Tetrahedron Vol. 36, pp. 2105 to 2111
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0040-4020/80/0715-2105/$02.00/0

STUDIES IN SESQUITERPENES—LVI†

ISOLONGIFOLENE (Part 7)‡: MECHANISM OF REARRANGEMENT OF LONGIFOLENE TO ISOLONGIFOLENE—II

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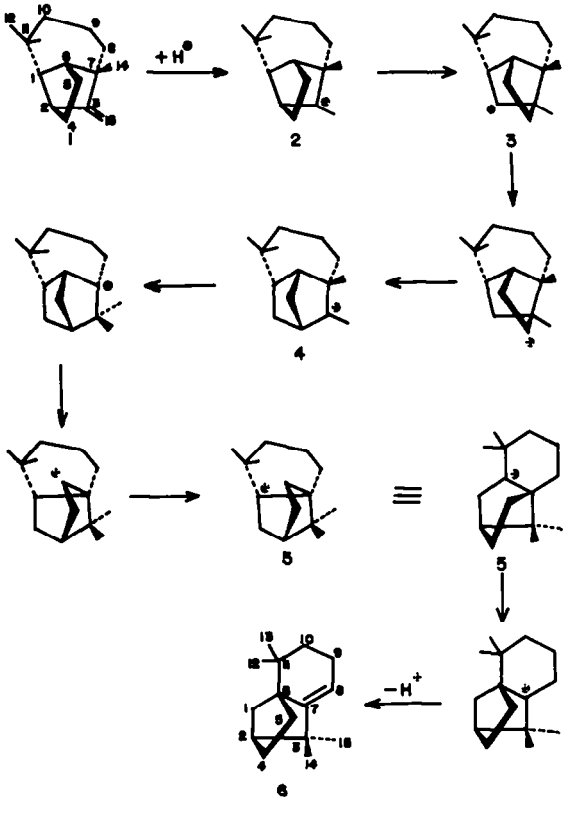
(*Received in UK* 19 *April* 1979)

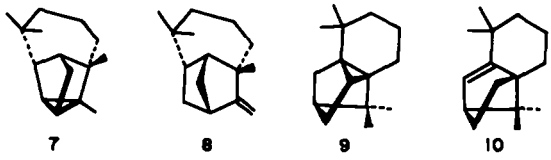
Abstract—The question of possible neutral intermediates which may lie on the reaction pathway in going from longifolene to isolongifolene has been investigated using BF_3·Et_2O–AcOD and D_3PO_4–dioxane, as reagents. It has been found that longicyclene is not an obligatory intermediate. The mode of cleavage of cyclopropane ring in longicyclene has been investigated.

IN THE preceding communication, we briefly outlined the problem of the mechanism of longifolene (**1**) to isolongifolene (**6**) rearrangement, and presented evidence in favour of the *exo exo* Me migration pathway (Scheme 1), as originally suggested by Berson *et al.*[1] The general question of possible neutral intermediates, which may lie on the reaction pathway, and specifically, the suggestion of McMurry[2] implicating longicyclene (**7**),[3] *via* **4**, in the rearrangement, was deferred. This aspect forms the subject matter of the present communication.



Scheme 1

An inspection of Scheme-1 reveals that if one considers the possibility of equilibration of the tertiary carbonium ions with the corresponding olefin (1,2-elimination) or cyclopropane (1,3-elimination),[4] there are then, besides longicyclene (**7**), at least three more compounds (**8**, **9**, **10**), which may



conceivably lie on the reaction pathway from longifolene to isolongifolene. If one carries out the isomerisation of longifolene in presence of a deutero-acid, then additional deuterium should get incorporated at certain specific sites (Scheme-2) which, in turn, should reveal if **7**, **9** and/or **10** are reaction intermediates. Specifically, the absence of any deuterium at C-1/C-2 would render McMurry's suggestion untenable. It may be noted that intermediacy of **8** cannot be probed by this method.

