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Cycloaddition Reactions of Substituted Cycloheptatrienes with Benzyne and Quinones: An Entry to the Substituted Benzhomobarrelenes

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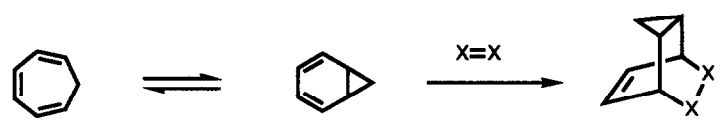
Abstract: Two cycloheptatriene derivatives ***8*** *and* ***9*** *react with benzyne to give adducts* ***10-12*** *having anti benzhomobarrelene geometry. On the other hand, cycloaddition reactions of benzoquinone and homobenzoquinone* ***16*** *with cycloheptarienes* ***1*** *and* ***8*** *resulted in the exclusive formation of* ***13, 17*** *and* ***18,*** *respectively.. The endo-configuration of benzoquinone ring in* ***13*** *was confirmed by photochemical (2+2)-cycloaddition to give the cage-molecule* ***15.***

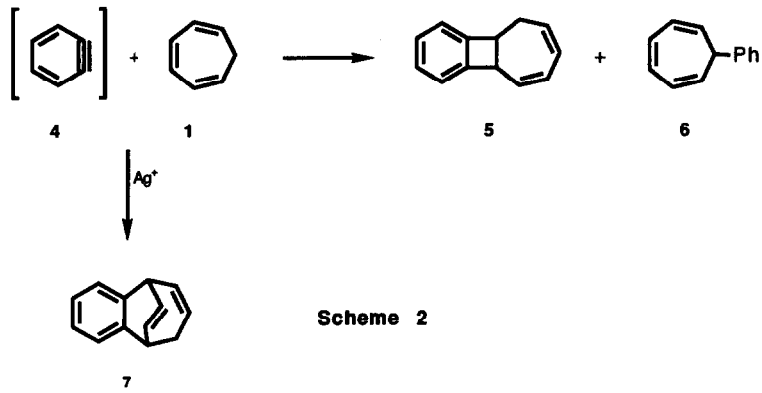
Cycloheptatriene **1** is in equilibrium with its valence isomer norcaradiene **2**[1]. The substituents at C-7 position in cycloheptatriene have a dramatic influence on the cycloheptatriene-norcaradiene (CHT-NOR) equilibrium. Hoffman[2] and Günther[3] have predicted that the π-acceptor substituents at C-7 of cycloheptatriene (such as CN, COOR, CHO etc.) shift CHT-NOR equilibrium to the side of norcaradiene, where electron donating substituents (such as OR, NR_2) stabilize the cycloheptatriene structure. By this theory, they have considered the interaction between the Walsh type HOMO and LUMO orbitals of cyclopropane and vacant or filled p orbitals of substituents. Valence isomerisation between CHT and NOR has been detected by dynamic NMR-spectroscopy. In cases where valence isomerization could not be detected by NMR, the existence of such valence tautomerization has been surmised from Diels-Alder products. Cycloheptatrienes gives in most cases norcaradiene-type adduct[4].



1 Cycloheptatriene **2** Norcaradiene **3**

Scheme 1

The course of benzyne reaction with unsubstituted cycloheptatriene has been examined. Crews and Beard[5] reported the characterization of two hydrocarbon products **5** and **6**. 7-phenyl-cycloheptatriene **6** results from ene-reaction, and cycloheptadiene derivative **5** arises from (2+2)-cycloaddition reaction. (2+4)-Cycloaddition products arising either from CHT or NOR were not observed.



