90. A (1,5)-Vinyl Shift

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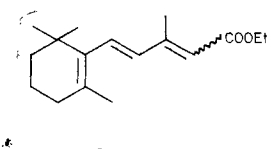
The structure of the by-product of the pyrolysis of **1** has been proved to be **3**. It is proposed that a (1,5) shift of an (alkoxycarbonyl)vinyl group (**8**⇄**10**) is the key step in the formation of **3**.

Introduction. – Earlier, we described the synthesis of ethyl dehydro-bicyclofarnesoate **2** by pyrolysis of the trienecarboxylate **1** [1]. Later, we found that the corresponding alcohol of **2**, upon treatment with acid, unexpectedly furnished herbertene [2]. In the course of our work on this latter rearrangement, we took the opportunity to eliminate an old obligation, namely elucidate the structure of a sizable by-product of the pyrolysis of **1**. Heating of **1** at 240° gave rise to **2** and this by-product in a ratio of 3:1 in an otherwise quite clean reaction in 70% yield [1]. In this paper, we describe formation and structure of this by-product.

Results. – The by-product was best isolated by controlled hydrolysis of the reaction mixture with KOH in MeOH at 50°. Under these conditions, the by-product is selectively hydrolysed to the acid, whereas the main product **2** is not. NMR experiments, conducted with the re-esterified product, established the structure of the by-product as **3** (see *Exper. Part*).



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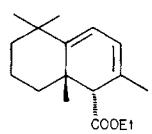

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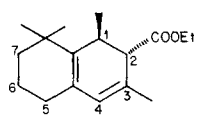

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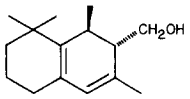
Especially helpful for the structure elucidation were beside the 2D-^{1}H,^{1}H-correlation (COSY), the 2D-^{13}C,^{1}H-correlation, and the 2D inadequate-experiment, the differential NOE experiments, which showed effects of 10–15% between CH_3–C(8)/H–C(1), H–C(2)/CH_3–C(3), and CH_3–C(3)/H–C(4). The *trans*-configuration followed from the small ^{1}H,^{1}H-coupling constant $J(1,2) = 2$ Hz and the even smaller, *i.e.* not observed, $J(2,4)$ which suggested H–C(2) to be in pseudoequatorial position (*cf.* **2** and *epi*-**2** in [1]).

Reduction of **3** with $LiAlH_4$ furnished the primary alcohol **4** which, upon treatment with acid (HCOOH, cat. $HClO_4$), afforded the hydrocarbon **5** (40%). An isomeric tetraline derivative was at our disposal from the acid-catalysed rearrangement of **6**, the hydride-reduction product of *epi*-**2** [1], and was identified as **7**[1]). The comparison of the

[1]) Note the different behaviour of the epimeric alcohol corresponding to **2** with a pseudoaxial CH_2OH group, which furnished herbertene as the main product [2].



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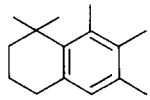

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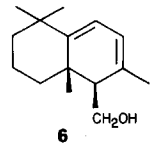

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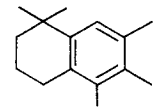

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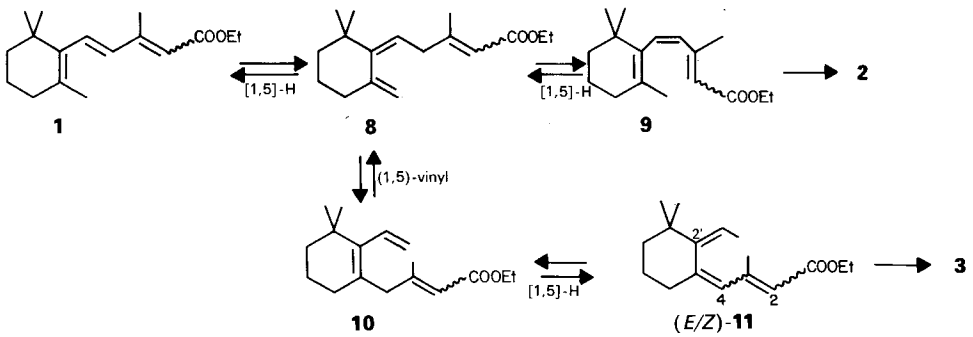
hydrocarbons was very valuable for the structure elucidation of **3**, as the position of the Me groups of both compounds was established by differential NOE experiments (see *Exper. Part*).