RESULTS AND DISCUSSION

Rearrangement of longifolene with BF_3–Et_2O–AcOD *and location of deuterium label.* Exposure of longifolene to BF_3·Et_2O–AcOD (30°, 20 min) generated deuterated isolongifolene having species up to 7 deuteriums (Table 1) as revealed by mass spectrometry. PMR spectrum of the product showed significant loss of the vinyl proton (5.14 ppm) and two (0.95 and 1.04 ppm) of the four Me group absorptions. To displace vinylic deuterium as well as any other possible labile deuterium by hydrogen, the product was treated with BF_3·Et_2O–AcOH (30°, 20 min) twice, when

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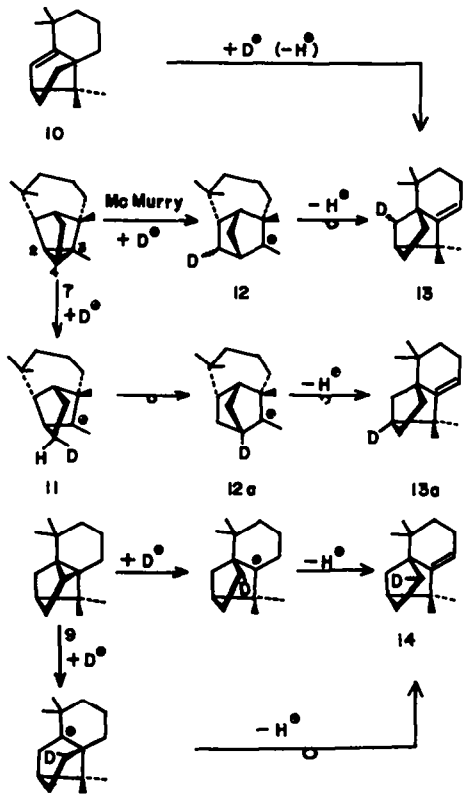


Scheme 2

the vinylic proton was almost fully regenerated without any significant effect on any other absorption (PMR) (Table 1). To confirm that isolongifolene, when exposed to BF_3·Et_2O–AcOD under the same conditions, incorporates deuterium to any significant degree only at the vinylic C(8), isolongifolene was treated with this reagent and the product, then, exposed to BF_3·Et_2O–AcOH, and both materials examined by mass spectrometry. The data (Table 1) fully bear out the contention that isolongifolene under the conditions of rearrangement, incorporates low amounts of deuterium and that too almost wholly at the vinylic C(8).

To decisively locate the sites of deuterium incorporation, it appeared worthwhile to probe each of the non-quaternary carbons for any deuterium label.

Deuterated isolongifolene, obtained as above, on catalytic oxidation (O_2/cobalt naphthenate)[5] gave unsaturated ketone **15**-d_x. This compound, as well as the product resulting after its exposure to aqueous ethanolic NaOH showed by mass spectrometry that there has been no loss of deuterium (Table 2). Furthermore, the unsaturated ketone **15** displays in its mass spectrum an important (83%) ion at *m/e* 162, which can reasonably[6] be assigned to the fragment **21** (Scheme-3); electron impact induced fragmentation of **15**-d_x generated a cluster of ions corresponding to this fragmentation, and having *m/e* and relative intensities consistent with no loss of deuterium. These results, thus, dictate that carbons 9, 10, 12, 13 carry no deuterium.

Compounds **16**, **17**, **18**, **19** appeared most appropriate for detecting any deuterium label at any of the remaining non-quaternary carbons. These derivatives were prepared from deuterated isolongifolene (as obtained by the BF_3·Et_2O–AcOD method) by following procedures disclosed earlier[7] and the compounds examined by mass spectrometry. From the results summarised in Table 2, it is obvious that no deuterium is lost in the formation of these compounds and in the case of **19**, also during its subsequent exposure to aqueous alkali. Furthermore, in the PMR spectrum of **16**-d_x, the signal due to the olefinic proton at 5.70 ppm is intact and appears as a doublet with the same coupling constant (J = 3.5 Hz) as in the non-deuterated **16** and hence, both C(1) and C(2) carry H atoms. Thus, from these data, it is clear that there can be no deuterium on carbons 1, 2, 4 and 5 and, that the entire deuterium label must be restricted to the two Me's on C(3)† (besides, of course, some labile deuterium at vinylic carbon).

The above results clearly preclude the involvement of the various possible intermediates considered earlier (Scheme-2) and specifically demonstrate that, under the reaction conditions investigated, the suggestion of McMurry[2] implicating longicyclene (**7**) is untenable. As stated earlier, the intermediacy of **8** cannot be proved by the present approach. The results are fully consistent with Scheme-1, when considered along with the racemization pathway[5a,7] and equilibration of **1,2** (*cf* Scheme-5).