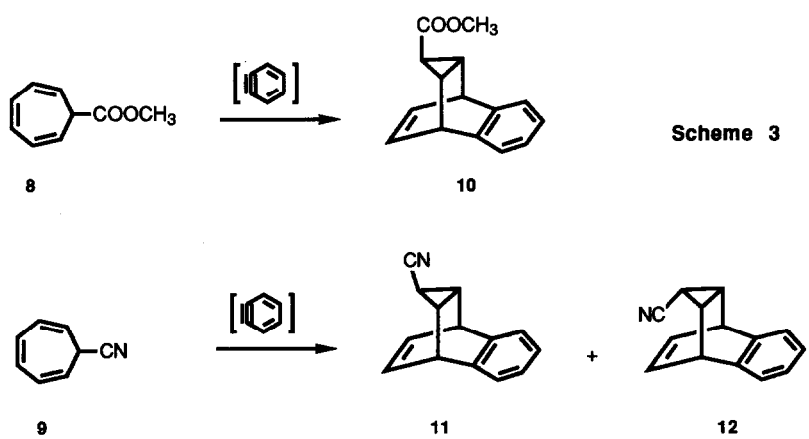
4 1 5 6

7

Scheme 2

In contrast to the cycloaddition reaction of benzyne with CHT, 1,3-cyclopentadiene[6] and 1,3-cyclohexadiene[5] gave (2+4)-cycloaddition products upon reaction with benzyne. The (2+4)-cycloaddition reaction between benzyne and 1,3-dienes is known to be concerted[7]. As the first assumption one would expect to find the net reaction for this type of cycloaddition to be sensitive to the extent of overlap in the transition state for the reacting π-orbitals (conformational factors). This product distribution (Scheme 2) has been explained on the basis of the fact that cycloheptatriene has a twist angle of 40^{o} between the carbon-carbon double bonds which have been shown by electron and X-ray diffraction work. As an extension of this work, Crews and Beard[8] examined the effect of the added Ag^{+} upon the course of benzyne addition to cyclic and acyclic polyenes. In the case of cycloheptatriene they have isolated only (2+4)-cycloaddition product **7** which was not observed in the absence of Ag^{+}. An ionic mechanism has been proposed to account the catalytic effect of silver ion and observed products.

To see the effect of the substituents in cycloheptatriene attached at C-7 carbon atom, on the course of the reaction, we have studied the cycloaddition reactions of benzyne to substituted cycloheptatrienes. As the model compounds, we chosed carboxymethyl- and cyano-cycloheptatrienes **8** and **9**. Furthermore, we have plannedto develop a simple synthetic methodology leading to the substituted benzhomobarrelene derivatives which are interesting molecules in view of the molecular rearrangements[9].



8 10

Scheme 3

9 11 12

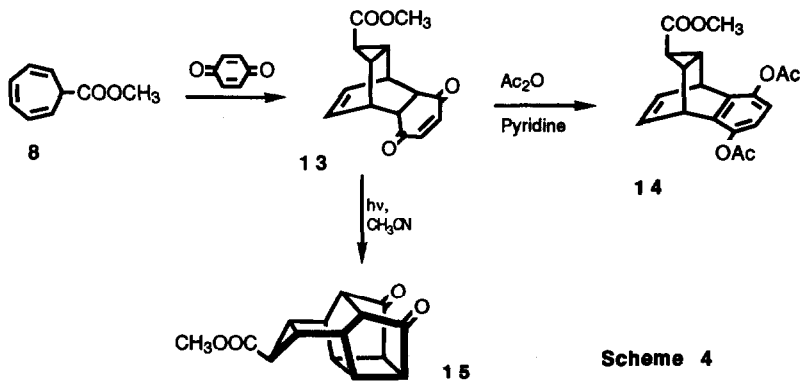
Benzyne generated from benzenediazonium-2-carboxylate hydrochloride[10] in refluxing ethylene dichloride, reacted with **8** to give **10**. Chromatography on silica gel permitted isolation of benzhomobarrelene derivative **10** as the sole product in a yield of 44 %. ^{1}H- and ^{13}C-NMR spectra of **10** are completely in agreement with the proposed structure. Aromatic protons are resonating as AA'BB' system (7.20-7.04) where olefinic protons and bridgehead protons give rise to an AA'XX'-system. XX'-part of this system shows further coupling with the neigboring cyclopropane protons. Furthermore, ^{1}H-NMR spectrum shows nearly degenerate cyclopropane protons. With the knowledge that cycloheptatriene enters into the Diels-Alder cycloadditions to give adduct having an anti cyclopropane orientation relative to the entering dienophile, we assume that the configuration of **10** is anti. On the other hand endo-isomer (carboxymethyl group) can not be formed because of the increased steric repulsion present in the endo-conformer of **8a** due to the bulkieness of the carboxyl group[11]. Therefore, we assign the compound **10** the configuration anti/exo.

8a

In our examination of the reaction between benzyne and **9**, a pair of adducts was formed after two days in refluxing ethylene chloride in a ratio 62:48. The ^{1}H- and ^{13}C-NMR spectra of **11** and **12** were completely in agreement with the proposed structures. A distinction between the exo- and endo-isomers in the benzhomobarrelene derivatives **11** and **12** is reliably founded on ^{1}H-NMR spectral data. The exo-orientation of the cyano group in **11** was deduced principally on the basis of the 3.30 Hz coupling constant (7.80 Hz in **12**) observed to exist between the trans cyclopropane protons.