Discussion. – In our first communication [1], we proposed a reversible [1,5]-H shift, **1**⇄**8**, to explain the *trans*⇄*cis* isomerisation of **1**, which is a prerequisite for the observed disrotatory electrocyclisation to **2** *(Scheme 1)*. In **8**, [1,5]-H shifts lead either to **1** or to (2*E*/*Z*)-**9**. The isomer (2*E*)-**9** is ideally disposed for an electrocyclisation to **2**, whereas (2*Z*)-**9** is not, and the latter isomerises to (2*E*)-**9** through reversible [1,7]-H shifts [1].

Scheme 1



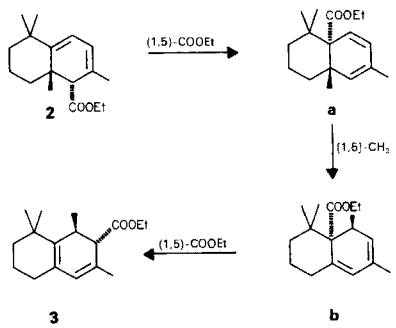
Now, we propose that in **8** a (1,5) shift of the (alkoxycarbonyl)vinyl group to **10** takes place in such a way that it can compete with the [1,5]-H shifts (**1**⇄**8**⇄**9**).

The $\Delta H^{\neq}$ of the [1,5]-H shift in our system is probably around 35 kcal/mol (for analogy, see [3]). On the other hand, very efficient (1,5)-vinyl migrations have already been reported [4–9] with $\Delta H^{\neq}$ *ca.* 21–26 kcal/mol. However, all these examples demonstrate rearrangements in bicyclic systems. In contrast to these reactions, our rearrangement takes place in a noncyclic system (concerning the π system), and the migrating vinyl moiety carries an additional alkoxycarbonyl group. The further fate of **10** is supposed to be very similar to that of **8**. A reversible [1,5]-H shift leads to the (2*E*/*Z*,4*E*/*Z*,2′*Z*)-triene-carboxylate **11**, from which only the (2*E*,4*Z*,2′*Z*)-isomer cyclises to **3** (see the case of **1**→**2** in [1]). The (2*Z*,4*E*,2′*Z*)-isomer is again supposed to isomerise to the (2*E*)-isomer through reversible [1,7]-H shifts, whereas the (4*E*)-isomers reversibly yield **10** again by [1,5]-H shifts.

An alternative mechanism for the formation of **3** can be formulated by three consecutive (1,5) migrations *(Scheme 2)*. First, a (1,5) migration of the alkoxycarbonyl group, **2**→**a**, followed by a (1,5)-CH_3 shift **a**→**b**, and finally a (1,5) shift of the alkoxycarbonyl group **b**→**3**. Both kinds of (1,5) shifts are well documented [3]. Such mechanism, however, could easily be excluded: heating of **2** at 260° for up to 45 h did not yield **3**, [1], whereas **3** was stable at this temperature. Furthermore, we pyrolyzed doubly labelled [1,2-$^3C_2$]-**1**[2]) to a mixture of labelled **2** and **3**.

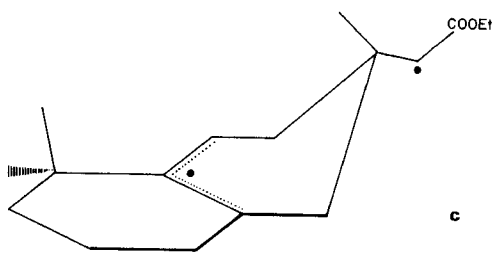
[2]) The synthesis will be published later.

Scheme 2



In the ^{13}C-NMR of the corresponding alcohols *epi*-**6** and **4**, one could observe a vicinal $J(^{13}C,^{13}C)$ of 35 Hz (from labelled **4**, 61.5 ppm (*t*) and 50.3 (*d*)). This means that in the course of the formation of **3** from **1**, C(1) and C(2) remain directly bonded.

Concerning the mechanism of the observed (1,5) shift of a (alkoxycarbonyl)vinyl group, different possibilities can be discussed. According to *Alder* and *Grimme*'s observations (*cf.* [9] and lit. cit. therein), a biradical intermediate of type **c** (or a corresponding transition state with biradical character) may be formulated[3]).



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Experimental Part

General. See [10]. Differential NOE: irradiated proton→affected proton (%).

