Synthesis of new anthraquinone and naphthohomobarrelene derivatives

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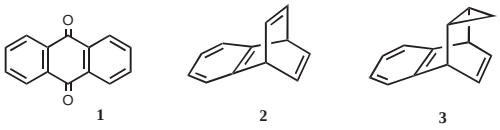
Cycloadditions of 1,4-naphthoquinone with cycloheptatriene and its 7-carbomethoxy and 7-cyano derivatives are investigated. The synthesis of new anthraquinone and naphthohomobarrelene derivatives is reported.

Keywords: norcaradienes, cycloheptatrienes, 1,4-naphthoquinone, anthraquinone, fused homobarrelenes, fused barrelenes.

The structures of anthraquinone (**1**), benzobarrelene (**2**) and benzohomobarrelene (**3**) are important in chemistry. Benzobarrelene (**2**), benzohomobarrelene (**3**) and their derivatives afford the possibility of several mechanistically interesting investigations. Their reactions such as bromination, di-π-methane rearrangement and solvolysis have been investigated.[1] Porphyrins possessing covalent linkages to quinones have become increasingly important in the study of photoinduced electron-transfer reactions. Adducts of 1,4-naphthoquinone are used in the preparation of porphyrin–quinone molecules.[2]



1 **2** **3**

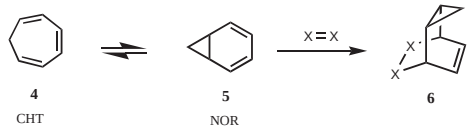
Cycloheptatriene (CHT, **4**) is in equilibrium with its valence isomer norcaradiene (NOR, **5**).[3] The substituents at the C-7 position in CHT have a dramatic influence on the CHT – NOR equilibrium. Hoffman and Günther have predicted that π-acceptor substituent(s) at C-7 of cycloheptatriene, such as CN, COOR and CHO, shift the CHT – NOR equilibrium to the side of norcaradiene, where electron donating substituents (such as OR, NR_2) stabilise the cycloheptatriene structure.[4] In cycloaddition reactions, cycloheptatrienes give in most cases norcaradiene-type adducts.[5]

Cycloaddition reactions of dienes with 1,4-naphthoquinone, a good dienophile, have been investigated.[6] Takeshita *et al.*[7] investigated the reaction of 1,4-naphthoquinone with cycloheptatriene (CHT) in toluene at high (reflux) temperatures (Scheme 2). The product yields obtained in this reaction are very low. However, adducts **8** and **9** are norcaradiene-type adducts.

We describe here further cycloaddition reactions of 1, 4-naphthoquinone with cycloheptatriene and 7-substituted cycloheptatrienes, with a view to the synthesis of anthraquinone and naphthohomobarrelene derivatives.

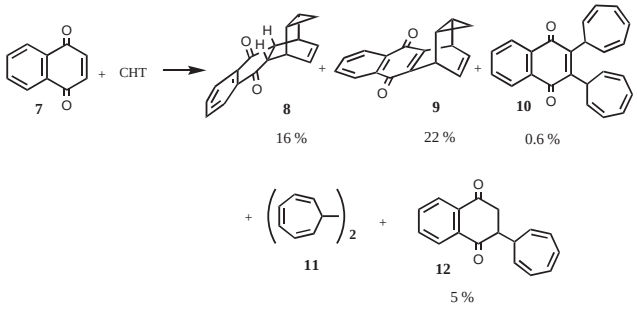
Results and discussion

A mixture of 1,4-naphthoquinone and CHT was heated in a sealed tube at 110 ºC for 17 days. The reaction mixture was cooled and the CHT in the mixture was removed. $CHCl_3$ was added to the residue and the dissolved part of it was subjected to silica gel column chromatography. Compounds **9** and **8** were separated, in that order. EtOAc (ethyl acetate) was added to the undissolved part of the residue and it was filtered. After solvent evaporation, the residue was reacted with pyridine and acetic anhydride (Ac_2O) at room temperature for 2 days. The reaction mixture was poured into a dilute HCl solution with ice and checked with pH paper. It was extracted with $CHCl_3$, washed with $NaHCO_3$ (5 %) and water and dried over $CaCl_2$, and then



