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Inter- and Intramolecular Hetero Diels-Alder Reactions, 31[1]

Synthesis of D-Homoestrone Derivatives by Tandem Knoevenagel Hetero Diels-Alder Reactions from Natural Estrone

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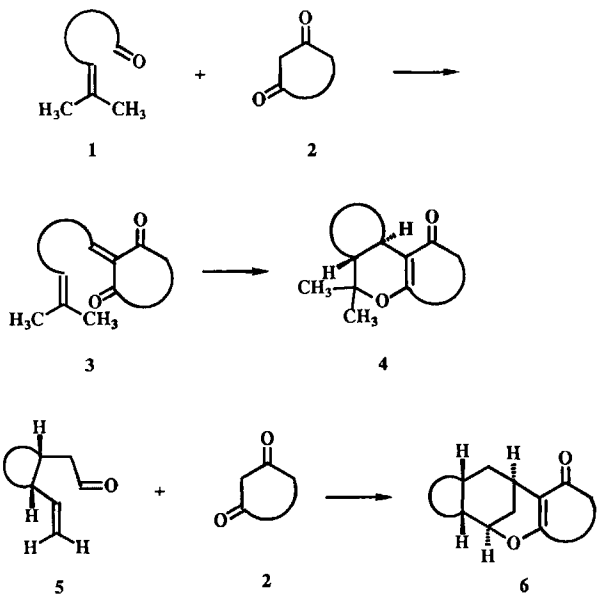
The tandem Knoevenagel hetero Diels-Alder reaction of the secoestrone derivative **8** with dimethylbarbituric acid (**9a**), Meldrum's acid (**9b**), and the pyrazolones **13a–c** stereoselectively affords the D-homoestrone derivatives **11a**, **12**, and **14a–c**, respectively, with the 16α,17aα configuration in excellent yield. In the reaction of **8** with **9a,b** only one diastereomer can be detected, whereas in the reaction of **8** with **13a–c** a small amount of the isomeric adducts **15a–c** has also been found.

The tandem Knoevenagel hetero Diels-Alder reaction[2], which has been developed by us, allows a highly efficient and stereoselective construction of polycyclic heterocycles. Thus, the condensation of a 1,3-dicarbonyl compound **2** with an aldehyde **1** bearing a dienophile moiety yields a 2-alkylidene-1,3-dioxo compound **3** which undergoes cyclization to give nearly exclusively the trans-annulated cycloadduct **4**. Recently, we have shown that by changing the substitution pattern of the dienophile moiety as in **5** bridged compounds **6** may be obtained[3]. This represents a new method for the synthesis of *cis*-1,3-disubstituted cyclohexanes. Moreover, it allows the formation of *cis*- or *trans*-decalins which are an integral part of steroids. In this paper we describe the synthesis of novel D-homoestrone derivatives using this new protocol.



D-homosteroids are of pharmacological interest[4]. Recently, a D-homoestra-4,16-dien-3-one has been found to be a potent orally active androgen[4a]. Several methods have been developed besides the total syntheses to obtain D-homosteroids from normal steroids[5]. The main procedures concern ring enlargement by rearrangements. However, many of these transformations are unselective though some efficient methods are also known as e.g. the base-catalyzed acyloin rearrangement of 17-hydroxypregnan-20-ones[6]. Furthermore, natural D-homosteroids are also known such as nicandrenone[7], which contains an aromatic ring D. This compound possesses strong repellent and mild insecticidal properties.

Our approach to the synthesis of D-homosteroids involves the cleavage of ring D of a steroid to give an allyl and a formyl group. Thus, condensation of estrone 3-methyl ether (**7**) with ethyl formate followed by reduction with $NaBH_4$, selective formation of the mono-*p*-toluenesulfonate of the primary hydroxy group of the *trans*-1,3-diol, and base-induced fragmentation yield the secoestrone derivative **8**[8]. This compound which is accessible in good yields is the starting material for the tandem Knoevenagel hetero Diels-Alder reaction. As 1,3-dicarbonyl compounds *N,N*-dimethylbarbituric acid (**9a**), Meldrum's acid (**9b**), as well as pyrazolones **13a–c** are used, and the reaction is performed in acetonitrile under reflux with ethylenediammonium diacetate as catalyst.

