6–3.8	14b

7, to be shifted downfield. This is consistent with the above assignment for the alcohol. Consequently, the correct structure for the orginal deuterated acetate in question must be (Va) (eqn. 3).

A firm confirmation of the above structural assignments was obtained by a detailed NMR analysis employing lanthanide-shift reagent. As this latter NMR study is part of an extensive investigation into the use of lanthanide shift reagents, it will be reported separately in a forthcoming paper by C.A. Reilly and E. F. Magoon.

exo-6-Deuterio-exo-5-acetoxybicyclo[2.2.1]*hept-2-ene*

Equimolar amounts (250 mmoles) of bicyclo[2.2.1]heptadiene and acetic acid-O-d_1 were heated together in a small autoclave for 17 h at 150° to give a 21% conversion to *exo*-5-acetoxybicyclo[2.2.1]hept-2-ene (87%), nortricyclyl acetate (9%) and bicycloheptadiene dimer (4%). This reaction unlike those carried out with a catalyst present, yields the acetate with the deuterium mostly in either the 5 or 6 position (mass spectroscopy). Even though the sample of *exo*-5-hydroxybicyclo[2.2.1]hept-2-ene was contaminated with 8% of the nortricyclyl alcohol, the NMR spectrum showed the deuterium to be in the *exo*-6-position, (Ve). This was concluded from the fact that the quartet from proton 5 (3.8 ppm) in the undeuterated alcohol collapsed to a doublet with a coupling constant of about 6.5 Hz (J_{5-6} 6.3 Hz and $J_{5-6'}$ 2.5 Hz), indicating that the proton at 6′ had been substituted.

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