4 CHT **5** NOR **6**

Scheme 1



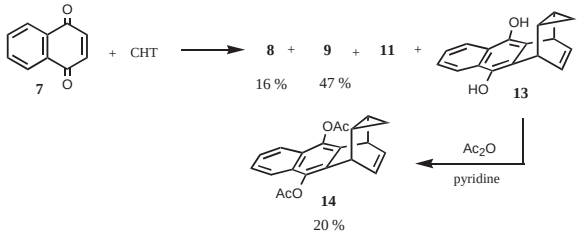
7 **8** 16 % **9** 22 % **10** 0.6 % **11** **12** 5 %

Scheme 2

the solvent was evaporated. The residue was subjected to silica gel column chromatography and compounds **9** and **14**, in that order, were separated. (Scheme 3)

The reaction products **8**, **9** and **11** were also obtained in this reaction. However, the amount of **11** was not determined. The yields of **11**[7,8a] are not written in Schemes 2 and 3 because they were not recorded in ref. 7. For compounds **8** and **9**, the yields that we obtained are higher than the yields of Takeshita *et al.*[7] To determine the structure of diol **13,** which was produced in this reaction and which has very low solubility in $CHCl_3$, it was converted into **14**. Diacetate **14** could be distinguished; it has a symmetrical structure and exhibits an *AA'BB'* system for aromatic protons, and is consistent with the ^{13}C NMR spectrum.

In the same way, 1,4-naphthoquinone (**7**) reacted with 7-carbomethoxy-CHT[8] (**15**) to give **16**, **17** and **18** (Scheme 4). The fraction of the reaction mixture soluble in $CHCl_3$ was subjected to silica gel column chromatography, and compounds **16** and **17** were separated, in that order. The remainder was reacted with Ac_2O, and **19** was obtained. Compound **16** is an *endo*- norcaradiene-type adduct. Products **16, 17** and **19** are symmetrical structures, and their ^1H and ^{13}C NMR spectra are in agreement with this.



7 **8** 16 % **9** 47 % **11** **13** **14** 20 %

Scheme 3

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The reaction of 1,4-naphthoquinone (**7**) with 7-cyano-CHT[8] (**20**) was performed. (Scheme 5) The ^{1}H NMR spectrum of the fraction of the reaction mixture soluble in $CHCl_3$ revealed that compounds **21**, **22**, **24** and **25** are present, and the ratios of **21** : **22** : **24** : **25** were 50 : 23 : 19 : 8, respectively. However, from the column chromatography of this mixture only compound **22** was obtained, in a yield of 8 %; the others were not isolated. However, compound **21** was also obtained in a purity of 93 % by fractional crystallisation. The molecular mass (HRMS) of **21** was 275.0935, and this HRMS is in good agreement with the proposed molecular formula. Compound **22** is produced by the oxidation of **21**, in which the CN group has an *exo* configuration. Two NOR structures are present in 7-cyano-CHT (**20**), and they give norcaradiene-type adducts where CN groups are in an *exo*- and *endo*- configuration in their cycloaddition reactions.[3,9,10] However, as with **13** and **18**, the reaction of **23** with Ac_2O in pyridine was performed, and **27** was prepared. Compounds **22** and **27** have symmetrical structures and their spectra are in complete agreement with these.

In cycloaddition reactions of 1,4-naphthoquinone with CHT or CHT derivatives such as $COOCH_3$ and CN, diols (**13**, **18** and **23**) were obtained in addition to adducts (**8**, **16** and **21**) and dihydroanthraquinones (**9**, **17** and **22**). For the formation of diols, the proposed mechanism may involve conversions of the adducts into their diols at high temperatures. Diols, naphthohomobarrelene derivatives, are *enol*-structures of the adducts. To determine the structures of the diols, they were converted into their diacetate derivatives (**14**, **19** and **27**). Dihydroanthraquinones (**9**, **17** and **22**) are produced by oxidations of adducts under the reaction conditions and during chromatography. Examples of the oxidation of adducts similar to **8**, **16** and **21** have been reported previously.[11]

In conclusion: the adducts **8**, **16** and **21**, prepared by the cycloaddition of 1,4-naphthoquinone with cycloheptadienes, are norcaradiene-type adducts and tetrahydroanthraquinone derivatives. In the syntheses of these adducts the CHT-NOR valence bond equilibrium participated.[3] Compounds **9**, **17** and **22** are dihydroanthraquinone derivatives. The diols (**13**, **18** and **23**) and diacetates (**14**, **19** and **27**) are naphthohomobarrelene derivatives. All except for compounds **8** and **9** are new.