The intermediate Knoevenagel products cannot be isolated since after their formation they immediately undergo intramolecular cyclization to the hetero Diels-Alder adducts. Thus, **8** reacts with **9a** via **10a** to give the cycloadduct **11a** in 94% yield. In a similar way **8** is condensed with **9b**; in

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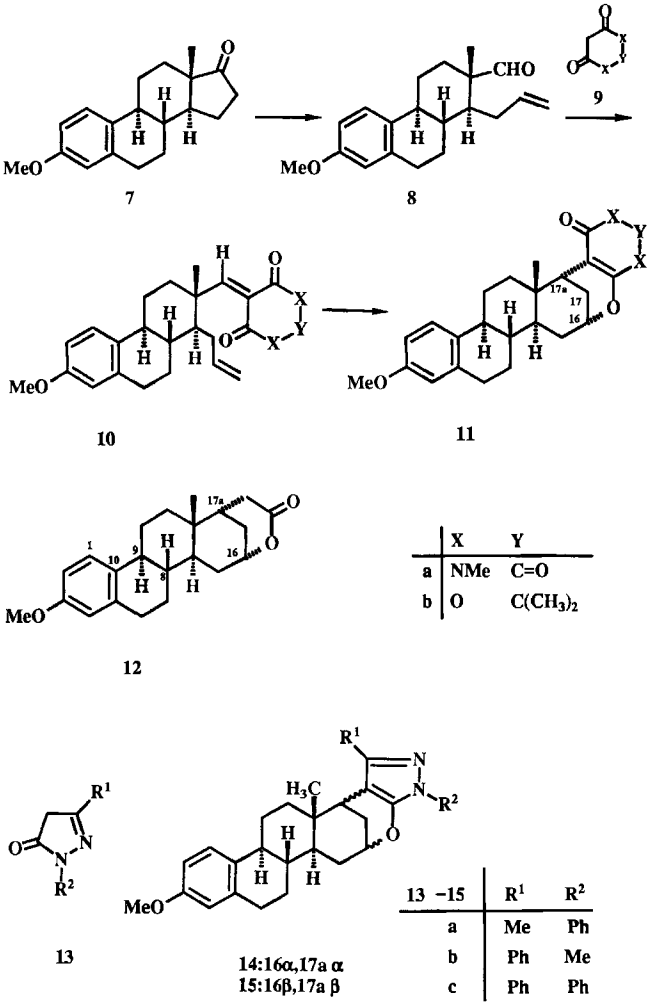
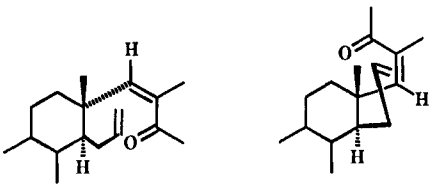
this case, however, the primarily formed adduct **11b** is not stable but liberates acetone and a C_1 moiety, leading to the formation of product **12** in 91% yield. The reactions of **8** with **9a** and **9b** proceed highly regio- and stereoselectively giving nearly exclusively the bridged compounds **11a** and **12** with the 16α,17aα configuration. The tandem Knoevenagel hetero Diels-Alder reaction of **8** with the pyrazolones **13a–c** again predominantely yields the cycloadducts **14a–c** with 16α,17aα configuration. However, in addition, a small amount of the 16β,17aβ diastereomers **15a–c** is obtained (**14:15** ≈ 5.5–8.5:1.0, overall yield 81–86%). The main products **14a–c** can be purified by chromatography.