Mass spectral fragmentation for locating deuterium label on isolongifolene. With the knowledge that isolongifolene resulting from the rearrangement of longifolene with BF_3·Et_2O–AcOD carries deuterium label at C(8), C(14) and C(15), we had on hand another site-specifically labelled deuterioisolongifolene, besides isolongifolene-1,2,4,4-d_4 described earlier.[7] By comparing the mass spectra of these compounds with that of non-deuterated isolongifolene, it has been possible to elucidate the major features of electron impact induced fragmentation of isolongifolene. These results proved to be of immense value in locating deuterium in isolongifolene derived from different substrates, such as longicyclene, or in deuteroisolongifolene obtained under different isomerisation conditions (*vide infra*), themes which are germane to the longifolene→isolongifolene rearrangement problem. Scheme-4 summarises the fragmentations, which are relevant to our present purpose. Details of elucidation of these and other fragmentation pathways will be reported elsewhere.

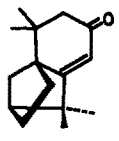
† The four tertiary Me's of isolongifolene appear (60 MHz) as 3H, 6H and 3H singlets at 0.84, 0.95 and 1.04 ppm in its PMR spectrum; at 90 MHz, the 6H signal resolves marginally. Thus, the PMR spectrum of deuterated isolongifolene did not clearly reveal the extent of deuterium incorporation in the Me's, and repeated integration of the signals suggested that at least two hydrogens have been replaced. During the course of subsequent work, it was found that the four Me signals resolve nicely in the PMR spectra of compounds **16**, **18**, **19**, **20**; the PMR spectra of these compounds derived from deuterated isolongifolene, show a significant loss of absorption (~66%) for one of the Me's and a loss of ~30% of the intensity of another Me absorption.

Table 1. Deuterated species in deuterated isolongifolene from different reactions

No.	Substrate	Reagent (BF_3–Et_2O+)	Reaction time (min)	No. of treat-ments	Rel. % deuterated species									Total D/mole-cule
					D_0	D_1	D_2	D_3	D_4	D_5	D_6	D_7	D_8	
1	Longifolene	AcOD	20	1	2	6	15	23	21	16	12	4	—	3.69
2	Product from 1	AcOH	20	2	6	10	21	26	16	14	7	—	—	3.06
3	Isolongifolene	AcOD	20	1	66	33	1	—	—	—	—	—	—	0.35
4	Product from 3	AcOH	20	2	98	1	1	—	—	—	—	—	—	0.03
5	Longicyclene	AcOD	65	1	1	6	9	14	18	17	16	13	6	4.58

Table 2. Deuterated species in different derivatives from deuterated isolongifolene

No.	Compound	Rel. % deuterated species								Total D/ molecule
		D_0	D_1	D_2	D_3	D_4	D_5	D_6	D_7	
1	Isolongifolene $-d_x$	2	6	15	23	21	16	12	4	3.69
2	Unsaturated ketone *15* $-d_x$	6	6	12	22	21	16	13	4	3.66
3	*15* $-d_x$ after exposure to aq. base	4	6	15	23	21	16	11	4	3.63
4	*16* $-d_x$	2	8	13	24	20	16	13	4	3.72
5	*17* $-d_x$	1	5	13	21	22	19	14	5	3.96
6	*18* $-d_x$	2	5	13	22	21	18	14	5	3.90
7	*19* $-d_x$	2	4	12	22	23	18	14	5	3.95
8	*19* $-d_x$ after exposure to aq. base	2	6	15	20	21	17	15	4	3.83



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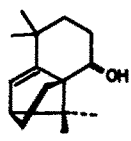

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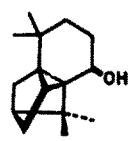

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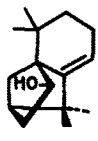

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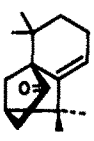

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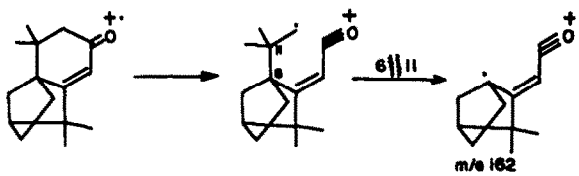