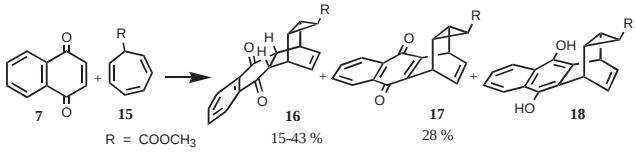
Experimental

Column chromatography (CC) was carried out on silica gel (60 mesh, Merck), amd preparative thick-layer chromatography (PLC) with 1 mm of silica gel 60 PF (Merck) on glass plates. A Thomas Hoover capillary melting apparatus was used. IR spectra: were obtained from solutions in 0.1 mm cells with a Perkin-Elmer spectrophotometer. The ^{1}H and ^{13}C NMR spectra were recorded on a 200(50)-MHz Varian spectrometer; δ are reported in in ppm, with Me_4Si as the internal standard. Mass spectra were determined with a VG ZabSpec instrument, range 1000 EI, 10000 for HRMS. Elemental analyses were performed on a Carlo Erba 1106 apparatus.

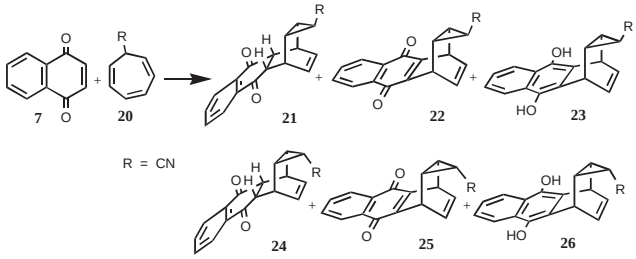
The reaction of 1,4-naphthoquinone with CHT

A mixture of 1,4-naphthoquinone (1.5 g) and CHT (5 ml) in a sealed tube was heated at 110 ± 5 °C for 17 days. The reaction mixture was cooled and excess of CHT in the mixture was removed. $CHCl_3$ (75 ml) was added to the residue and the soluble part was separated on a silica gel column chromatography, eluting with ether / hexane (5 / 95). Compound **9** (1.03 g, 44 %) and 8 (370 mg, 16 %) were separated, in that order. Compound **11** was also detected in the first fraction.

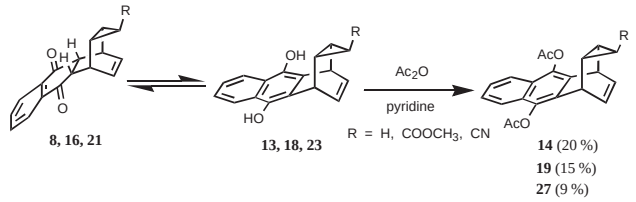
EtOAc (75 ml) was added to the residue which was not dissolved in the $CHCl_3$. After filtration the EtOAc was removed, and the residue (2.05 g) was allowed to react at room temperature for 2 days with pyridine (2.5 ml) and acetic anhydride (Ac_2O) (3.75 ml). The reaction mixture was poured into dilute aqueous HCl (200 g) with ice and checked with pH paper. It was extracted with $CHCl_3$ (2 × 50 ml), the extract was washed with $NaHCO_3$ (5 %, 100 ml) and water (100 ml), and dried over $CaCl_2$. The solvent was evaporated and the residue was submitted to silica gel column chromatography with EtOAc / hexane (2 / 8) elution. Compounds 9 (72 mg, 3 %) and 14 (620 mg, 20 %) were separated.



Scheme 4



Scheme 5



Scheme 6

Compounds **8** and **9** are known.[7] The NMR data of compound **8** and **9** are consistent with reported[7] data. The structure of **11** was checked by its NMR spectra we obtained.

8: Colourless crystals from ethyl acetate; m.p. 161–163 °C (Lit.[7] 165-166.5 °C); δ_C (50 MHz, $CDCl_3$): 198.34 (CO), 136.02, 134.51, 129.50, 127.34, 50.94, 38.27, 10.34, 2.90. ^{13}C NMR data of compound **8** are given here because they have not been reported previously.