	X	Y
a	NMe	C=O
b	O	$C(CH_3)_2$

13 –15	R^1	R^2
a	Me	Ph
b	Ph	Me
c	Ph	Ph

We assume that the cycloadducts **11a**, **12**, and **14** are formed via an *endo*-(*Z*) transition structure (TS 1) involving attack of the dienophile at the hetero diene moiety from above (*Re* face). The transition structure (TS 2) which would lead to the 16β,17aβ diastereomers displays a strong interaction between the angular methyl group at C-13 and the reacting carbonyl moiety. However, this interaction is less pronounced in the transition structure derived from **8** with the pyrazolones **13**, compared to those from **8** with **9** resulting in the formation of a small amount of the diastereomers **15a–c**.



The determination of the configuration of **11a**, **12**, **14a–b**, and **15b** is based on the ^{1}H-NMR spectra and an X-ray analysis[9] of **12**. A signal at δ = 4.79–4.97 for 16-H in **11a**, **14a–b**, and **15b** and at δ = 5.79 for 16-H in **12**, which integrates for one proton, indicates the bridged structure. For an annulated system resonances at δ = 4.5–5.0 for two protons should be found. Also, in the ^{13}C-NMR spectra a resonance is observed at δ = 74.9–77.1, which can only be assigned to the tertiary carbon C-16. The configuration of C-16 and consequently of C-17a can be deduced from the couplings of 16-H. For **11a**, **12**, and **14a–c** the resonance of 16-H appears almost as a quintuplet with a coupling constant of J = 3 Hz, whereas the ^{13}C-NMR spectrum of the diastereomer, e.g. **15b**, reveals a doublet of a doublet with J = 8 Hz and J = 3 Hz. Interestingly, a strong anisotropy effect is observed for the diastereomer **15b**. Usually – as in the ^{1}H-NMR spectra of **11a**, **12**, and **14a–c** – the angular methyl group at C-13 resonates around δ = 1.0, whereas in the spectrum of **15b** a singlet at δ = 0.48 is observed for this group. This can only be explained by assuming that the methyl group at C-13 in **15b** lies above the plane of the pyrazol moiety.

The described procedure for the synthesis of D-homoestrone derivatives is a general method for the enlargement of ring D in steroids and can also be applied to other types of steroids. In addition, the obtained cycloadducts, especially **12**, can be further transformed in many different ways.

We thank the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie* for their generous support. J. W. is grateful to the *Hungarian Academy of Sciences* for a scholarship.

Experimental

Melting points: Kofler melting point apparatus (corrected values). – IR: Bruker IFS 25. – UV: Varian Cary 219. – ^{1}H and ^{13}C NMR: Varian XL-200, VXR-200, and FT-80 A; multiplicities were determined with the APT pulse sequence. – MS: Varian MAT 311 A and Varian MAT 731 (high resolution). – Elemental analyses were carried out in the analytical laboratory of the university at Göttingen. – All solvents were distilled prior to use. All reactions were carried out under nitrogen and monitored by TLC (Macherey-Nagel Alugram Sil G/UV_{254}). Products were isolated by column or flash chromatography (CC of FC) on SiO_2 (CC: ICN Silica 63–200, 60 A, ICN Biochemicals, Eschwege; FC: Baker 30–60 active). – Solvents used for TLC and column chromatography: A: ethyl acetate/petroleum ether (1:1), B: (1:2), C: (1:4), D: (1:10).

Tandem Knoevenagel Hetero Diels-Alder Reaction of **8** *with* **9a**, **9b**, *and* **13a–c**. – *General Procedure:* To a stirred solution of the aldehyde **8** (298 mg, 1.00 mmol) in anhydrous acetonitrile (10 ml) was added 1.10 mmol of **9a**, **9b**, or **13a–c**, ethylenediammonium diacetate (10 mg) and anhydrous Na_2SO_4 (500 mg) at 20°C under nitrogen. The mixture was then heated to reflux and kept at this

temperature until completion of the reaction (12–20 h, TLC, solvent as indicated). The solvent was evaporated in vacuo and the residue purified by chromatography on silica gel. Recrystallization was performed from chloroform/petroleum ether.