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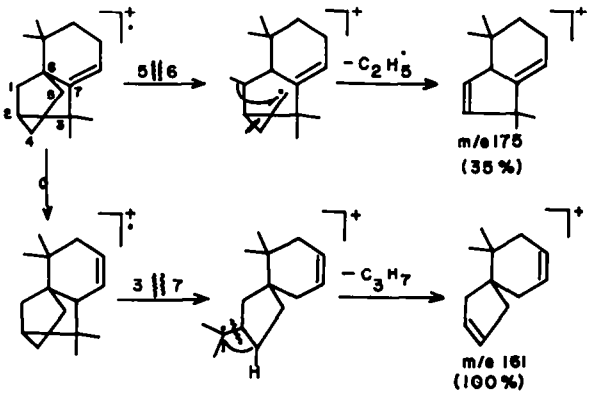
Scheme 3

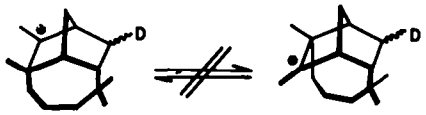


Scheme 4

Rearrangement of longicyclene to isolongifolene. Though, it has been shown that longicyclene (**7**) is not an intermediate in the BF_3Et_2O-catalyzed rearrangement of longifolene to isolongifolene, isomerisation of longicyclene, under acid catalysis, is still germane to longifolene→isolongifolene transformation, as will become apparent from the results described in the next section.

Longicyclene on being refluxed (22 hr) with cupric acetate in acetic acid is known[3] to furnish, besides longifolene (51%) and longicyclene (20%), some 15% isolongifolene. Though rearrangement of longicyclene in presence of a strong protic or Lewis acid has not been investigated, it is obvious that it should smoothly rearrange to isolongifolene, as indeed, it has been found to be the case. Obviously, the first step would be the cleavage of the 3-membered ring, generating a carbonium ion (or its equiv). Of the various possibilities, McMurry,[2] while discussing the intermediacy of longicyclene in the longifolene isolongifolene rearrangement, postulated direct cleavage to the cation **4**, a pathway, which from theoretical reasonings appears to be less likely. It is now widely accepted[8] that acid catalysed cleavage of cyclopropanes to the corresponding carbonium ions proceeds by way of edge-protonation. In longicyclene, the C(2), C(3) bond is almost completely shielded by the 7-membered ring, hence its protonation should be sterically inhibited in comparison to protonation of the much more accessible C(3), C(4) bond, leading to the longifolyl cation **2**.† Thus, one would anticipate that the *preferred* pathway for the rearrangement of longicyclene to isolongifolene would converge at the longifolene→isolongifolene mechanism (Scheme-1) at the first protonation step (**1** ⇌ **2**). Experimental support for this has been forthcoming from the following.

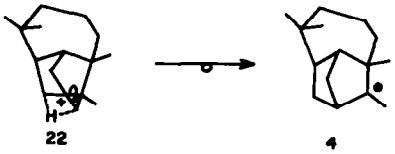
If longicyclene, during exposure to $BF_3{\cdot}Et_2O$–AcOD, were to open to **4**, only C(3)–Me would be deuterated, unlike longifolene, wherein by virtue of the racemisation pathway, the Me group originally located at C(7) also gets deuterated. This is because the shift **23** to **24**, which corresponds to the racemization pathway in case of longifolyl cation (**2**), would be inhibited as it involves an *endo, endo* migration.[10] Thus, if direct ring-opening to **4** (by one step or "two-step" mechanism) were the preferred pathway, one would expect *lesser* incorporation of deuterium, than what would have been incorporated had the preferred route lay *via* **2**. In practice, exposure of longicyclene to $BF_3{\cdot}Et_2O$–AcOD under conditions exactly identical‡ to those



23(≡ 4/12) 24

employed for longifolene yielded deuteroisolongifolene containing 4.58 deuterium/molecule (Table 1). Taking into account one additional deuterium atom acquired in cyclopropane cleavage, the remaining label is very close to that (3.69) incorporated by isolongifolene, when longifolene is the substrate (Table 1). This clearly favours ring-opening to longifolyl cation **2**/**11**. In further confirmation of this, deuteroisolongifolene from longicyclene, on electron impact induced fragmentation, gave the *m/e* 161 ion-cluster (Scheme-4) containing a total of 1.4D/'molecule' (Table 3), which corresponds to the expected loss of at least 3D/'molecule', required to be located at the two C(3) Me's, as per cleavage to longifolyl cation.

