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LITERATURVERZEICHNIS

[1] 84. Mitt.: *G. Ohloff, C. Vial, H. R. Wolf & O. Jeger*, Helv. *59*, 75 (1976).
[2] *B. R. von Wartburg, H. R. Wolf & O. Jeger*, Helv. *56*, 1948 (1973).
[3] *J. Ehrenfreund, Y. Gaoni & O. Jeger*, Helv. *57*, 2704 (1974).
[4] *A. P. Alder & H. R. Wolf*, Helv. *58*, 1048 (1975).
[5] *Z. Chabudzinski & M. Skwarek*, Roczniki chem. Ann. Soc. chim. Polonorum *45*, 1907 (1971).
[6] *H. Labhart & G. Wagnière*, Helv. *42*, 2219 (1959).
[7] *J. Hill, J. Iriarte, K. Schaffner & O. Jeger*, Helv. *49*, 292 (1966).
[8] *E. Baggiolini, H. P. Hamlow & K. Schaffner*, J. Amer. chem. Soc. *92*, 4906 (1970).
[9] *O. L. Chapman* in 'Organic Photochemistry', *3*, 115 (1973), Marcel Decker, New York 1973.
[10] *D. C. Nonhebel & J. C. Walton* in 'Free-radical-chemistry', S. 510, At The University Press, Cambridge 1974.
[11] *R. L. Cargill, T. E. Jackson, N. P. Peet & D. M. Pond*, Accounts chem. Res. *7*, 106 (1974).
[12] *P. Scribe, C. Nouet & J. Wiemann*, Tetrahedron Letters *1970*, 4375; *P. Scribe, D. Hourdin & J. Wiemann*, C. r. hebd. séances Acad. Sci. *268*, 178 (1969).
[13] *D. E. McGeer, M. G. Vinje & R. S. McDaniel*, Canad. J. Chemistry *43*, 1417 (1965).
[14] *W. G. Dauben, G. Lodder & J. Ipaktschi*, Fortschritte der chemischen Forschung *54*, 73 (1975).
[15] *K. B. Sharpless & R. Rodehorst*, J. Amer. chem. Soc. *95*, 6136 (1973).
[16] *J. R. B. Campbell, A. M. Islam & R. A. Raphael*, J. chem. Soc. *1956*, 4096.
[17] *E. J. Corey, H. J. Burke & W. A. Remers*, J. Amer. chem. Soc. *78*, 180 (1956).
[18] *G. Büchi & E. M. Burgess*, J. Amer. chem. Soc. *82*, 4333 (1960).
[19] *M. P. Zink, H. R. Wolf, E. P. Müller, W. B. Schweizer & O. Jeger*, Helv. *59*, 32 (1976).
[20] *T. Norin*, Acta chem. Scand. *19*, 1289 (1965).
[21] *R. S. Monson* in 'Advanced Organic Synthesis', S. 3, Academic Press, N.Y. 1971.
[22] *J. R. Neff, R. G. Grützmacher & J. E. Nordlander*, J. org. Chemistry *39*, 3814 (1974).
[23] *K. Ohno & J. Tsuji*, J. Amer. chem. Soc. *90*, 99 (1968).
[24] *C. A. Brown & D. Barton*, Synthesis *1974*, 434.

7. Twista-4,9-diene

Preliminary Communication

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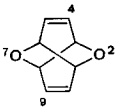
(10. XI. 75)

Summary. A synthesis of twista-4,9-diene (**17**) from tricyclo[4.3.1.$0^{3,8}$]dec-4-en-10-one (**2**) is described.

In connection with our studies on bridged polycyclic hydrocarbons and hetero analogs[1]) we here describe a synthesis of twista-4,9-diene (tricyclo[4.4.0.$0^{3,8}$]deca-4,9-diene) (**17**)[2]).

[1]) See *e.g.* [1–3].

[2]) As the first example of a twista-4,9-diene we recently prepared the heterocyclic analog 2,7-dioxa-twista-4,9-diene (**1**) [3].



