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THERMAL REARRANGEMENTS OF TRICYCLO[4.2.2.$0^{2,5}$]DECATRIENE DERIVATIVES

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Abstract —The behaviour of tricyclodecatriene derivatives **1** and **8** in short-time and/or static thermolysis was investigated. The intermediate **8** in the transformation of **1** in naphthalene derivatives and the reversible rearrangement **1** ⇄ **8** were evidenced. Some mechanistic aspects of **1** or **8** rearrangement into naphthalene derivatives are discussed.

The application of the concept of orbital symmetry to the interpretation of the concerted reactions—a fundamental contribution to chemical theory due to Woodward and Hoffmann[1]—has stimulated the investigation of the thermal and photochemical interconversions of the $(CH)_n$ hydrocarbons. Among $(CH)_n$ hydrocarbons, the $(CH)_{10}$ valence isomer with tricyclo[4.2.2.$0^{2,5}$]deca-3,7,9-triene skeleton, namely Nenitzescu's hydrocarbon,[2] as well as its benzo and dibenzo derivatives, have received considerable attention.[3]

There are, however, few data concerning the mechanism of the rearrangement of 7,8-dicarbomethoxy-tricyclo [4.2.2.02.5]deca-3,7,9-triene (**1**),[4] the first compound of the series to have been converted into naphthalene derivatives.[2b,5]

The mechanism by which **1** rearranges to naphthalene derivatives **2–4**, proposed by C. D. Nenitzescu,[2b,5] involves the following key steps: (a) *anti* → *syn* rearrangement of cyclobutene ring and formation of tricyclo[4.4.0.$0^{2,5}$]decatriene **5**; (b) rearrangement of **5** to a [10]annulene **6**; (c) rearrangement of [10]annulene **6** to 9,10-dihydronaphthalene **7**; (d) transformation of **7** in the naphthalene **4** and dihydroderivatives, for which the structures **2** and **3** were established.[6]

The mechanistic hypothesis accounted for the unexpected rearrangement during which the two COOR groups change from vicinal positions in the starting compound (**1**) to the distant positions in the final products (**2–4**).

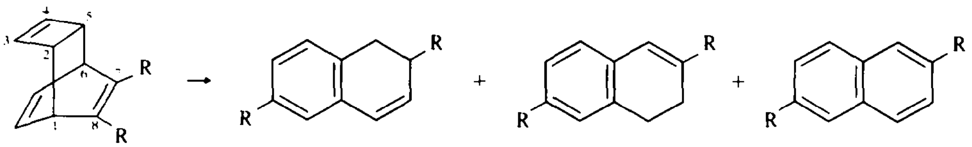
Although the key steps of the process were correctly formulated, the proposed configurations as well as the mechanistic details are somewhat different from those expected on the basis of modern chemical concepts.[1]

In order to gain some insight into the mechanism, we tried to detect unstable intermediates and to establish whether the compounds previously isolated (in the thermolysis of **1** in static system) are primary products or are formed in subsequent reactions. The thermolysis of **1** was therefore reinvestigated. Two experimental techniques were adopted: the short-time thermolysis and the thermolysis in a static system.

The preliminary thermolysis of **1** using both techniques revealed a new reactive intermediate **8**, together with the earlier described[5,6] ones, **2**, **3** and **4**, as well as two new products, **9** and **10**.

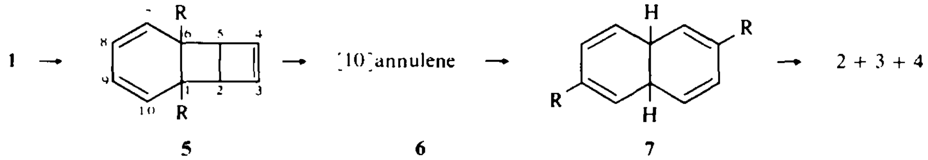
The intermediate **8** was isolated in a pure state by preparative glc; the starting material was a mixture (**1** 70% and **8** 30%) resulting from distillation of crude **1** on a very efficient column. Large amounts of **8** were prepared by treating the mixture of **1** and **8** with bis-benzonitrile · $PdCl_2$ (BNP) and removing the instantly formed **1** · $PdCl_2$ complex.[7]

The structure and configuration of **8** were based on spectral data and chemical behaviour.