Ethyl trans-*1,2,5,6,7,8-Hexahydro-1,3,8,8-tetramethyl-2-naphthoate* (**3**). A mixture of **1** (388 g) in *N,N*-diethylaniline (1.6 l) was refluxed at 220° during 70 h (conversion to **2**/**3** *ca.* 92%[4])). After workup (hexane, 2N H_2SO_4, drying over $MgSO_4$), the crude product was hydrolysed in CH_3OH (1 l) with KOH (100 g) at reflux until all **3** disappeared (GLC, 1.5 h). Workup for the acids yielded 71 g of a mixture of carboxylic acids, which were esterified in hexamethylphosphoric triamide (HMPA)/H_2O 9:1 in the presence of KOH and EtI furnishing **3**/(2*E*/*Z*)-**1** *ca.* 4:1, besides 4 small impurities. This mixture was carefully distilled on a column: 35 g of **3** at 112–114°/0.75 Torr (> 95%) and 16 g of **3** at 114–115°/0.75 Torr contaminated with 15% of **1**. The residue (8.5 g) contained mainly **1**,

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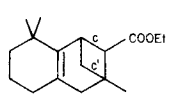
[3]) An ionic analogue of **c** could also be formulated. An intramolecular *Diels-Alder* addition of **8** to yield **d** with subsequent opening of the cyclobutane ring at c,c', possibly *via* **c**, would also be in agreement with the observed vinyl shift.



d

[4]) Later we found that refluxing at 273° in tetraethylenglycol dimethyl ether is much more advantageous ($t_{1/2}$ only 25–30 min; workup with H_2O/hexane).

the 4 smaller impurities, and *ca.* 15% of **3**. **3**: IR (film): 1730. UV (EtOH): 265 ($5.25 \cdot 10^3$). ^{1}H-NMR: 5.62–5.59 (*m*, H–C(4)); 4.15–4.0 (*m*, CH_3CH_2O); 2.79–2.71 (*m*, H–C(1)); 2.57–2.55 (*d*, $J \approx 2$, H–C(2)); 2.1–1.95 (*m*, 2 H–C(5)); 1.86–1.84 (*d*, $J \approx 2$, CH_3–C(3)); 1.62–1.53 (*m*, 2 H–C(6)); 1.48–1.41 (*m*, 2 H–C(7)); 1.23 (*t*, CH_3CH_2O); 1.06, 0.97 (2*s*, 2 CH_3–C(8)); 1.02 (*d*, CH_3–C(1)). ^{13}C-NMR: 172.4 (*s*); 137.9 (*s*); 127.5 (*s*); 125.5 (*s*, and *d*); 60.0 (*t*); 52.8 (*d*); 39.9 (*t*); 33.8 (*s*); 31.2 (*d*); 29.25 (*t*); 29.1 (*q*); 27.8 (*q*); 23.2 (*q*); 19.5 (*t* and *q*); 14.3 (*q*). Differential NOE: 2 CH_3–C(8)→H–C(1) (11); CH_3–C(3)→H–C(2) (10) and H–C(4) (15). MS: 262 (22, $M^{+\cdot}$), 247 (31), 189 (18), 173 (34), 159 (23), 147 (11), 133 (17), 119 (100), 105 (16).

trans-*1,2,5,6,7,8-Hexahydro-1,3,8,8-tetramethyl-2-naphthalenemethanol* (**4**). At r.t., **3** (1.5 g, 5.7 mmol) in THF (30 ml) was reduced with $LiAlH_4$ (0.5 g). Normal workup yielded 1.2 g of an oil. B.p. 100–110°/0.05 Torr (bulb-to-bulb dist.). ^{1}H-NMR: 5.48–5.45 (*m*, H–C(4)); 3.51 (*dd*, $J \approx 10, 5$, 1 H, CH_2OH); 3.33 (*dd*, $J \approx 10, 10$, 1 H CH_2OH); 2.41–2.35 (br. *q*, H–C(1)); 2.06–1.83 (*m*); 1.77 (*d*, $J \approx 2$, CH_3–C(3)); 1.66–1.39 (*m*, 5 H); 1.06, 1.02 (2*s*, 2 CH_3–C(8)); 0.99 (*d*, CH_3–C(1)). ^{13}C-NMR: 137.1 (*s*); 131.1 (*s*); 124.6 (*s*); 124.4 (*d*); 61.5 (*t*); 50.3 (*d*); 39.9 (*t*); 33.8 (*s*); 29.22 (*t*); 29.15 (*q*); 29.05 (*d*); 27.8 (*q*); 22.6 (*q*); 19.5 (*t*); 19.1 (*q*). MS: 220 (11, $M^{+\cdot}$), 205 (15), 189 (11), 175 (4), 145 (6), 133 (11), 119 (100), 105 (25), 91 (10).