1

As starting material we used tricyclo[4.3.1.$0^{3,8}$]dec-4-en-10-one (protoadamant-4-en-10-one or isotwist-4-en-10-one) (**2**) which is conveniently prepared by pyrolysis of 7-allyloxycycloheptatriene [4]. Reduction of ketone **2** yielded almost quantitatively the two epimeric alcohols **3**[3][4] (m.p. 253°) and **4** (m.p. 232°), in a proportion depending on the applied reaction conditions (*e.g.* $LiAlH_4$/ether or Na/CH_3OH). However, **3** was always the major product. **3** and **4** were also characterized as their acetates **5** [IR.: 3040, 1732, 1636. NMR.: 4.93/$d\times d$, $J_{1,10^{C(7)}5}$) = 4 and $J_{6,10^{C(7)}} = 5$, or *vice versa*, H–C(10)$^{C(7)}$] and **6** [IR.: 3035, 1736, 1639. NMR.: 4.76/m ($W^{1/2}$ approx. 6), H–C(10)$^{C(2)5}$)].

Treatment of alcohols **3** and **4** with thionyl chloride yielded in both cases as main product (> 90%) the same 10$^{C(7)}$-chloro isomer **7** [m.p. 135°. IR.: 3045, 1635. NMR.: 4.17/m ($W^{1/2}$ approx. 6), H–C(10)$^{C(2)}$][6]. To avoid participation of the double bond C(4)–C(5) in the subsequent rearrangement reaction, **7** was transformed by hydroxymercuration [$Hg(OAc)_2/H_2O$/THF] followed by $NaBH_4$-reduction in aqu. NaOH to the hydroxy-chloride **8**[7][8] [m.p. 179°. IR.: 3620, 3560–3200. NMR.: 4.03/m ($W^{1/2}$ approx. 7), H–C(10)$^{C(2)}$; 4.19/m ($W^{1/2}$ approx. 12), H–C(4)$^{C(2)}$] which was easily converted to the corresponding acetate **9** [IR.: 1737. NMR.: 4.03/m ($W^{1/2}$ approx. 7), H–C(10)$^{C(2)}$; 5.11/m ($W^{1/2}$ approx. 12, among others $J_{4^{C(2)},5^{C(2)}} = 6$ and $J_{3,4^{C(2)}} = 4$), H–C(4)$^{C(2)}$].

Rearrangement to the twistane skeleton was accomplished by treatment of the hydroxy-chloride **8** or the acetoxy-chloride **9** with silver acetate in acetic acid[9].

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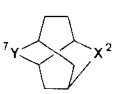
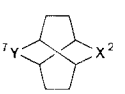
[3] **3** and all the compounds described hereafter gave satisfactory elemental analyses; all m.p. are uncorrected; IR. (CCl_4): ν_{max} in cm^{-1}; NMR. ($CDCl_3$): chemical shifts are reported in δ units relative to internal TMS (δ = 0.00 ppm), coupling constants are given in Hz, $W^{1/2}$ means line width at half height.

[4] The structural assignments of the compounds **3**–**17** are based mainly on comparisons among spectral data from a wide variety of 2,7-dihetero-isotwistanes (**a**) and 2,7-dihetero-twistanes (**b**) of known structures (see [3] and earlier papers on heterotricyclodecanes cited therein).



a



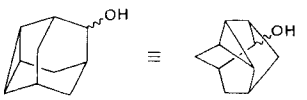
b

[5] The indices C(2) and C(7) indicate the carbon atom towards which a substituent is orientated.

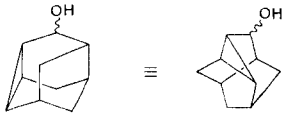
[6] A by-product (approx. 1–5%) could be characterized as 2,6-dichloro-adamantane.

[7] For an analogous transformation see the sequential treatment of the corresponding C(10)-unsubstituted protoadamant-4-ene with $Hg(OAc)_2$ and $NaBH_4$, which gave predominantly 4$^{C(7)}$-hydroxy-protoadamantane [5].

[8] In addition to **8** (60%), 35% of a tetracyclic alcohol, probably with a dehydroadamantane (**c**) or a dehydroprotoadamantane (**d**) skeleton, could be isolated.