1 **2** **3** **4**

R = $COOCH_3$



5 **6** **7**

The spectral data (Table 1) correspond to a structure involving five olefinic protons (but two of them are non-equivalent cyclobutenic protons), three saturated protons and two different carbomethoxy groups (one of them included in a α,β-unsaturated system).

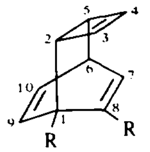
Among the 12 valence isomers which could be formed by Cope rearrangements of **1**, only 1,8-dicarbomethoxy-*syn*-tricyclo[4.2.2.$0^{2,5}$]deca-3,7,9-triene is acceptable as **8** and supported by its chemical behaviour which is characteristic of tricyclo[4.2.2.$0^{2,5}$] decadiene and triene derivatives. The treatment of **8** with BNP affords the complex **8**·$PdCl_2$ (**11**). **8** was regenerated from **11** by stirring with 20% aqueous NaCN.

Alternatively, by reducing the carbomethoxy groups with $LiAlD_4$ and acetylating the diol formed (**12**) with $(CD_3CO)_2O$, the bis-deuterioacetyl derivative **13** was prepared. The spectral parameters of **12** and **13**, shown in Table 2, confirm the proposed structure of **8**.

One should note the *exo-cis* addition of deuterium to the 7,8 double bond, which is reflected in the *endo* configuration of H-7 (unshielded by the neighbouring cyclobutene double bond) and of the 8-acetoxymethyl-d_5 group (H-3 and H-4 are magnetically equivalent).

In order to obtain more information on the conversion of **1** to **8** and to elucidate the role of **8** in the thermal transformation of **1** to naphthalene derivatives, the thermal behaviour of **1** and **8** over a broad range of temperature and thermolysis time was investigated.

The short-time thermolysis was carried out between 200° and 400°; below 200° there is no significant transformation. The results of the short-time thermolysis of **1** and **8** show that the thermolysis of **1** leads to significant amounts of **8**, while **8** undergoes isomerization to **1**. The maximum amount of isomerization (nearly 25%) is reached at 350°. Above this temperature, **1** and **8** rapidly decay to naphthalene derivatives. The observed reversible isomerization



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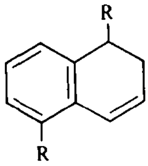

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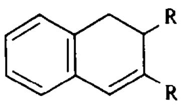
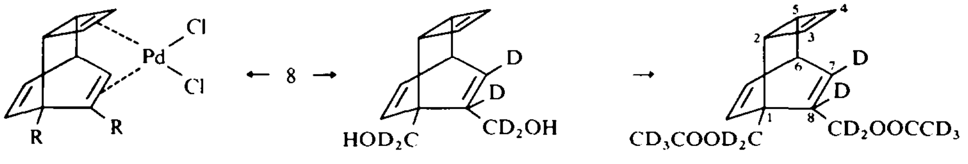


10

Table 1. Spectral parameters of **8**

<table>
<tr><td>IR (CCl_4) cm^{-1}</td><td colspan="4">1723 (α,β-unsaturated ester), 1740 (saturated ester)
1590, 1612 (C=C)</td></tr>
<tr><td rowspan="3">NMR
(C_6D_6,
δ, ppm)</td><td colspan="2">olefinic H</td><td>saturated H</td><td>$COOCH_3$</td></tr>
<tr><td>5.87, 6.37
system AB
(H-3, H-4)</td><td>6.14 (t, H-10)
6.70 (d, H-9)
6.98 (d, H-7)</td><td>2.44 (t, H-5)
2.88 (d, H-2)
3.20–3.70 m
(H-6 covered)</td><td>3.88 s
3.70 s</td></tr>
<tr><td colspan="4">coupling (J, Hz): $J_{9.10}=7.0$; $J_{6.10}=J_{6.7}=6.5$;
$J_{2.5}=J_{5.6}=4.0$</td></tr>
<tr><td>UV (EtOH)</td><td colspan="4">λ_{max} 223.4 nm (ε=3366) (α,β-unsaturated carbonyl)</td></tr>
</table>