Isolation of two cycloaddition products[12] (**11** and **12**) in the case of 7-cyano-cycloheptatriene can be explained on the basis of small and linear cyano group which does not show any steric interaction with double bond orbitals in endo-conformer[13].

The above mentioned cycloaddition reactions have been carried out also in the presence of catalytic amounts of Ag^+. We did not notice any effect on product distribution. Therefore, we can conclude that benzyne

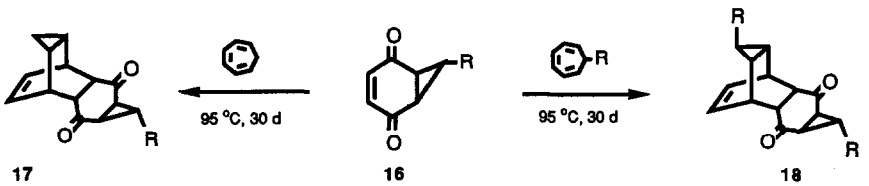


Scheme 4

undergoes a (2+4)-cycloaddition reaction with the nearly planar norcaradiene isomers in a concerted fashion to give benzhomobarrelene derivatives. Similar cycloaddition reactions between benzyne and substituted bis-cycloheptatriene derivatives (heptalen) has recently been observed[14].

Reaction of 7-carboxymethly-cycloheptatriene **8** with p-benzoquinone[15] in an ultrasonic apparatus followed by crystallization of the formed product resulted in the formation of cycloaddact **13**. Due to the structural components present in this molecule, its endo configuration has been established by chemical method. Photocyclization of **13** to **15** is completely in agreement for the endo-configuration of the starting material. Furthermore, the oxygenated ring was aromatized by means of simple O-acetylation. **14** has been characterized well by spectroscopic methods. This sequence is a very simple way to entry to the at aromatic ring susbstituted benzhomobarrelene derivatives such as **14**.

These results are in sharp contrast to Takeshita's observation for the reaction of cycloheptatriene and p-benzoquinone[16]. Thermal cycloaddition reaction of cycloheptatriene and p-benzoquinone afforded vicinal *ditropylation product together with a trace of the 1:1 adduct (1%) even under more drastic condition. Our* results indicate clearly that **8** is equilibrating with its valence isomer norcaradiene and nearly planar structure of the corresponding norcaradiene can add easily to p-benzoquinone to form **13**.

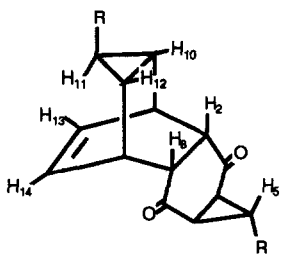


17 **16** **18**

R = $COOCH_3$

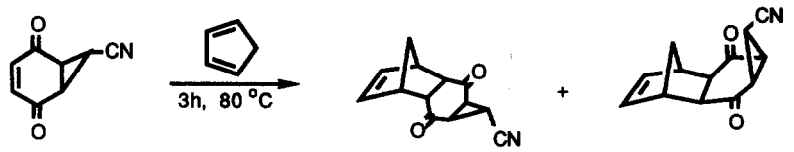
Scheme 5

In a similar manner, we reacted homobenzoquinone **16**[17] *with* **1** *and* **8**. *Both reactions were completed* in nearly one month and at 95 °C and gave only one isolable product in each case with high yield. In principle four stereoisomers are possible, namely endo/anti, endo/syn, exo/anti, and exo/syn. In our case, we isolated only one product. The other possible cycloaddition products were not observed. It is very well known that the preferential formation of a endo [2 + 4] π cycloadducts as in the case of **17** and **18** might be controlled by the secondary orbital interactions in transition state[18].



18 R = $COOCH_3$

The structure of **18** has been confirmed by differential ^{1}H-NMR Nuclear Overhauser Enhancement (NOE) studies. Irradiation of H_{11} at δ = 1.21 induces an enhancement of the olefinic resonances which indicates clearly the exo-orientation of the ester group at C_{11} atom. Irradiation of H_2 and H_8 protons at



19 20 endo/anti 4:1 21 exo-syn **Scheme 6**

δ = 3.02 causes enhacement of the cyclopropane protons (H_{10} and H_{12}) and the other cyclopropane proton H_5 which reveal the formation of the endo-addition product and the exo-configuration of the second cyclopropane ring. These results have been also established in the reverse experiment.