D-Homoestrone N,N-Dimethylbarbituric Acid Adduct **11a**: The reaction of **8** (298 mg, 1.00 mmol) with **9a** (172 mg, 1.10 mmol) for 14 h according to the general procedure yielded 410 mg (94%) of **11a** as colorless needles after chromatography (solvent A). – R_f = 0.16 (solvent B). – M.p. 249–250°C. – $[\alpha]_D^{20}$ = +183.5 (*c* = 1 in $CHCl_3$). – IR (KBr): $\tilde{\nu}$ = 2930 cm^{-1} (CH), 2870 (CH), 1700, 1670–1590 (C=O, C=C), 1520, 1400. – UV (CH_3CN): λ_{max} (lg ε) = 263 nm (4.031), 286 (3.330). – ^1H NMR (200 MHz, $CDCl_3$): δ = 1.03 (s, 3H, 18-CH_3), 1.0–3.0 (m, 14H), 3.39 (s, 3H, NCH_3), 3.41 (s, 3H, NCH_3), 3.80 (s, 3H, OCH_3), 4.97 (m, 1H, 16-H), 6.64 (d, $J_{2,4}$ = 3 Hz, 1H, 4-H), 6.75 (dd, $J_{1,2}$ = 8.5, $J_{2,4}$ = 3 Hz, 1H, 2-H), 7.22 (d, $J_{1,2}$ = 8.5 Hz, 1H, 1-H). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 17.5 (C-18), 28.1 and 28.7 (N-1′- and N-3′-CH_3), 29.9 (C-6), 38.8 (C-13), 43.3 (C-9), 55.2 (3-OCH_3), 77.1 (C-16), 89.3 (C-5′), 111.5 (C-2), 113.4 (C-4), 126.3 (C-1), 132.7 (C-10), 137.4 (C-5), 151.2 (C-2′), 157.4 (C-6′), 157.5 (C-3), 162.9 (C-4′). – MS (70 eV): *m/z* (%) = 436 (100) [M^+], 227 (10), 225 (14), 100 (12), 73 (22).

$C_{26}H_{32}N_2O_4$ (436.6) Calcd. C 71.53 H 7.39 N 6.42
Found C 71.40 H 7.38 N 6.32

D-Homoestrone Meldrum's Acid Adduct **12**: The reaction of **8** (298 mg, 1.00 mmol) with **9b** (159 mg, 1.10 mmol) for 12 h according to the general procedure afforded 310 mg (91%) of **12** as colorless prisms after chromatography (solvent A). – R_f = 0.21 (solvent B). – M.p. 230–234°C. – $[\alpha]_D^{20}$ = +77.3 (*c* = 1 in $CHCl_3$). – IR (KBr): $\tilde{\nu}$ = 2930 cm^{-1} (CH), 2870 (CH), 1720 (C=O), 1610, 1500, 1390, 1240 (C–O). – UV (CH_3CN): λ_{max} (lg ε) = 277 nm (3.341), 285 (3.302). – ^1H NMR (200 MHz, $CDCl_3$): δ = 0.97 (s, 3H, 18-CH_3), 1.0–3.0 (m, 14H), 3.78 (s, 3H, OCH_3), 5.79 (m, 1H, 16-H), 6.63 (d, $J_{2,4}$ = 3 Hz, 1H, 4-H), 6.74 (dd, $J_{1,2}$ = 8.5, $J_{2,4}$ = 3 Hz, 1H, 2-H), 7.23 (d, $J_{1,2}$ = 8.5 Hz, 1H, 1-H). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 18.0 (C-19), 29.9 (C-6), 43.4 (C-9), 55.2 (3-OCH_3), 75.6 (C-16), 111.7 (C-2), 113.4 (C-4), 126.2 (C-1), 132.3 (C-10), 137.7 (C-5), 157.5 (C-3), 171.6 (C-21). – MS (70 eV): *m/z* (%) = 341 (24), 340 (100) [M^+], 227 (11), 187 (12), 186 (30).