3,10-Diacetoxy-1R(S),12S(R),13R(S),15S(R)-pentacyclo [10.3.2.0^{2,11}.0^{4,9}.0^{13,15}]heptadeca-2(11),3,5,7,9,16-hexaene (**14**): white crystals from ether/$CHCl_3$; m.p. 198–200 °C; ν_{max} (KBr) 3077, 3014, 2969, 1764, 1654, 1618, 1513, 1425, 1361, 1284, 1226, 1187, 1174, 1097, 1047, 1020 cm^{-1}; δ_H (200 MHz-$CDCl_3$): 7.89–7.40 (*AA'* of *AA'BB'*, 2 arom. H), 7.49–7.41 (*BB'* of *AA'BB'*, 2 arom. H), 6.18–6.14 (m, 2 olef. H), 4.15–4.10 (m, H-C(1), H-C(12)), 2.52 (s, 2 Me.), 1.36–1.30 (m, H-C(13), H-C(15)), 0.77 (dt, *A* of *AB*, ^2J = 5.58, ^3J = 3.68, *exo* H-C(14)), 0.62 (dt, *B* of *AB*, ^2J = 5.58, ^3J = 7.18, *endo* H-C(14)); δ_C (50 MHz, $CDCl_3$): 170.70 (CO), 139.51, 137.57, 132.31, 127.92 (2 C), 123.15, 37.79, 22.56, 16.26, 13.13; *m/z* 334 (20), 292 (38), 250 (100), 209 (12), 202 (7). Anal: calc. for $C_{21}H_{18}O_4$: C 75.43, H 5.43; found: C 75.33, H 5.45 %.

The reaction of 1,4-naphthoquinone with 7-methoxycarbonyl-CHT (15)

This reaction was studied under two conditions.

(**a**) A mixture of 1,4-naphthoquinone (1.0 g), 7-carbomethoxy-CHT[8] (1.0 g) and $CHCl_3$ (13 ml) in a sealed tube was heated at 95 ± 5 °C for 7 days. The reaction mixture was cooled and $CHCl_3$ (75 ml) was added, and solid material was separated. After solvent evaporation, the residue was submitted to column chromatography on silica gel (50 g) with EtOAc / hexane (5 / 95). Compounds **16** (300 mg, 15 %) and **17** (470 mg, 24 %) were eluted, in that order. EtOAc (ethyl acetate) (75 ml) was added to the other residue mixture and it was filtrated. After EtOAc removed, the residue (860 g) with pyridine (2.5 g) and Ac_2O (1.8 g) was reacted at room temperature for 2 days. Work-up of this was studied like that of **14**. Crude product was submitted on silica gel (50 g) column chromatography with EtOAc / hexane (1/5). Compound **17** (75 mg, 4 %) and **19** (367 mg, 15 %) were separated, respectively.

14-exo-Methoxycarbonyl-1S(R),2S(R),11R(S),12R(S),13R(S),15S(R) -pentacyclo[10.3.2.0^{2,11}.0^{4,9}.0^{13,15}]heptadeca-2(11),4,6,8,16-pentaene-3,10-dione (**16**): Colourless crystals from hexane/$CHCl_3$; m.p. 148–150 °C; ν_{max} ($CHCl_3$) 3080, 3029, 3004, 2978, 1753, 1702, 1600, 1446, 1421, 1344, 1319, 1293, 1268, 1217, 1165, 1012, 961 cm^{-1};

δ_H (200 MHz-$CDCl_3$): 8.02–7.94 (AA' of AA'BB', 2 arom. H), 7.71–7.26 (BB' of AA'BB', 2 arom. H), 5.80–571 (m, 2 olef. H), 3.72–3.70 (m, H-C(1), H-C(12)), 3.62 (s, OMe), 3.25 (m, H-C(2), H-C(11)), 1.87–1.84 (m, H-C(13), H-C(15)), 1.24 (t, ^3J = 2.77, H-C(14)); δ_C (50 MHz, $CDCl_3$): 198.65 (CO), 175.24 (CO), 1367.33, 136.17, 131.84, 128.93, 53.76, 51.52, 38.61, 22.64, 19.83.