Furthermore, structural assingments to the compounds **17** and **18** have been supported by comparison with the results obtained by Adam et al.[19]. They have reacted homobenzoquinones with cyano-substituted cyclopropane rings **19** and cyclopentadiene and obtained the endo/anti and exo/syn cycloadducts **20** and **21** where the former is dominating (Scheme 6). The fact, that we have isolated only one isomer is an indication that secondary orbital effect is operating strongly in the case of cycloheptatriene. The lower reactivity of homobenzoquinone **16** compared to benzoquinone is probably attributed to unfavorable steric effects. Furthermore, , the LUMO-HOMO gap is unquestionably larger for the homobenzoquinone derivative **16** and thus its dienophilicity lower[19].

Experimental Section

General Methods: Melting points were determined on a Thomas-Hoover capillary melting point apparatus. Solvents were concentrated at reduced pressure. Infrared spectra were obtained from KBr pellets or from solution in 0,1 mm cells on a Perkin-Elmer 337 Infrared recording spectrophotometer. ^{1}H-NMR spectra were recorded on 200 MHz Varian and Bruker spectrometer and are reported in δ units TMS as internal standart. All column choromatograph was performed on silica gel (60-Mesh, Merck).

Exo-7-carbomethoxy-2,5-benzo-tricyclo[4.1.0]hepta-3-ene 10. To a solution of 7-carbomethoxy-CHT (2.89 g, 19.2 mmol) in 180 mL of ethylene dichloride were added 14.2 g (77 mmol) of benzenediazonium 2-carboxylate hydrochloride. The formed mixture was refluxed, under nitrogen atmosphere for 2 days. The colorless mixture became dark. The reaction mixture was cooled and the solvent evaporated. Chromatography of the residue on silicagel (50 g), eluting with ether/hexane (1:9) gave **10** (870 mg, 44%) which was crystallized from ether/$CHCl_3$; colorless crystals, mp 101-103 °C; ν_{max} (KBr) 3080, 2975, 1720, 1440, 1400, 1300, 1220, 1160, 1050, 910, 760,700 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.20-7.04 (AA'BB'-system, aromatic protons, 4H), 6.20 (AA'-part of AA'XX'-system, olefinic protons, 2H), 4.10 (XX'-part of AA'XX'-system, bridgehead protons, 2H), 3.61 (s, OCH_3, 3H), 1,90 (m, cyclopropane protons, 3H); ^{13}C-NMR (50MHz, $CDCl_3$) δ 172.40 (CO), 145.82 (C), 131.68 (CH), 124.86 (CH), 123.27 (CH), 51.59 (CH_3), 48.89 (CH), 28.19 (CH), 26.54 (CH); Anal. Calcd for $C_{15}H_{14}O_2$: C, 80.62; H, 6.24; O, 14.14. Found: C, 80.45; H, 6.28.

Exo-7-cyano-2,5-benzo-tricyclo[4.1.0]hepta-3-ene 11 and endo-7-cyano-2,5-benzo-

tricyclo[4.1.0]hepta-3-ene 12. To a solution of 7-cyano-CHT[20] (3.0 g, 25,6 mmol) in 160 mL of ethylene dichloride were added 15.2 g (82.4 mmol) of benzenediazonium 2-carboxylate hydrochloride. The formed mixture was refluxed under nitrogen atmosphere for 2 days. The colorless mixture became dark. The reaction mixture was cooled and the solvent evaporated. The residue was subjected to column chromatography on silica gel (50 g). Eluting with ether/hexane (1:9) afforded **11** as the first fraction (1.088 g, 22 %). Further eluting gave **12** (722 mg, 16 %). Both adducts were crystallized from ether/$CHCl_3$.

11: Colorless crystals, mp 108-110 °C; ν_{max} (KBr) 3040, 3020, 3000, 2240, 1465, 1380, 1350, 1030, 790, 760, 720 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.22-7.07 (AA'BB'-system, aromatic protons 4H), 6.20 (AA'-part of AA'XX'-system, olefinic protons, 2H), 4.14 (XX'-part of AA'XX'-system, bridgehead protons, 2H), 1.94 (m, cyclopropane protons, 2H), 1.63 (t, J 3.30 Hz, cyclopropane proton, 1H); ^{13}C-NMR (50MHz, $CDCl_3$) δ 144.47 (C), 131.27 (CH), 125.35 (CH), 123.65 (CH), 120.08 (CN), 40.24 (CH), 24.72 (CH), 10.35 (CH); Anal. Calcd for $C_{14}H_{11}N$: C, 87.01; H, 5.74; N, 7.25. Found: C, 86.91; H, 5.59.