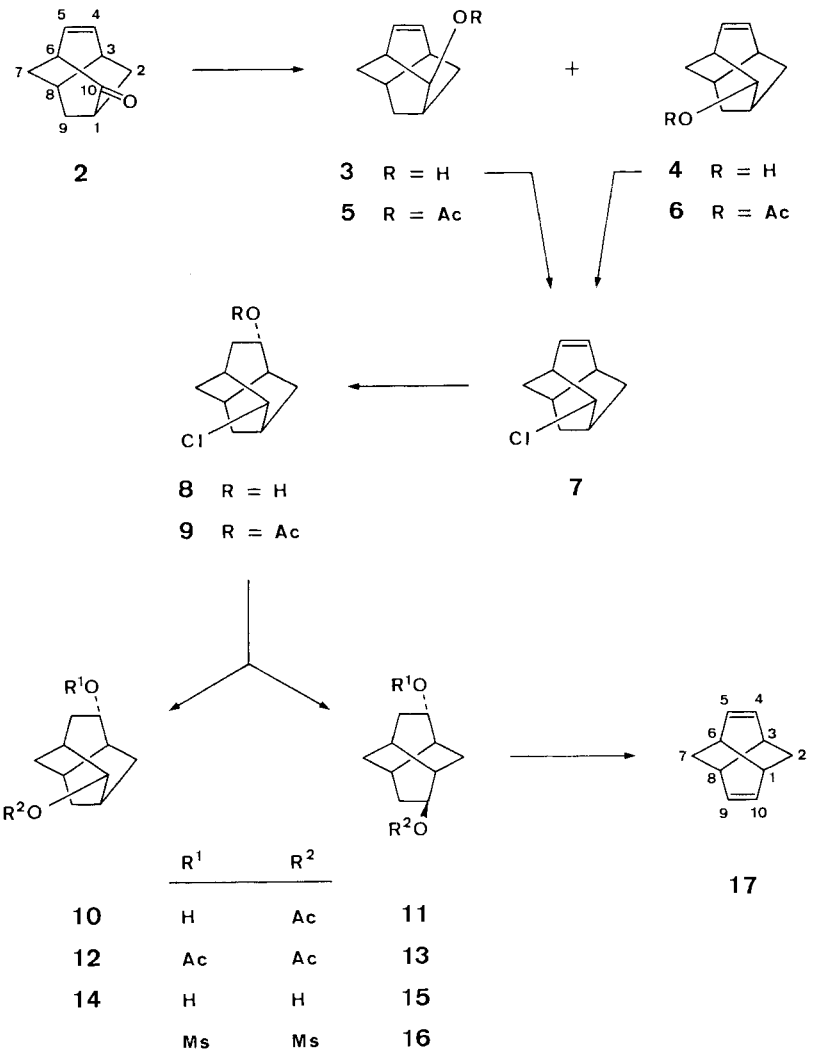


c



d

[9] For analogous rearrangements under solvolytic conditions of the corresponding 4-unsubstituted 10$^{C(2)}$- and 10$^{C,(7)}$-brosylates as well as the 10$^{C(2)}$-tosylate see [6] and [7], respectively.



in the former case a mixture of mono- and diacetates (**10** + **11** and **12** + **13**) was formed, whereas in the latter isotwistane diacetate **12** [IR.: 1736. NMR.: 4.66/*m* ($W^{1/2}$ approx. 7). H–C(10)$^{C(2)}$; 5.12/*m* ($W^{1/2}$ approx. 12, among others $J_{4^{C(2)},5^{C(2)}}$ = 6.5 and $J_{3,4^{C(2)}}$ = 4), H–C(4)$^{C(2)}$] and twistane diacetate **13** [m.p. 65–66°. IR.: 1737. NMR.: 5.04/*m* ($W^{1/2}$ approx. 14, among others $J_{4^{C(2)},5^{C(2)}} = J_{9^{C(2)},10^{C(2)}}$ = 7.5 and $J_{1,10^{C(2)}} = J_{3,4^{C(2)}}$ = 4), H–C(4)$^{C(2)}$ and –C(10)$^{C(2)}$] were obtained in 85% yield (ratio approx. 65:35). The above compounds **10**–**13** were reduced with $LiAlH_4$ to the corresponding diols **14** (m.p. 290°) and **15** (m.p. 227°).