14-exo-Methoxycarbonyl-1S(R),12R(S),13R(S),15S(R)-pentacyclo[10.3.2.0^{2,11}.0^{4,9}.0^{13,15}]heptadeca-4,6,8,16-tetraene-3,10-dione (**17**): pale yellow crystals from ether/$CHCl_3$, m.p. 187–189 °C; ν_{max} (KBr) 3080, 3029, 2978, 2953, 1753, 1727, 1676, 1651, 1600, 1574, 1474, 1421, 1344, 1319, 1293, 1268, 1242, 1165, 910, 757, 731 cm^{-1}; δ_H (200 MHz, $CDCl_3$): 8.09–8.04 (*AA'* of *AA'BB'*, 2 arom. H), 7.71–7.27 (*BB'* of *AA'BB'*, 2 arom. H), 6.21–6.16 (m, 2 olef. H), 4.75–4.70 (m, H-C(1), H-C(12)), 3.61 (s, OMe), 2.01–1.97 (m, H-C(13), H-C(15)), 1.88 (t, ^3J = 2.77, H-C(14)); δ_C (50 MHz, $CDCl_3$): 182.94 (CO), 173.01 (CO), 157.14, 135.34, 134.17, 133.08, 128.35, 53.60, 37.73, 31.28, 28.73; Anal: calc. for $C_{19}H_{14}O_4$: C 74.50, H 4.61; found: C 74.71, H 4.60 %.

3,10-Diacetoxy-14-exo-methoxycarbonyl-1S(R),12R(S),13R(S),15S(R)-pentacyclo[10.3.2.0^{2,11}.0^{4,9}.0^{13,15}]heptadeca-2(11),3,5,7,9,16-hexaene (**19**): colourless crystals from hexane/$CHCl_3$; m.p. 86–88 °C; ν_{max} (KBr) 3080, 3029, 3004, 1778, 1727, 1625, 1523, 1446, 1395, 1370, 1319, 1244, 1217, 1165, 1140, 1063, 1012, 961, 936, 885 cm^{-1}. δ_H (200 MHz, $CDCl_3$): 7.78–7.72 (AA' of AA'BB', 2 arom. H), 7.51–7.43 (BB' of AA'BB', 2 arom. H), 6.25–6.21 (m, 2 olef. H); 4.27–4.21 (m, H-C(1), H-C(12)), 3.60 (s, OMe), 2.49 (s, 2 Me), 2.07–2.02 (m, H-C(13), H-C(15)), 1.84 (t, ^{3}J = 2.93 Hz, H-C(14)); δ_C (50 MHz, $CDCl_3$): 173.52 (CO), 170.55 (CO), 139.87, 135.98, 133.20, 128.26, 128.13, 123.44, 53.43, 37.64, 27.83, 25.87, 22.50; m/z 393/392 (2/6), 351/350 (2/10), 319 (4), 308 (50), 277 (10), 276 (45), 248 (34), 231 (28), 210 (100), 209 (32), 189 (24), 165 (18), 152 (14), 98 (17). Anal: calc. for $C_{23}H_{20}O_6$: C 70.40, H 5.14; found: C 70.37, H 5.16 %.

(**b**) A mixture of 1,4-naphthoquinone (1.0 g), 7-carbomethoxy-CHT[8] (2.0 g) and $CHCl_3$ (30–40 ml) was refluxed for 7 days. The reaction mixture was cooled and the solvent was evaporated. The residue was submitted to silica gel (10 g) column chromatography, eluting successively with CCl_4, $CHCl_3$ and EtOAc. In CCl_4 the first fraction was **15**. The other fractions were combined and the solvent was evaporated. Anthraquinone derivative **16** (830 mg, 43 %) was obtained by crystallisation (ether/$CHCl_3$) from the residue.

The reaction of 1,4-naphthoquinone with 7-cyano-CHT (20)

This reaction was also studied under two conditions.

(**a**) A mixture of 1,4-naphthoquinone (1.0 g), 7-cyano-CHT[8] (1.2 g) and $CHCl_3$ (15 ml) in sealed tube was heated at 95 °C for 18 days. The reaction mixture was cooled and $CHCl_3$ (75 ml) was added, and then solid was separated. After solvent evaporated, the residue was submitted on silica gel (50 g) column chromatography with EtOAc / hexane (1/9). Compound **22** (100 mg, 6 %) was separated. The other parts of the reaction were studied in the same manner as that of **15**. Crude product was submitted on silica gel (50 g) column chromatography with EtOAc / hexane (3/7). Compound **22** (40 mg, 2 %) and **27** (200 mg, 9 %) were separated, respectively.