† However, it may be noted that conceivably cation **4** can arise from a process involving attack at the still more accessible (but less reactive) C(2)–C(4), followed by a Wagner–Meerwein rearrangement (**22** → **4**).



22 4

These considerations receive support from our recent work on the N-bromo-succinimide cleavage of longicyclene, in which the ratio of C(3)–C(4), C(2)–C(3) cleavage is ~4.[9] Since, the steric requirements of Br^+ are more profound in comparison to those of H^+, the "two-step" cleavage assumes significance in the present context.

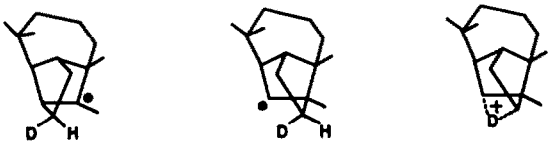
‡ Except for the time of the reaction, which had to be increased to 65 min. instead of 20 min., as after 20 min the reaction was still incomplete.

Table 3. Deuterated species in selected mass spectral fragments of deuteroisolongifolene from different reactions

No.	Reaction	'Ion'[a] (m/e)	Rel. % deuterated species													Total D/ 'mole-cule'
			D_0	D_1	D_2	D_3	D_4	D_5	D_6	D_7	D_8	D_9	D_{10}	D_{11}	D_{12}	D_{13}	
1	Longifolene/BF_3·Et_2O–AcOD	204	2	6	15	23	21	16	12	4	—	—	—	—	—	—	3.69
		175	2	7	15	25	22	15	11	3	—	—	—	—	—	—	3.62
		161	47	47	3	3	—	—	—	—	—	—	—	—	—	—	0.62
2	Longicyclene/BF_3·Et_2O–AcOD	204	1	6	9	14	18	17	16	13	6	—	—	—	—	—	4.58
		175	2	9	9	16	22	16	16	10	—	—	—	—	—	—	4.09
		161	12	49	29	7	3	—	—	—	—	—	—	—	—	—	1.40
3	Longifolene/D_3PO_4–dioxane	204	0	0	0.5	3	7	11	15	15	16	14	11	5	2	0.5	7.33
		175	0	0	1	6	15	21	18	19	14	5	1	—	—	—	5.93
		161	1	8	23	25	21	14	5	2	1	—	—	—	—	—	3.35

[a] Refers to the ion from non-deuterated isolongifolene (Scheme-4); the M^+ is given in this Table again for ready reference.

However, since in the generation of *m/e* 175 ion-cluster, there is some 10% deuterium loss (Table 3; *cf* entry 1 for the same fragment, where there is no such loss), part of deuterium acquired at ring-cleavage must be located at C(1), necessitating intervention of cations such as **25**, **26** arising from **27**†; alternatively this deuterium must be located at C(4) (see following section).



25 **26** **27**

Further support for unimportance of C(2)-C(3) cleavage was forthcoming from the fact that isolongifolene obtained from rearrangement of longicyclene was recemized to almost the same extent as that obtained from longifolene under the same conditions (BF_3·Et_2O–AcOH). This conclusion follows from the fact that if longicyclene were to cleave directly to **4**, racemization would be bypassed.

Rearrangement of longifolene to isolongifolene in D_3PO_4-dioxane. Isomerisation of longifolene to isolongifolene with BF_3·Et_2O–AcOH is quite fast, the isomerisation being complete in ~20 min at ~30°. It was thought worthwhile to examine also the isomerisation reaction under conditions which will permit the reaction to be carried out at an acceptable slow rate. While checking some possible reagent/reaction condition combinations and keeping in mind that the system should be readily adaptable for deuterium labelling, it was found that by using ~20% H_3PO_4 in dioxane, the rearrangement was complete only after 85–95 hr at reflux. This system was finally selected for further probing the longifofolene→isolongifolene rearrangement.