11 **12** **13**

Table 2. Spectral parameters of products obtained by reduction of **8**

<table>
<tr><td></td><td>H-3
H-4</td><td>H-9</td><td>H-10</td><td>H-2</td><td>H-5</td><td>H-6</td><td>H-7</td><td>IR</td></tr>
<tr><td>12</td><td>6.03
s</td><td colspan="2">5.80 – 6.50
m</td><td>2.20
d</td><td>2.53
t</td><td>3.20
m</td><td>1.95
d</td><td>3575 (OH)
3620</td></tr>
<tr><td rowspan="2">13</td><td>6.13
s</td><td>6.20
dd</td><td>6.50
dd</td><td>2.40
d</td><td>2.60
t</td><td>3.33
m</td><td>2.00
d</td><td>1718 (CO)</td></tr>
<tr><td colspan="8">$J_{6.7}=J_{2.5}=4.0$, $J_{5.6}=3.5$, $J_{9.10}=6.0$, $J_{6.9}=1.5$, $J_{6.10}=7.5$</td></tr>
</table>

Table 3. The thermolysis of esters **1** and **8**

	Products (μ moles)							
	phthalic ester	esters		naphthalene derivatives				
		8	**1**	**10**	**9**	**2**	**3**	**4**
The short-time thermolysis of ester **1**								
200°	0.6	4.3	90.9					
250	0.7	5.0	90.0					
300	0.8	10.3	85.0		0.6	0.1		0.1
350	1.0	26.5	55.8	0.1	1.8	4.9	2.9	1.0
400	1.8	8.6	12.0	0.7	7.4	23.4	17.4	2.0
The short-time thermolysis of ester **8**								
200°	0.4	92.6	2.0					
250	1.3	92.4	1.7			0.1		0.1
300	1.4	79.7	7.5	1.3	1.3	2.3	1.3	0.9
350	1.6	29.4	27.3	2.5	1.8	16.4	9.9	3.7
400	2.2	4.5	9.0	2.8	6.2	34.2	21.8	3.8
The static thermolysis of ester **1** at 250°								
0 min		3.9	96.1					
2.5	4.3	28.0	52.0	1.0	1.2	6.4	4.0	3.1
5	9.7	23.9	38.2	1.3	1.4	6.9	7.9	7.7
10	15.7	11.0	15.0	2.3	2.6	16.4	16.9	17.6
20	23.7	4.9	6.7	2.5	2.3	14.8	19.7	25.5
30	26.1	2.3	2.9	3.0	1.7	9.9	17.4	34.6
60	29.7	0.4	1.1	3.1	1.1	3.4	15.2	42.8
120	29.7			3.2	0.8	0.1	8.8	55.0
The static thermolysis of ester **8** at 250°								
0 min		99.0	1.0					
3	11.5	21.8	24.1	1.0	1.9	18.9	14.4	6.4
5	15.4	11.5	13.5	1.1	2.9	25.1	20.2	9.5
10	16.3	5.9	7.8	1.9	3.0	28.6	23.6	11.8
20	19.2	0.6	2.1	3.9	3.2	27.7	25.7	16.9
25	20.0		1.0	4.0	3.2	25.1	25.9	19.6

1 ⇄ **8** was proved by separation of both components.

Other important observations are the formation of naphthalene compounds above 300° and the fact that the major components are the dihydro derivatives **2** and **3**.

The thermolysis of **1** and **8** was carried out in a static system at 150°, 200° and 250°. The results obtained at 250° (where the reaction is more significant) indicate that the maximum of interconversion **1** ⇄ **8** is reached after 2.5–3 min of heating.

Concerning the distribution of naphthalene derivatives, the results clearly indicate that the primary products are the dihydro derivatives **2** and **3**; a subsequent step (experimentally proved) involves the dehydrogenation of **2** and **3** (easier for the former compound), leading to the stable derivative **4**.

DISCUSSION

The conversion of **1** to naphthalene compounds is a multistep process. Experimental results show that the isomerization of **1** and **8** take place in two ranges of temperature. The formation of isomeric esters **8** and **1**, respectively, predominate and that of naphthalene compounds is not significant at lower temperatures. The latter derivatives become the main products over a critical range of temperature (300–350°). For this reason, two series of reactions can be considered.

(a) The interconversion of **1** and **8** involves the reversible change of the *anti* cyclobutene ring orientation in **1** to *syn* in **8**.