14-exo-Cyano-1S(R),12R(S),13R(S),15S(R)-pentacyclo[10.3.2.0^{2,11}.0^{4,9}.0^{13,15}]heptadeca-4,6,8,16-tetraene-3,10-dione (**22**): pale yellow crystals from ether/$CHCl_3$, m.p. 214–216 °C; ν_{max} (KBr) 3016, 3055, 3029, 2263, 2238, 1676, 1651, 1600, 1344, 1319, 1293, 1242, 910, 808, 757, 731, 655 cm^{-1}; δ_H (200 MHz, $CDCl_3$): 8.12–8.04 (*AA'* of *AA'BB'*, 2 arom. H), 7.75–7.70 (*BB'* of *AA'BB'*, 2 arom. H), 6.24–6.17 (m, 2 olef. H), 4.81–4.75 (m, H-C(1), H-C(12)), 2.07–2.03 (m, H-C(13), H-C(15)), 1.65 (t, ^3J = 3.22 Hz, H-C(14)); δ_C (50 MHz, $CDCl_3$): 182.90 (CO), 156.18, 135.74, 133.97, 132.74, 128.50, 120.98, 37.20, 27.14, 14.00 (CH); Anal: calc. for $C_{18}H_{11}NO_2$: C 79.11, H 4.06, N 5.13; found: C 78.99, H 4.07, N 5.09 %.

3,10-Diacetoxy-14-exo-cyano-1S(R),12R(S),13R(S),15S(R)-pentacyclo[10.3.2.0^{2,11}.0^{4,9}.0^{13,15}]heptadeca-2(11),3,5,7,9,16-hexaene (**27**): White crystals from ether/$CHCl_3$/hexane; m.p. 147–149 °C; ν_{max} (KBr) 3071, 3020, 2937, 2238, 1770, 1655, 1617, 1585, 1513, 1430, 1367, 1302, 1276, 1206, 1174, 1104, 1046, 1014, 892, 789, 745 cm^{-1}; δ_H (200 MHz, $CDCl_3$): 7.82–7.77 (*AA'* of *AA'BB'*, 2 arom. H), 7.54–7.50 (*BB'* of *AA'BB'*, 2 arom. H), 6.25–6.21 (m, 2 olef. H), 4.31–4.26 (m, H-C(1), H-C(12)), 2.54 (s, 2 Me), 2.12–2.08 (m, H-C(13), H-C(15)), 1.62 (t, ^3J = 3.30 Hz, H-C(14)); δ_C (50 MHz, $CDCl_3$): 171.23 (CO), 140.21, 134.63, 132.86, 128.78, 128.21, 123.50, 121.72, 37.11, 24.51, 22.68, 10.38. Anal: calc. for $C_{22}H_{17}NO_4$: C 73.53, H 4.77, N 3.90; found: C 73.42, H 4.75, N 3.88 %.

(**b**) A mixture of 1,4-naphthoquinone (1.3 g), 7-cyano-CHT (3.2 g) and $CHCl_3$ (30–40 ml) was refluxed for 7 days. The reaction mixture was cooled and the solvent was evaporated. The residue was submitted to silica gel (10 g) column chromatography with CCl_4, $CHCl_3$ and EtOAc, successively. With CCl_4, the first fraction was compound **20**. The other fractions were combined and the solvent was evaporated. ^{1}H NMR spectrum of the residue revealed that compounds **21**, **22**, **24** and **25** are present, in ratios 50 : 23 : 19 : 8, respectively. When it was sequentially crystallised (4 times) from ether/$CHCl_3$, the anthraquinone derivative **21** (80 mg) was obtained as a mixture together with **24** (**21** : **24** = 13 : 1).

14-exo-Cyano-1S(R),12R(S),13R(S),15S(R)-pentacyclo[10.3.2.0^{2,11}.0^{4,9}.0^{13,15}]heptadeca-4,6,8,16-tetraene-3,10-dione (**21**): δ_H (200 MHz-$CDCl_3$): 8.03–7.87 (AA' of AA'BB', 2 arom. H), 7.73–7.68 (BB' of AA'BB', 2 arom. H), 5.81–5.77 (m, 2 olef. H), 3.81–3.78 (m, H-C(1), H-C(12)), 3.25 (bs, H-(C-2), H-(C-11)), 1.96–1.93 (m, H-C(13), H-C(15)), 1.03 (t, ^3J = 3.18 Hz, H-C(14)); δ_C (50 MHz, $CDCl_3$): 197.92 (CO), 156.18, 136.45, 131.01, 129.04, 122.40, 50.85, 37.86, 20.92, 3.09; HRMS: found 275.0935, calc. for $C_{18}H_{13}NO_2$ 275.0946.