1,2,3,4-Tetrahydro-1,1,6,7,8-pentamethylnaphthalene (**5**). For 30 min, **4** (1.1 g, 5 mmol) was refluxed in HCOOH (20 ml) containing 70% $HClO_4$ soln. (0.2 ml). Short chromatography on silica gel with hexane and distillation furnished 370 mg (37%) of **5**. ^{1}H-NMR: 6.77 (*s*, H–C(5)); 2.77–2.71 (*m*, 2 H–C(4)); 2.38 (*s*, CH_3–C(8)); 2.22 (*s*, CH_3–C(6)); 2.13 (*s*, CH_3–C(7)); 1.76–1.62 (*m*, CH_2(2), CH_2(3)); 1.42 (*s*, 2 CH_3–C(1)). ^{13}C-NMR: 141.0 (*s*); 135.4 (*s*); 134.07 (*s*); 134.05 (*s*); 133.2 (*s*); 129.1 (*d*); 45.0 (*t*); 34.5 (*s*); 32.3 (*t*); 29.85 (2*q*); 20.5 (*q*); 19.6 (*t*); 19.4 (*q*); 16.0 (*q*). Differential NOE: 2 CH_3–C(1)→CH_3–C(8) (8); CH_3–C(8)→CH_3–C(1) (6) and CH_3–C(7) (9); CH_3–C(7)→CH_3–C(6) (12); CH_3–C(6)→H–C(5) (13). MS: 202 (17, $M^{+\cdot}$), 187 (100), 172 (17), 159 (9).

cis-*1,5,6,7,8,8a-Hexahydro-2,5,5,8a-tetramethyl-1-naphthalenemethanol* (**6**). At 40–50°, *epi*-**2** [1] (1.25 g, 5 mmol) in THF (30 ml) was reduced with $LiAlH_4$ (0.3 g) for 4 h. Usual workup yielded 1.1 g (*ca.* 100%) of an oil. B.p. 125–130°/0.1 Torr. IR (film): 3350. ^{1}H-NMR: 5.82 (*d*, $J \approx 6$, H–C(4)); 5.76–5.72 (*m*, H–C(3)); 3.98–3.84 (*AB* of *ABX*, CH_2O); 2.16–2.11 (*m*, H–C(1)); 1.98–1.96 (*m*, CH_3–C(2)); 2.02–1.95 (*m*, 1 H); 1.75–1.54 (*m*, 2 H); 1.48–1.26 (*m*, 4 H). MS: 220 (8, $M^{+\cdot}$), 189 (3), 159 (6), 133 (11), 119 (100), 105 (24), 91 (10), 57 (40), 41 (62).

1,2,3,4-Tetrahydro-1,1,5,6,7-pentamethylnaphthalene (**7**). For 30 min, **6** (250 mg, 1.15 mmol) was refluxed in HCOOH (10 ml) containing 0.1 ml of 70% $HClO_4$ soln. After usual workup, 120 mg (50%) of 90% pure **7** were distilled at 80°/0.05 Torr. ^{1}H-NMR: 7.03 (*s*, H–C(8)); 2.65–2.60 (*m*, 2 H–C(4)); 2.27 (*s*, CH_3–C(7)); 2.17 (*s*, CH_3–C(6)); 2.14 (*s*, CH_3–C(5)); 1.86–1.78 (*m*, 2 H–C(3)); 1.63–1.58 (*m*, 2 H–C(2)); 1.28 (*s*, 2 CH_3–C(1)). ^{13}C-NMR: 142.6 (*s*); 134.1 (*s*); 133.2 (*s*); 131.8 (*s*); 131.7 (*s*); 125.4 (*d*); 38.8 (*t*); 33.7 (*s*); 31.9 (2*q*); 28.5 (*t*); 20.9 (*q*); 19.8 (*t*); 15.7 (*q*); 15.5 (*t*). Differential NOE: 2 CH_3–C(1)→H–C(8) (28); H–C(7)→H–C(8) (9.5); CH_3–C(5)→2 H–C(4) (3.5). MS: 202 (19, $M^{+\cdot}$), 187 (100), 172 (15), 157 (12).

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