12: Colorless crystals, mp 163-165 °C; ν_{max} (KBr) 3008, 2980, 2210, 1465, 1450, 1350, 1050, 800, 500 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.25-6.50 (AA'BB'-system, aromatic protons, 4H), 6.48 (AA'-part of AA'XX'-system, olefinic protons, 2H), 4.29 (XX'-part of AA'XX'-system, bridgehead protons, 2H), 1.87-1.63 (m, cyclopropane protons, 3H); ^{13}C-NMR (50MHz, $CDCl_3$) δ 145.66 (C), 134.56 (CH), 129.06 (CH), 123.46 (CH), 120.04 (CN), 40.37 (CH), 28.58 (CH), 14.07 (CH);

Exo-10-carbomethoxy-tetracyclo[6.3.2.0^{2,7}.0^{9,11}]trideca-4,12-diene-3,5-dione 13: 540 mg (5 mmol) of p-benzoquinone and 1.0 g (6.67 mmol) of 7-carbomethoxy-CHT were dissolved in 5 mL of $CHCl_3$. The formed solution was placed into an ultrasonic apparatus (Branson 3200) and heated at 40 °C for 7 days. The reaction mixture was cooled and the solvent evaporated. The adduct **13** was purified by crystallization from ether/$CHCl_3$. Light yellow crystals (1.15 g, 89 %); mp 114-116 °C; ν_{max} (KBr) 3020, 2980, 1730, 1670, 1450, 1410, 1340, 1260, 1170, 950, 720; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 6.64 (s, olefinic protons, 2H), 5.86 (AA'-part of AA'XX'-system, olefinic protons, 2H), 3.64 (s, OCH_3, 3H), 3.62 (XX'-part of AA'XX'-system, bridgehead protons, 2H), 3.07 (m, 2H), 1.82 (m, cyclopropane protons, 2H), 1.26 (t, J 2.83 Hz, cyclopropane proton, 1H); ^{13}C-NMR (50MHz, $CDCl_3$) δ 199.22 (CO), 173.21 (CO), 141.03 (CH), 129.58 (CH), 51. 82 (CH_3), 50.11 (CH), 36.15 (CH), 20.50 (CH), 17.81 (CH); Anal. Calcd for $C_{15}H_{14}O_4$: C, 69.76; H, 5.46; O, 24.78. Found: C, 69.97; H, 5.60.

Exo-7-carbomethoxy-2,5-p-diacetoxybenzo-tricyclo[4.1.0]hepta-3-ene 14: A mixture of 450 mg (1.74 mmol) of **13** , 2.0 g of acetic anhydride and, 2.5 g pyridine were stirred at room temperature for 12 days. A to 5 °C cooled solution of 0.01 N HCl (100 mL) was added to the reaction mixture. The resulting mixture was exracted with $CHCl_3$. The combined organic extracts were washed with water, dried, and removed under reduced pressure. Crystallization of the residue from ether/$CHCl_3$ gave **14** (482.5 g, 60 %); Colorless crystal, mp 154-156 °C; ν_{max} (KBr) 3000, 2970, 1765, 1725, 1580, 1540, 1380, 1200, 1040 cm-1; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 6.79 (s, aromatic protons , 2H), 6.19 (AA'-part of AA'XX'-system, olefinic protons, 2H), 4.17 (XX'-part of AA'XX'-system, bridgehead protons, 2H), 3.58 (s, OCH_3 ,3H), 2.34 (s, $COCH_3$, 3H), 1.97 (m, cyclopropane protons, 2H), 1.85 (t, J 2.90 Hz, cyclopropane proton, 1H); ^{13}C-NMR (50MHz, $CDCl_3$) δ 172.31 (CO), 169.78 (CO), 143.32 (C), 139.79 (C), 131.88

(CH), 119.64 (CH), 52.08 (CH_3), 36.17 (CH), 28.29 (CH), 25.53 (CH), 21.27 (CH_3); Anal. Calcd for $C_{19}H_{18}O_6$: C, 67.66; H, 5.30; O, 28.04. Found: C, 67.94; H, 5.19.