Determined peaks for **24** and **25** in ^{1}H NMR of the reaction mixture are 6.12–5.95 (m, 2 olef. H), 4.06–3.88 (m, H-C(1), H-C(12)); for **24** and 6.55–6.47 (m, 2 olef. H), 4.85-4.83 (m, H-C(1), H-C(12)); for **25**.

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References

1 (a) M. Balcı, O. Çakmak and T. Hökelek, *J Org. Chem.*, 1992, **57**, 6640; (b) R Altundaş and M. Balcı, *Tetrahedron*, 1993, **49**, 6521; (c) A. Daştan, M. Balcı, T. Hökelek, D. Ülkü and O. Büyükgüngör, *Tetrahedron*, 1994, **50**, 10555; (d) A. Menzek, N. Saraçoğlu, A. Daştan, M. Balcı and R. Abbasooğlu, *Tetrahedron*, 1997, **53**, 14451; (e) A. Menzek, *Tetrahedron*, 2000, **56**, 8505; (f) A. Menzek and M. Gökmen, *J. Chem. Res. (S).*, 2002, 475.

2 (a) M.R. Wasielevski and M.P. Niemeczyk, *J. Am. Chem. Soc*., 1984, **106**, 5043; (b) M.R. Wasielevski, M.P. Niemeczyk, D.G. Johnson, W.A. Swec and D.W. Minsek, *Tetrahedron*, 1989, **45**, 4785.

3 (a) M. Balcı, Turk. J. Chem., 1992, **16**, 42; (b) W. J. Le Noble, Hightlights of Organic Chemistry, Marcel Dekker Inc., New York, 1974, 402; (c) G. Maier, Angew. Chem. Int.. Ed. Engl., 1967, **6**, 402.

4 (a) R. Hoffman, *Tetrahedron Lett*., 1970, 2907; (b) H. Günther, *Tetrahedron Lett*., 1970, 5173.

5 (a) H. Kessler, in W. -M., Houben, *Methoden der Organischen Chemie*, 1972, 5/d 376; (b) A. Menzek and M. Balcı, *Aust. J. Chem*., 1993, **46**, 1613; (c) A. Menzek, N. Saraçoğlu, M. Kraweic, W.H. Watson and M. Balcı, *J Org. Chem.*, 1995, **60**, 829; (d) M. Balcı, S.A. Bourna, A. Menzek, N. Saraçoğlu and W.H. Watson *J Chem. Cryst.*, 1995, **25**, 107; (e) M. Balcı and B. Atasoy, *Tetrahedron Lett*., 1984, **25**, 4033.

6 (a) J.W. Wijen and J.B.N. Engberts, *J Org. Chem.*, 1997, **61**, 4438; (b) G. Desimoni, G. Faita, D. Posini and P.P. Righetti, *Tetrahedron*, 1992, **48**, 1667; (c) B.S. Poncin, A. -H. H. Prisque and L. Ghosez, *Tetrahedron Lett.*, 1982, **23**, 3261.

7 A. Mori, H. Nametsuka, and H. Takeshita, *Bull. Chem. Soc. Jpn*., 1985, **58**, 2072.

8 (a) W. von E. Doering and L.H. Knox, *J. Am. Chem. Soc*., 1957, **79**, 352; (b) F.G. Klaerner, S. Yaslak and M. Wette, *Chem. Ber*., 1977, **110**, 107.

9 A. Menzek and M. Balcı, *Tetrahedron*, 1993, **49**, 6071.

10 W. Adam and M. Balcı, *J Org. Chem*., 1979, **44**, 1189.

11 (a) N. Saraçoğlu, A. Menzek and M. Balcı, *Turk. J Chem.*, 2001, **25**, 123; (b) A. Wiehe, M.O. Senge and H. Kurreck, *Liebigs Ann./Recueil*, 1997, 1951.