Since the interconversion **1** ⇄ **8** occurs at relatively low temperature, and no other major products could be found, we assume that a concerted reaction takes place, involving [3.3]sigmatropic (Cope) rearrangement,[1,8–10] governed by the conservation of orbital symmetry rules. The demonstration of the reversible isomerization **1** ⇄ **8**, for the first time proved in the $(CH)_{10}$ series by direct isolation of the isomers, is a decisive argument in favour of this reaction route.

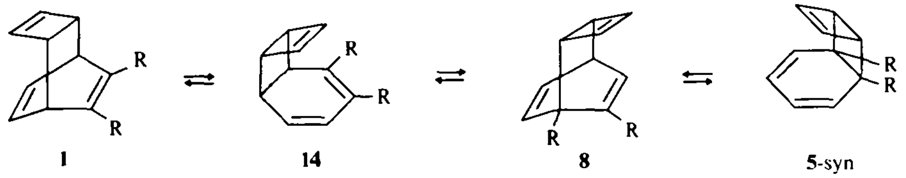
In this interpretation, the esters **1** and **8** are thermally equilibrated with tricyclo[4.4.0.0^{2,5}]decatriene valence isomers **14** and **5**-*syn*, the latter[2b,5] having been earlier proposed as key intermediate in the conversion of **1** to naphthalene derivatives.

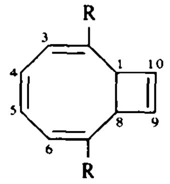
The failure to detect the intermediates **14** and **5**-*syn* is undoubtedly due to the greater thermal stability of [4.2.2.0^{2,5}] systems as compared to [4.4.0.0^{2,5}] systems.[9,10]

(b) For the further isomerization of **5**-*syn* into naphthalene compounds, only hypothetical mechanistic aspects can be taken into account.

A disrotatory, thermally forbidden, cyclobutene ring opening of **5**-*syn* to 9,10-dicarbomethoxy-*cis*-9,10-dihydronaphthalene can be *a priori* excluded on theoretical as well as experimental grounds; studies concerning the thermal behaviour of the latter compound[11] show a different distribution of naphthalene derivatives from that observed in the thermolysis of **1** and **8**.

The formation of dihydronaphthalenes **2**, **3** and **9** as final products supports the formation of *trans*-9,10-dihydronaphthalene derivatives as intermediates. For this reason, the following intermediates were considered to be involved: **15**, **16**, **17** and **18**.





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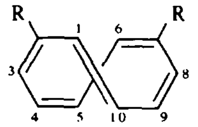

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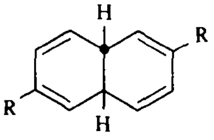
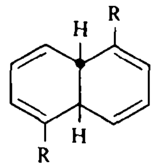
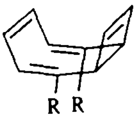


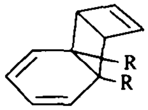
17



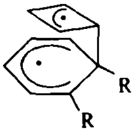
18



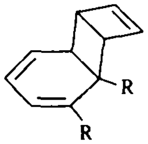
15



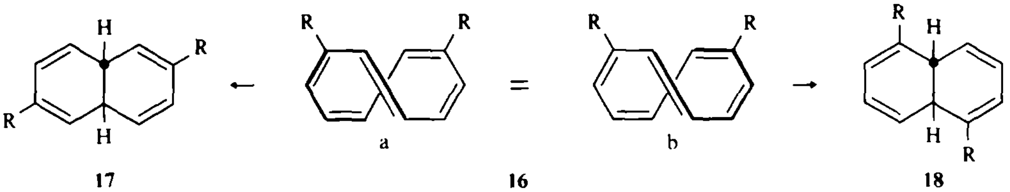
5-anti



19



20

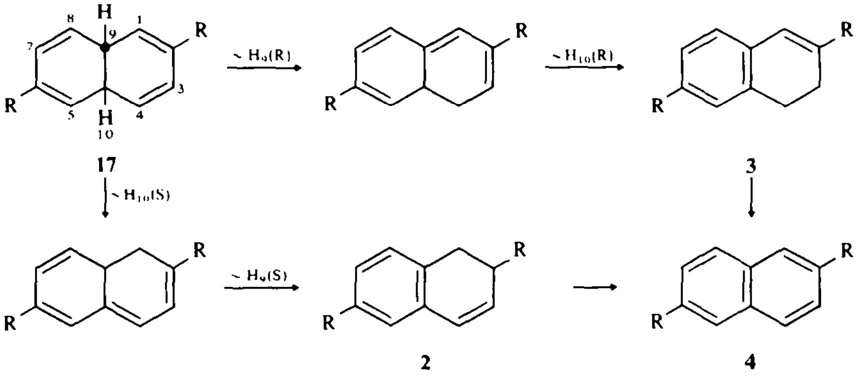


Electrocyclic or homolytic ring opening of **5**-*syn* involving the bond between the two carbomethoxy groups,[12] leading to **15**, may be favoured by the presence and vicinal position of these groups.