Treatment of the twistane dimesylate **16** [prepared from the diol **15** with methanesulfonyl chloride in pyridine (90%), m.p. 198–200°] with *t*-BuOK/DMSO afforded as main component approx. 40% of twista-4,9-diene (**17**) [m.p. 70–72°. IR.: 3045, 1640,

1465, 1358, 1300, 1197, 1057, 1019, 848, 714. ^{1}H-NMR.: 1.52/*m* ($W^{1/2}$ approx. 8), H_2–C(2) and –C(7); 2.38/*m* ($W^{1/2}$ approx. 8), H–C(1), –C(3), –C(6) and –C(8); 6.20/*m* ($W^{1/2}$ approx. 8), H–C(4), –C(5), –C(9) and –C(10); the signals at 1.52 and 6.20 are changed to singlets in double irradiation experiments (simultaneous irradiation of the H–C(1), –C(3), –C(6) and –C(8) nuclei). ^{13}C–NMR.: only three signals due to the high symmetry (point group D_2) at 28.61/*d*, C(1), C(3), C(6) and C(8); 49.10/*t*, C(2) and C(7); 134.94/*d*, C(4), C(5), C(9) and C(10)].

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REFERENCES

[1] *H. Tobler, R. O. Klaus & C. Ganter*, Helv. *58*, 1455 (1975).
[2] *R. O. Klaus, H. Tobler & C. Ganter*, Helv. *57*, 2517 (1974).
[3] *P. Ackermann & C. Ganter*, Helv. *56*, 3054 (1973).
[4] *C. A. Cupas W. Schumann & W. E. Heyd*, J. Amer. chem. Soc. *92*, 3237 (1970).
[5] *B. D. Cuddy, D. Grant & M. A. McKervey*, Chem. Commun. *1971*, 27.
[6] *L. A. Spurlock & K. P. Clark*, J. Amer. chem. Soc. *94*, 5349 (1972).
[7] *M. Tichý, L. Kniežo & J. Hapala*, Tetrahedron Letters *1972*, 699.

8. Synthesis of Bromo-substituted 2-Buten- and 2-Penten-4-olides

by **Christopher B. Chapleo**[1], **Karen L. Svanholt**[2], **Roger Martin** and **André S. Dreiding**

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(4. XI. 75)

Zusammenfassung. Durch Erhitzen mit Bromwasserstoffsäure lassen sich aus Methyl (2*Z*)-4-Brom-2-brommethyl-2-butenoat (**1**) bzw. -2-pentenoat (**3**) die Lactone 2-Brommethyl-2-buten-4-olid (**2**) bzw. -2-penten-4-olid (**4**) gewinnen. Unter den gleichen Bedingungen werden Methyl (2*Z*)- und (2*E*)-4,4-Dibrom-2-brommethyl-2-butenoat (**5** und **6**) nur zu den entsprechenden Säuren **7** und **8** hydrolysiert. Die (2*Z*)- resp. (2*E*)-Konfiguration von **7** und **8** werden durch die folgenden (*trans*/*cis* > 1) ^{13}C zu ^{1}H Kopplungen zwischen den an der Doppelbindung vicinal gelegenen Kohlenstoff- und Wasserstoffatomen im ^{13}C-NMR.-Spektrum bestätigt: ^{13}COO zu H—C(3) 5,7 Hz in **7** und 10,2 Hz in **8**; $^{13}CH_2Br$ zu H—C(3) 8,7 Hz in **7** und 6,9 Hz in **8**.

Mittels N-Bromsuccinimid werden 2-Buten-4-olid (**10**) bzw. sein 2-Methylderivat **12** in 4-Brom-2-buten-4-olid (**11**) bzw. sein 2-Methylderivat **13** übergeführt. Mit Methanol entsteht aus **13** 4-Methoxy-2-methyl-2-buten-4-olid (**14**). Die Bromierung von 2-Penten-4-olid (**15**) oder von 3-Penten-4-olid (**16**) unter denselben Bedingungen gibt hingegen 4,5-Dibrom-2-penten-4-olid (**17**), während aus 2-Brommethyl-2-penten-4-olid (**4**) ein Gemisch von 4-Brom-2-brommethyl-2-penten-4-olid (**20**) und 4,5-Dibrom-2-brommethyl-2-penten-4-olid (**21**) entsteht.

1. Introduction. – Brominated butenolides might be useful synthons for natural products containing an unsaturated butyrolactone moiety[3]. We describe here our

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[3] Recent attention has been directed towards the synthesis of α-methylidene-butyrolactone derivatives [1], strigol [2] and related compounds [3] as well as freelingyne [4].