$C_{22}H_{28}O_3$ (340.5) Calcd. C 77.61 H 8.29
Found C 77.50 H 8.34

D-Homoestrone Pyrazolone Adduct **14a**: The reaction of **8** (298 mg, 1.00 mmol) with **13a** (192 mg, 1.10 mmol) for 16 h according to the general procedure yielded 391 mg (86%) of a mixture of **14a** and **15a** (8.5:1.0, ^{13}C NMR) after single chromatography (solvent D, broad cut). A second chromatography (solvent D) and subsequent crystallization afforded 212 mg (47%, not optimized) of pure **14a** as colorless prisms. – R_f = 0.17 (solvent D) [**15a**: R_f = 0.20 (solvent D)]. – M.p. 250–253°C. – $[\alpha]_D^{20}$ = –35.7 (*c* = 1 in $CHCl_3$). – IR (KBr): $\tilde{\nu}$ = 2940 cm^{-1} (CH), 2890 (CH), 1610 (C=N), 1530, 1460. – ^1H NMR (200 MHz, $CDCl_3$): δ = 1.03 (s, 3H, 18-CH_3), 1.0–2.8 (m, 13H), 2.26 (s, 3H, CH_3), 2.45 (br. t, *J* = 1.5 Hz, 1H, 17a-H), 3.75 (s, 3H, OCH_3), 4.86 (br. s, 1H, 16-H), 6.59 (d, $J_{2,4}$ = 3 Hz, 1H, 4-H), 6.69 (dd, $J_{1,2}$ = 8.5, $J_{2,4}$ = 3 Hz, 1H, 2-H), 7.15 (d, $J_{1,2}$ = 8.5 Hz, 1H, 1-H), 7.18–7.77 (m, 5, Ph-H). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.1 (3′-CH_3), 17.6 (C-18), 30.0 (C-6), 43.1 (C-9), 55.1 (3-OCH_3), 75.6 (C-16), 99.4 (C-4′), 111.5 (C-2), 113.4 (C-4), 119.8 (C-2″), 125.0 (C-4″), 126.2 (C-1), 128.9 (C-3″), 132.9 (C-10), 137.6 (C-5), 139.0 (C-1″), 146.5 (C-3′), 151.3 (C-5′), 157.4 (C-3). – MS (70 eV): *m/z* (%) = 455 (31), 454 (100) [M^+], 227 (72), 226 (60), 225 (42), 213 (45), 211 (58), 187 (67), 77 (46).

$C_{30}H_{34}N_2O_2$ (454.6) Calcd. C 79.26 H 7.54 N 6.16
Found C 79.09 H 7.46 N 6.04

D-Homoestrone Pyrazolone Adduct **14b** *and* **15b**: The reaction of **8** (298 mg, 1.00 mmol) with **13b** (192 mg, 1.10 mmol) for 22 h according to the general procedure yielded 386 mg (85%) of a mixture of **14b** and **15b** (5.52:1.00, ^{13}C NMR) after single chromatography (solvent D, broad cut). A second chromatography (solvent D) and subsequent crystallization afforded 230 mg (51%, not optimized) of pure **14b** as colorless prisms. **15b** was obtained as colorless oil from the mother liquor by repeated chromatography (solvent D).

14b: R_f = 0.22 (solvent C), – M.p. 261–264°C. – $[\alpha]_D^{20}$ = +190.6 (*c* = 1 in $CHCl_3$). – IR (KBr): $\tilde{\nu}$ = 2940 cm^{-1} (CH), 2890 (CH), 1620 (C=N), 1570, 1510, 1460. – ^1H NMR (200 MHz, $CDCl_3$): δ = 1.02 (s, 3H, 18-CH_3), 1.0–2.8 (m, 13H), 2.98 (br. t, *J* = 1.5 Hz, 1H, 17a-H), 3.71 (s, 3H, NCH_3), 3.74 (s, 3H, OCH_3), 4.79 (br. s, 1H, 16-H), 6.57 (d, $J_{2,4}$ = 3 Hz, 1H, 4-H), 6.64 (dd, $J_{1,2}$ = 8.5, $J_{2,4}$ = 3 Hz, 1H, 2-H), 7.04 (d, $J_{1,2}$ = 8.5 Hz, 1H, 1-H), 7.28–7.77 (m, 5H, Ph-H). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 17.9 (C-18), 30.0 (C-6), 42.9 (C-9), 55.1 (3-OCH_3), 74.9 (C-16), 96.4 (C-4′), 111.4 (C-2), 113.4 (C-4), 126.2 (C-1), 126.8 (C-2″), 127.1 (C-4″), 128.2 (C-3″), 132.9 (C-10), 135.3 (C-1″), 137.6 (C-5), 146.6 (C-3′), 151.8 (C-5′), 157.3 (C-3). – MS (70 eV): *m/z* (%) = 455 (30), 454 (100) [M^+], 227 (42), 226 (29), 225 (26), 213 (22), 211 (30), 187 (24).