The 1,2 bond cleavage leading to the free rotating diradical **19**, although less favoured, could take place in minor amounts. Reclosure of **19** to **5**-*anti* seems to be sterically hindered by the vecinity of carbomethoxy groups; reclosure to **20** could explain the small quantities (less than 5 %) of **10** observed, but **10** could be formed also from **14**.

Furthermore, **15** undergoes a thermally allowed electrocyclic conrotatory opening process to *trans*-*cis*^{4}-cyclodecapentaene (**16**). In the latter, there are two possibilities of transannular ring closure in a disrotatory process. Both involve hexatriene systems having in common the *trans*-1,10 double bond. The experimental evidence that the closure of the hexatriene system unsubstituted at the terminal double bond (**16a**), namely that leading to 2,6-disubstituted *trans*-9,10-dihydronaphthalene **17**, is prefered.

A consecutive [1.5]sigmatropic suprafacial hydrogen migration[13] in **17** and **18** explains the formation of dihydro derivatives **2**, **3** and **9**, respectively, as primary products of thermolysis. These compounds undergo further aromatization only at higher temperature or after prolonged heating.



EXPERIMENTAL

All m.ps and b.ps are uncorrected. IR spectra were obtained with a Jena UR 20 spectrometer. UV spectra were taken with a Jena Specord spectrophotometer. ^1H NMR spectra were measured with a Varian A-60A instrument, with signals reported to internal TMS, δ 0.00 ppm; coupling constants given in Hz. Glc analysis were carried out on a Carlo Erba 2450 chromatograph, equipped with a flame ionization detector, using a 2 m × 3 mm of 10% QFl on Gas Chrom Q glass column; carrier gas: nitrogen, 30 ml/min. Preparative glc were carried out on a Carlo Erba GV chromatograph, equipped with catharometer, using a 2 m × 10 mm of 20% QFl on Chromosorb W column; detector temp 200°; carrier gas: hydrogen, 300 ml/min.

Starting material. Compound **1** was prepared from cyclooctatetraene and dimethyl acetylenedicarboxylate, using a procedure similar to that developed by Reppe.[4] NMR (C_6D_6): 2.61 (bs, H-1, H-6), 3.55–3.90 (bs, H-2, H-5), 3.51 (s, two carbomethoxy groups), 5.84 (s, H-3, H-4), 5.95 (m, H-9, H-10).

Static thermolysis of **1**. The ester **1** was heated at 330° for 5 min; from the product (composition: **1** 0.5–1.5%, **8** 0.4–0.5%, **10** 2.4–3.7%, **9** 1.8–2.4%, **2** 9.0–12.0%, **3** 18.7–23.7%, **4** 30.0–39.5%) the naphthalene derivatives **2**, **3**, **4**, **9** and **10** were obtained by preparative glc.

2,3-*Dicarbomethoxy*-1,2-*dihydronaphthalene* (**10**). NMR ($CDCl_3$): 3.30 (m, H-1), 3.50–4.00 (m, H-1, H-2 and two groups $COOCH_3$ which appear as singlets at 3.60 and 3.83), 7.21 (s, 4 aromatic H), 7.64 (s, H-4).

1,5-*Dicarbomethoxy*-1,2-*dihydronaphthalene* (**9**). NMR ($CDCl_3$): 3.20–3.80 (m, H-1, 2H-2), 3.73 and 3.91 (s, two $COOCH_3$ groups), 6.11 and 6.55 (2bd, H-3, H-4, $J_{3,4}$ = 10.0), 7.25–8.15 (m, 3 aromatic H).

