Substance I: quantité isolée: 28 mg. F. 216° (déc.), recristallisé dans l'eau, Rf = 0,70 (polyamide, MeOH/H_2O 9:1), Rf = 0,55 (cellulose, AcOH 15%).

$C_{27}H_{30}O_{16}$ (610,35) Calc. C 53,15 H 4,93% Tr. C 51,30 H 4,95%

Substance II: quantité isolée: 40 mg. F. 206–207° (déc.) recristallisé dans le méthanol, Rf = 0,80 (polyamide, MeOH/H_2O 9:1), Rf = 0,68 (cellulose, AcOH 15%).

$C_{27}H_{30}O_{15}$ (594,36) Calc. C 54,58 H 5,02% Tr. C 52,45 H 5,48%

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316. Heterotricyclodecanes XVII[1]) 2,7-Dioxa-twist-4-ene and 2,7-dioxa-twista-4,9-diene

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(9. XI. 73)

Summary. 2,7-Dioxa-twist-4-ene (**3**) and 2,7-dioxa-twista-4,9-diene (**6**) were prepared.

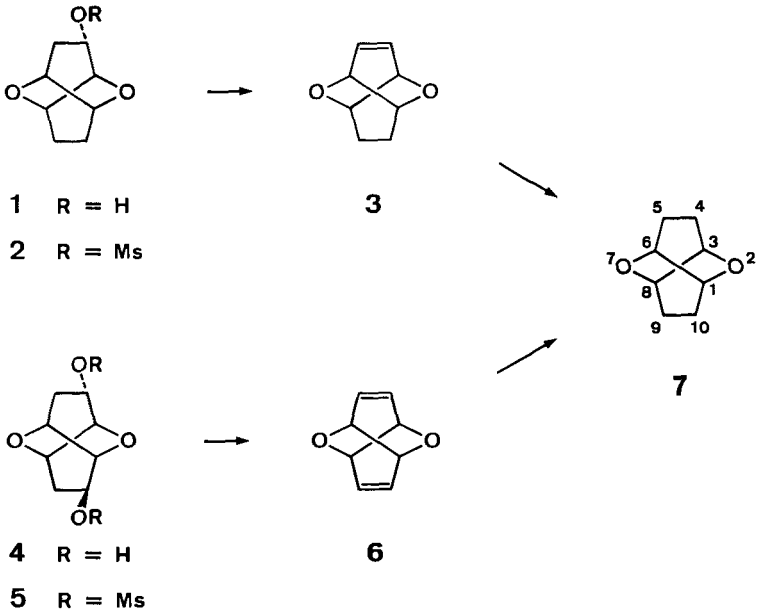
In connection with our studies on diheterotricyclodecanes we describe here the synthesis of 2,7-dioxa-twist-4-ene (**3**) and 2,7-dioxa-twista-4,9-diene (**6**). Whereas the mono-unsaturated compound **3** is the first example of a heterotwistene (pure carbocyclic twistene has already been synthesized earlier [2]), 2,7-dioxa-twista-4,9-diene (**6**) represents the first twistadiene prepared thus far.

Treatment of the twistane-mesylate **2** (prepared from twistanol **1** [3]) with *t*-BuOK/Me_2SO gave almost quantitatively 2,7-dioxa-twist-4-ene (**3**), m.p. 46°. By a similar reaction sequence 2,7-dioxa-twista-4,9-diene (**6**) (m.p. 84°) was prepared in excellent yield starting from the twistane-diol **4**[2]) *via* its dimesylate **5**.

[1]) For part XVI, see [1].

[2]) The synthesis of **4** will be described shortly in *Helv.*

Structural assignments of the compounds **3** and **6** are based on chemical conversion to the known saturated 2,7-dioxa-twistane (**7**) [3] by catalytic hydrogenation (Pd/C in EtOH) and on spectroscopical measurements. Mainly NMR. spectra (δ, 100 MHz, $CDCl_3$) give a full proof of the structures of **3** and **6**. The spectrum of **3** shows the following signals: 1.7–2.4/*m*, H_2–C(9), H_2–C(10) (typical $AA'BB'$-spectrum on simul-



taneous irradiation of the H–C(1) and –C(8) nuclei in a double resonance experiment); 3.64/*d*, $J_{1,10} = J_{8,9} = 2.4$ Hz [further splitting by $J_{1,6} = J_{3,8} = 1.7$ Hz and $J_{1,3} = J_{6,8} = 0.6$ Hz) H–C(1), –C(8)]; 4.42/*q*, $J_{1,6} = J_{3,8} = 1.7$ Hz, $J_{3,4} = J_{5,6} = 1.7$ Hz, $J_{3,5} = J_{4,6} = 1.7$ Hz (further splitting by $J_{1,3} = J_{6,8} = 0.6$ Hz) H–C(3), –C(6); 6.70/*t*, $J_{3,4} = J_{5,6} = 1.7$ Hz, $J_{3,5} = J_{4,6} = 1.7$ Hz, H–C(4), –C(5). The NMR.-spectrum of the diene **6** consists of two multiplets at 4.24 [$W^1/_2$ 6 Hz, H–C(1), –C(3), –C(6), –C(8)] and 6.61 [$W^1/_2$ 6 Hz, H–C(4), –C(5), –C(9), –C(10)]. Both signals are changed to singlets in double irradiation experiments.

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