$C_{30}H_{34}N_2O_2$ (454.6) Calcd. C 79.26 H 7.54 N 6.16
Found C 79.02 H 7.43 N 5.98

15b: R_f = 0.25 (solvent C). – ^1H NMR (200 MHz, $CDCl_3$): δ = 0.48 (s, 3H, 18-CH_3), 1.0–2.9 (m, 13H), 3.10 (d, *J* = 9 Hz, 1H, 17a-H), 3.70 (s, 3H, NCH_3), 3.75 (s, 3H, OCH_3), 4.37 (dd, *J* = 11, 6.5 Hz, 1H, 16-H), 6.59 (d, $J_{2,4}$ = 3 Hz, 1H, 4-H), 6.65 (dd, $J_{1,2}$ = 8.5, $J_{2,4}$ = 3 Hz, 1H, 2-H), 7.09 (d, $J_{1,2}$ = 8.5 Hz, 1H, 1-H), 7.36–7.54 (m, 5H, Ph-H).

D-Homoestrone Pyrazolone Adduct **14c**: The reaction of **8** (298 mg, 1.00 mmol) with **13c** (260 mg, 1.10 mmol) for 20 h according to the general procedure yielded 419 mg (81%) of a mixture of **14c** and **15c** (7.7:1.0, ^{13}C NMR) after single chromatography (solvent D, broad cut). A second chromatography (solvent D) and subsequent crystallization afforded 190 mg (37%, not optimized) of nearly pure **14c** as colorless prisms. – R_f = 0.27 (solvent D) [**15c**: R_f = 0.29 (solvent D)]. – IR (KBr): $\tilde{\nu}$ = 2950 cm^{-1} (CH), 2890 (CH), 1610 (C=N), 1580, 1520, 1460. – ^1H NMR (200 MHz, $CDCl_3$): δ = 1.04 (s, 3H, 18-CH_3), 1.0–2.8 (m, 13H), 3.05 (br. t, *J* = 1.5 Hz, 1H, 17a-H), 3.73 (s, 3H, OCH_3), 4.92 (br. s, 1H, 16-H), 6.56 (d, $J_{2,4}$ = 3 Hz, 1H, 4-H), 6.63 (dd, $J_{1,2}$ = 8.5 Hz, $J_{2,4}$ = 3 Hz, 1H, 2-H), 7.04 (d, $J_{1,2}$ = 8.5 Hz, 1H, 1-H), 7.22–7.97 (m, 10H). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 17.9 (C-18), 30.0 (C-6), 43.0 (C-9), 55.1 (3-OCH_3), 75.4 (C-16), 98.3 (C-4′), 111.4 (C-2), 113.4 (C-4), 120.4 (C-2″), 125.5 (C-4″), 126.2 (C-1), 127.3 (C-2‴), 127.6 (C-4‴), 128.3 (C-3‴), 128.9 (C-3″), 132.9 (C-10), 135.0 (C-1‴), 137.6 (C-5), 139.0 (C-1″), 148.4 (C-3′), 151.8 (C-5′), 157.4 (C-3). – MS (70 eV): *m/z* (%) = 517 (42), 516 (100) [M^+], 273 (18), 258 (17), 249 (21), 44 (28), 43 (22).