2,6-*Dicarbomethoxy*-1,2-*dihydronaphthalene* (**2**). M.p. 75°; NMR (CCl_4): 2.90–3.55 (m, 2H-1, H-2), 3.70 and 3.85 (s, two $COOCH_3$ groups), 6.08 (dd, H-3, $J_{2,3}$ = 2.5, $J_{3,4}$ = 10.0), 6.56 (dd, H-4, $J_{2,4}$ = 1.5, $J_{3,4}$ = 10.0), 7.15 (d, H-8, $J_{7,8}$ = 7.0), 7.60–7.90 (m, H-5, H-7).

2,6-*Dicarbomethoxy*-3,4-*dihydronaphthalene* (**3**). M.p. 126°; NMR (CCl_4): 2.40–3.20 (m, 2H-3, 2H-4), 3.81 and 3.90 (s, two $COOCH_3$ groups), 7.21 (d, H-8, $J_{7,8}$ = 8.0), 7.48 (s, H-1), 7.75–8.00 (m, H-5, H-7).

2,6-*Dicarbomethoxy-naphthalene* (**4**). M.p. 188°; NMR ($CDCl_3$): 4.03 (s, two $COOCH_3$ groups), 8.11 (s, H-3, H-4, H-7, H-8), 8.65 (s, H-1, H-5).

Thermolysis experiments. The static thermolysis technique consisted of heating the compound to the desired temperature for a definite time. The short-time thermolysis technique used a modified vaporizer of a Carlo Erba 5460 gas chromatograph, heated at the desired temp. Time of pyrolysis was about 0.75 sec. The method allows direct analysis of the products (carrier gas: argon; the above described column was heated at 180°). The products formed in both types of thermolysis of **1** and **8** are presented in Table 3.

1,8-*Dicarbomethoxy-syn-tricyclo* $[4.2.2.0^{2,5}]$-*deca*-3,7,9-*triene* (**8**). Distillation *in vacuo* of the crude starting material on a spinning band column Normag–Wingler–Fritz, afforded a fraction with b.p. 153–158°/4 mm, containing (glc) 70% **1** and 30% **8**. Pure **8** was isolated by preparative glc. IR, NMR and UV data are shown in Table 1.

A preparative route to **8**. Bis-benzonitrile · $PdCl_2$ (6.0 g, 15.6 mmoles) was dissolved in 250 ml benzene and 5.0 g of the above fraction (containing 3.5 g, 14.2 mmoles, **1** and 1.5 g, 6.1 mmoles, **8**) were added. The mixture was allowed to stand at room temp for 24 hr, and the yellow crystalline ppt of **1** · $PdCl_2$ was filtered off and washed with benzene. The solvent was removed *in vacuo* and the oily residue was dissolved in petroleum ether–ether (3:1) and chromatographed on alumina Grade II. The colourless soln was evaporated and the residue heated at 70°/1 mm until all benzonitrile was removed; 1.1–1.2 g (73–80%) **8** were obtained.

The complex of **8** *with* $PdCl_2$ (**11**). A soln of 0.50 g (2 mmoles) **8** in 2 ml benzene was treated with a soln of 0.85 g (2.2 mmoles) BNP in 40 ml benzene, and the mixture allowed to stand for 48 hr at room temp. The yellow–orange crystals were filtered off and washed with 3 ml benzene, yielding 0.35 g (41%) complex **11**, m.p. 205° (dec); IR (KBr): 1630, 1410, 1486 (complexed C=C), 1728, 1740 (C=O) cm^{-1}. (Found: C, 40.31; H, 3.43; Cl, 15.14; Pd, 25.24. Calc. for $C_{14}H_{12}Cl_2O_4Pd$: C, 39.89; H, 2.87; Cl, 16.82, Pd, 25.24%.)

The complex **11** treated with an aqueous soln of KCN yielded **8** in a 80% yield.

1,endo-8-*Di*-(*acetoxymethyl*-d_5)-exo-cis-7,8-*dideuterio-tricyclo*$[4.2.2.0^{2,5}]$*deca*-3,9-*diene* (**13**). The reduction of **8** with $LiAlD_4$ afforded the dihydroxy-derivative **12** in a 80% yield. Crude **12** treated with perdeuterioacetanhydride, in presence of catalytic amounts of pyridine, afforded **13** in a 80% yield. Spectral properties are shown in Table 2.

Acknowledgement—We are indebted to Dr. Ing. M. Elian for helpful discussions.

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