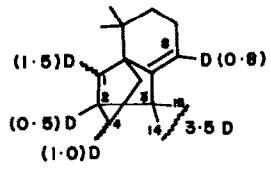
Exposure of longifolene to D_3PO_4–dioxane (reflux, 96 h) furnished deuterated isolongifolene having species containing upto 12 D atoms (Table 3), and a total average deuterium uptake of 7.33 D/molecule. A comparison of these figures with those obtaining for deuterated isolongifolene from BF_3·Et_2O–AcOD isomerisation (Table 3), reveals almost double deuterium incorporation, clearly suggesting new equilibration of intermediate carbonium ions with the corresponding olefin/cyclopropane. It may be pointed out that under these reaction conditions, isolongifolene takes up an average total of 1.6 D/molecule, of which 0.8 D is located (PMR) at the vinylic carbon. ‡

The position of D label in this product could be established by a study of its mass spectral fragmentation and spectral (PMR, mass) characteristics of its derivatives **16**, **18** and **19**. In the mass spectrum of this isolongifolene-d_x, the ion *m/e* 175-cluster shows a loss of 1.4 D (Table 3), which as per the rationale of this fragmentation (Scheme-4), requires that this deuterium must be located at C(1), C(4) and/or C(5). Compound **19** prepared from this deuteroisolongifolene shows 98% retention of deuterium, thus, there is no deuterium at C(5), a finding which also rules out the intermediacy of cycloisolongifolene (**9**). A comparison of the methyl absorptions in the PMR spectra of **16**, **18** and **19** (see footnote *a*) prepared from natural abundance isolongifolene, BF_3·Et_2O–AcOD-derived isolongifolene and the present isolongifolene-d_x clearly shows some 3.5 D located in the two Me's on C(3). Further, the ion *m/e* 161-cluster in the mass spectrum of this isolongifolene-d_x shows (Table 3) a loss of almost 4D and, since this fragmentation entails loss of C(3), C(14), C(15) and a H/D from C(4) (Scheme-4), some D must be located at C(4). In the PMR spectrum of compound **16** derived from deuterisolongifolene from the present reaction, the signal due to the olefinic proton at 5.70 ppm corresponds to only 0.4H and the signal is a clear

† Intervention of **4**/**12** would be inconsistent with the extent of deuteration of C(3) Me's.

‡ See footnote on next page.

superimposition of a doublet and a singlet and hence there should be some D at C(2). Also, mass spectrum reveals that compound **16** derived from this isolongifolene-d_x has lost one deuterium during its preparation; this considered along with earlier PMR data, leads to the conclusion that we have at least 1.5 D located at C(1). All these data lead us to conclude that during rearrangement of longifolene to isolongifolene under these reaction conditions deuterium gets incorporated at carbons 1, 2, 4, 14, 15 and 8, with the approximate average deuterium distribution as shown in **28**.



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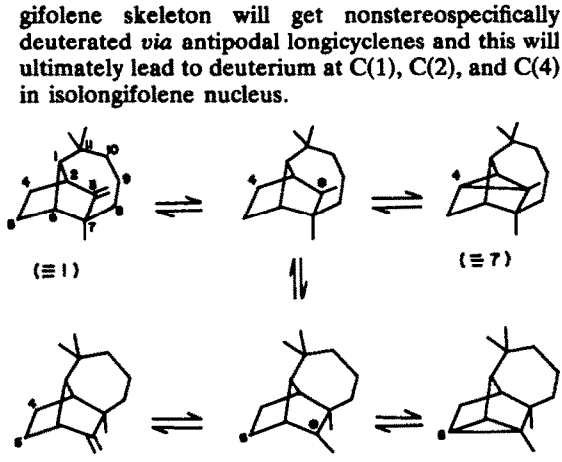
Deuterium incorporation at C(8), C(14) and C(15) was anticipated from results earlier obtained in the BF_3·Et_2O–catalysed rearrangement, while deuterium label at C(2) would necessitate the intermediacy of longicyclene (Scheme-2). The label at C(1) can arise *via* longicyclene and/or neoisolongifolene (**10**) (Scheme-2), most probably by both routes.† Deuterium incorporation at C(4) was unanticipated, but again, arises by way of longicyclene, as will be clear from Scheme-5. It is obvious from this Scheme that *both* C(4) and C(5) in longifolene skeleton will get nonstereospecifically deuterated *via* antipodal longicyclenes and this will ultimately lead to deuterium at C(1), C(2), and C(4) in isolongifolene nucleus.