$C_{35}H_{36}N_2O_2$ (516.7) Calcd. C 81.36 H 7.02 N 5.42
Found C 81.20 H 7.11 N 5.29

CAS Registry Numbers

7: 1624-62-0 / **8**: 118335-53-8 / **9a**: 769-42-6 / **9b**: 2033-24-1 / **11a**: 129570-36-1 / **12**: 129570-39-4 / **13a**: 89-25-8 / **13b**: 41927-50-8 / **13c**: 4845-49-2 / **14a**: 129704-17-2 / **14b**: 129570-38-3 / **14c**: 129570-40-7 / **15a**: 129570-37-2 / **15b**: 129646-49-7 / **15c**: 129646-50-0

[1] Part 30: L. F. Tietze, S. Brand, T. Brumby, J. Fennen, *Angew. Chem.* **102** (1990) 675; *Angew. Chem. Int. Ed. Engl.* **29** (1990) 665.
[2] L. F. Tietze, *J. Heterocycl. Chem.* **27** (1990) 47.

[3] [3a] L. F. Tietze, H. Stegelmeier, K. Harms, T. Brumby, *Angew. Chem.* **94** (1982) 868; *Angew. Chem. Int. Ed. Engl.* **21** (1982) 863. – [3b] L. F. Tietze, C. Bärtels, unpublished results.

[4] [4a] M. A. Avery, M. Tanabe, D. F. Crowe, G. Detre, R. H. Peters, W. K. M. Chong, *Steroids* **55** (1990) 59. – [4b] R. E. Dolle, H. S. Allaudeen, L. I. Kruse, *J. Med. Chem.* **33** (1990) 877. – [4c] S. Itoh, H. Ichikawa, H. Takagi, I. Yoshizawa, *Chem. Pharm. Bull.* **36** (1988) 4261.

[5] Reviews on homosteroids: E. Brown, M. Ragault, *Tetrahedron* **35** (1979) 911; P. Kocovský, *Chem. Listy* **73** (1979) 583; T. Masamune *Int. Rev. Sci.: Org. Chem., Ser. Two,* **8** (1976) 237; H. O. Huisman, W. N. Speckamp, *ibid.* **8** (1976) 207; D. N. Kirk, *Terpenoids Steroids* **4** (1974) 311.

[6] Newer work on the synthesis of homosteroids: [6a] V. M. Rzheznikov, T. I. Ivanenko, V. P. Fedotov, S. N. Pestovskii, S. N. Ananchenko, *Khim. Farm. Zh.* **22** (1988) 1462; *Chem. Abstr.* **110** (1989) 108353. – [6b] E. Brown, J. Lebreton, *Tetrahedron* **43** (1987) 5827. – [6c] R. Pellicciari, B. Natalini, R. Fringuelli, *Steroids* **49** (1987) 433. – [6d] S. A. Campbell, T. A. Crabb, R. O. Williams, *Magn. Reson. Chem.* **24** (1986) 803. – [6e] C. Aubert, J. P. Bégué, D. Bonnet-Delpon, *Tetrahedron* **41** (1985) 2665. – [6f] N. G. Steinberg, G. H. Rasmusson, G. F. Reynolds, J. H. Hirshfield, B. H. Arison, *J. Org. Chem.* **49** (1984) 4731. – [6g] M. B. Groen, F. J. Zeelen, *Recl. Trav. Chim. Pays-Bas* **103** (1984) 169. – [6h] K. Takaki, M. Ohsugi, M. Okada, M. Yasumura, K. Negoro, *J. Chem. Soc., Perkin Trans. 1* **1984**, 741. – [6i] M. Fetizon, G. Sozzi, *Tetrahedron* **37** (1981) 61. – [6j] G. Haffer, U. Eder, G. Neef, G. Sauer, R. Wiechert, *Liebigs Ann. Chem.* **1981**, 425.

[7] R. B. Bates, D. J. Eckert, *J. Am. Chem. Soc.* **94** (1972) 8258.

[8] G. Schneider, S. Bottka, L. Hackler, J. Wölfling, P. Sohár, *Liebigs Ann. Chem.* **1989**, 263.

[9] J. Antel, G. M. Sheldrick, L. F. Tietze, J. Wölfling, *Acta Crystallogr., Sect. C,* **44** (1988) 2229.

[250/90]