Photocyclization of 13: A solution of **13** (193.5 mg, 0.75 mmol) in acetonitrile (110 mL) was placed in an immersion apparatus (quartz) and irradiated with 1800-3500 A lamp at 20 °C for 13 h. Evaporation of solvent gave **15** (90 %). **15** decomposes slowly at room temperature; ν_{max} ($CHCl_3$) 2260, 1750, 1715, 1290, 890; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 3.69 (s, OCH_3, 3H), 2.94 (m, 2H), 2.86 (m, 2H), 2.57 (m, 4H), 1.88 (m, cyclopropane protons, 2H), 1.63 (t, J 2.99 Hz, cyclopropane proton, 1H); ^{13}C-NMR (50MHz, $CDCl_3$) δ 210.72 (CO), 173.50 (CO), 52.50 (CH_3), 48.38 (CH), 46.29 (CH), 35.42 (CH), 32.23 (CH), 18.90 (CH), 16.32 (CH).

5-exo-Carbomethoxy-pentacyclo[7.3.2.0^{4,6}.0^{2,8}.0^{10,12}]tetradeca-13-ene-3,7-dione 17: Homoquinone **16** (540 mg, 3 mmol) and CHT (9.2 g, 0.1 mol) were placed into a constricted test tube, sealed and heated at 95 °C for 30 days. After cooling to room temperature CHT was evaporated. Crystallization of the residue from ether/$CHCl_3$ gave **17**(1.0 g, 90 %). Colorless crystals, mp 180-181 °C; ν_{max} (KBr) 3030, 3000, 2900, 1735, 1700, 1450, 1300, 1200, 995, 740 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 5.71 (AA'-part of AA'XX'-system, olefinic protons, 2H), 3.72 (s, OCH_3, 3H), 3.49 (XX'-part of AA'XX'-system, bridgehead protons, 2H), 3.06 (t, J 4.60 Hz, cyclopropane proton, 1H), 2.95 (bs, 2H), 2.65 (d, J 4.60 Hz, cyclopropane protons, 2H), 0.87 (m, cyclopropane protons, 2H), 0.14-0.03 (m, cyclopropane protons, 2H); ^{13}C-NMR (50MHz, $CDCl_3$) δ 201.62 (CO), 166.52 (CO), 129.70 (CH), 52.94 (CH_3), 49.41 (CH), 37.32 (CH), 31.76 (CH), 27.04 (CH), 8.14 (CH), 2.15 (CH); Anal. Calcd for $C_{16}H_{16}O_4$: C, 70.57; H, 5.92; O, 23.51. Found: C, 70.25; H, 5.76.

5,11-exo/exo-dicarbomethoxy-pentacyclo[7.3.2.0^{4,6}.0^{2,8}.0^{10,12}]tetradeca-13-ene-3,7-dione 18: Homoquinone **16** (360 mg, 2 mmol) and 7-carbomethoxy-CHT **8** (1.5 g, 10 mmol) were placed into a constricted test tube, sealed and heated at 95 °C for 30 days. After cooling to room temperature the residue was crystallized from ether/$CHCl_3$. Colorless crystals (745 mg, 85 %) mp 207-209 °C; ν_{max} (KBr) 3020, 2980, 2940, 1740, 1720, 1705, 1450, 1390, 1210, 1070, 750 5,80 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 5.80 (AA'-part of AA'XX'-system, olefinic protons, 2H), 3.73 (s, OCH_3, 3H), 3.61 (XX'-part of AA'XX'-system, bridgehead protons, 2H), 3.61(s, OCH_3, 3H), 3.09 (t, J 4.63 Hz, cyclopropane proton, 1H), 3.02 (br. s, methine protons, 2H), 2.67 (d, J 4.63 Hz, cyclopropane protons, 2H), 1,57 (m, cyclopropane protons , 2H), 1.21 (t, J 2.75 Hz, cyclopropane proton, 1H); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 188.92 (CO), 173.93 (CO), 168.77 (CO), 130.87 (CH), 53.40 (CH_3), 52.24 (CH_3), 49.15 (CH), 37.71 (CH), 31 .85 (CH), 27.49 (CH), 19.90 (CH), 18.09 (CH); Anal. Calcd for $C_{18}H_{18}O_6$: C, 65.45 H, 5.49; O, 29.06. Found: C, 65.71; H, 5.65

Acknowledgments

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