Scheme 5

Thus, it is evident that under these reaction conditions, longicyclene gets involved with the longifolene→isolongifolene rearrangement. In fact, in one experiment using natural abundance materials, the reaction was worked up after 2 hr (when, from a glc monitoring study, it was known that, the concentration of longicyclens is 20% and is optimal) and longicyclene isolated and identified (IR, PMR). There is no evidence for involvement of cycloisolongifolene (**9**), and there is a distinct possibility that neoisolongifolene (**10**) partakes in the reaction.

CONCLUSION

It is evident that longicyclene is not an obligatory intermediate in the longifolene→isolongifolene rearrangement. Further, longicyclene preferably opens to longifolyl cation rather than to **4**. These findings make McMurry's suggestion[2] untenable. Under H_3PO_4–dioxane catalysis, longicyclene gets involved, by superimposition of a faster longifolene→longicyclene isomerisation.

EXPERIMENTAL

For general remarks see the preceding communication.

Materials. Commercial longifolene was further purified by fractionation and finally by chromatography over 10% $AgNO_3$–silica gel to remove minor amounts of (−)-caryophyllene.[11] Material, thus purified, was glc and tlc (Ag^+) pure: b.p. 85–86°/2 mm, $[\alpha]_D$ + 54.06° (c = 3.1).

Longicyclene used was glc and tlc pure: b.p. 81°/2 mm, $[\alpha]_D$ + 31.21° (c = 1.3).

Isomerisation with boron trifluoride

To a mixture of longifolene (26.64 g) and AcOD (125 ml; 98% isotopic purity), BF_3·Et_2O (25 ml) was added (10 min) with stirring and maintaining the temp at 30 ± 1°, under usual precautions for rigorous exclusion of moisture. After an additional 20 min stirring at the same temp, the now homogenous red soln was transferred to a separatory funnel containing ice-water (250 ml) and pentane/ether (1:1, 100 ml). After thorough shaking the solvent layer was removed and the aqueous phase extracted with the same solvent mixture (100 ml × 2). The mixed extracts were washed with water (100 ml × 3), 10% $NaHCO_3$aq (50 ml × 2), brine and dried. The solvent was flashed off and the product (29.09) separated into hydrocarbon and acetate fractions by filtration through a column of alumina (grade I, 6.0 cm × 16.0 cm). The hydrocarbon fraction, eluted with hexane, was distilled to furnish deuterated isolongifolene (17.92 g), b.p. 104–106°/6 mm. The product was glc, tlc (Ag^+) pure.

This procedure was followed with other substrates.

Isomerisation with deutrophosphoric acid. Longifolene (8.0 g) was added to a soln of D_3PO_4 (90%, 25 g; prepared by cautiously adding 10 ml D_2O to 23.6 g P_2O_5) in dry purified dioxane (125 ml) and the clear soln refluxed (bath temp 110–112°) for 96 hr when longifolene had completely disappeared (glc). The mixture was cooled, poured into 10% Na_2CO_3aq (1000 ml) and worked up as above to get glc, tlc (Ag^+) pure deutroisolongifolene (7.0 g).

Allylic oxidation of deuteroisolongifolene. Isolongifolene-d_x (*ex* BF_3·Et_2O reaction) (2.59 g), cobalt naphthenate (6 mg) and anhyd. Na_2CO_3 (27 mg) were heated in a suitable set-up at 90° (16 h) and later at 110° (6 hr), while passing a slow stream of O_2. After cooling, the product was taken up in ether, filtered and, the filtrate freed of solvent to furnish a product (2.4 g), which (in hexane) was chromatographed over silica gel (1.8 cm × 30 cm). Elution was carried out with hexane and later with benzene with tlc monitoring (solvent: benzene). The required unsaturated ketone was eluted with benzene and was distilled: b.p. 170–180° (bath)/7 mm, yield 0.78 g (tlc, glc pure). IR: 2250 (—CD_3), 2175 (—CD_2), 2080 (—CD), 1675 (C=O). PMR: 1.00 (*s*, 3H), 1.07 (*bs*, ~4 H), 1.16 (*s*, ~2H), 5.5 (*s*, ~0.4H).

† This is based on the results of a study on degenerate isolongifolene rearrangement, which will be reported elsewhere. In connection with this, it may be noted that isolongifolene when exposed to D_3PO_4–dioxane under the same reaction conditions takes up deuterium at C(1), besides C(8), almost to an equal extent.

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