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Isomerization of Dihydroazulenes to Substituted Azulenes - Naked Eye Observation of a Novel COPE-Type Rearrangement.[1, 2]

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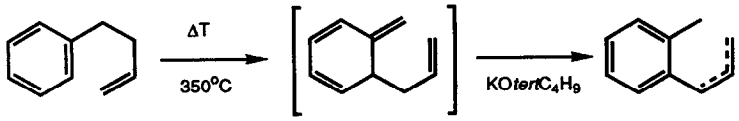
Key Words: [3,3]-Sigmatropic Rearrangement; Dihydroazulenes; Azulenes; Allylic Compounds; Propadienes.

Abstract: Readily accessible 3a-bridgehead allylic or propargylic substituted dihydroazulenes **9** rearrange at room temperature to thermodynamic more stable substituted azulenes. This process is paralleled by a gradual change in color: the yellow solution of the starting pentaenes e.g. **9a** smoothly turns to green and finally to the brilliant blue of **10a** at the end of the reaction. Activation parameters for one example of this type of reaction are given. The synthesis of **9a** and some derivatives which are subjected to this rearrangement process are described.

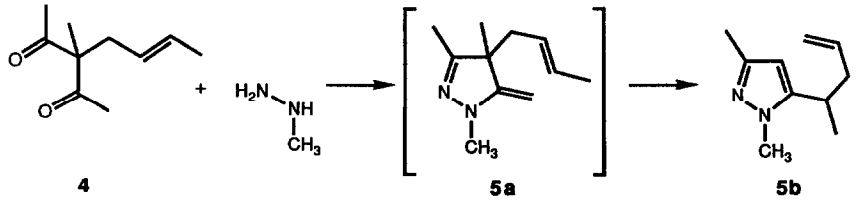
COPE rearrangements commonly are reversible processes based on cleavages of one C,C-single and two C,C-double bonds and respective formation of two C,C-double and one C,C-single bond in the 1,5-hexadiene part of an organic molecule ([3,3]-sigmatropic rearrangement).[3] The ratio of isomers at a given temperature is governed by thermodynamic parameters.

If one double bond of the parent 1,5-hexadiene derivative is part of an aromatic system, any COPE rearrangement will abolish its resonance stabilization. This is reflected in a higher enthalpy of activation and therefore in a smaller rate constant of this process. Thus 4-phenyl-1-butene (**1**) gives only toluene and propylene at 500°C under conditions where the expected product o-allyltoluene (**3**) should be stable. If additional dilute potassium *tert*-butoxide is present to enable tautomerization of methyleneallylcyclohexadiene (**2**) to **3**, substituted benzene **1** isomerizes to **3** at 350°C.[4]



1 **2** **3**

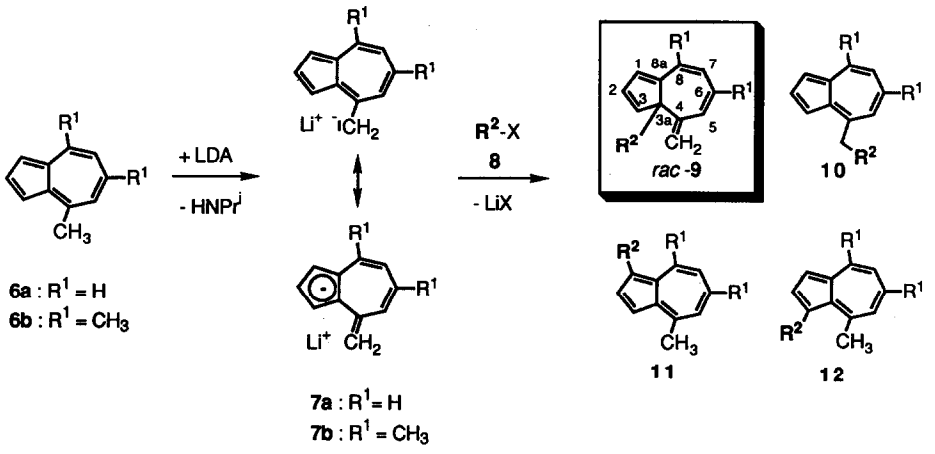
Vice versa any [3,3]-sigmatropic reaction that leads to an aromatic compound starting from a polyolefin should result in the formation of its aromatic isomer in high yields: N-methyl-5-methylene-3,4-dimethyl-4(2'-butenyl)-4,5-dihydropyrazole (**5a**) which is the intermediate in condensation of substituted diketone **4** and methyl hydrazine, rearranges in refluxing ethanol smoothly to the aromatic pyrazole **5b**.[5]



4 **5a** **5b**

According to our knowledge no example of this kind of reaction is described so far in the literature where a polyolefinic hydrocarbon rearranges to its aromatic isomer. Appropriate model compounds for studying

COPE-rearrangements, that lead to substituted aromatic compounds, starting with polyolefins should be certain 3a-substituted 3a,4-dihydro-4-methyleneazulenes **9**. These are readily available via a bridgehead alkylation reaction of lithium-4-methyleneazulenides **7** with appropriate alkyl halides or -sulfonic acid esters **8** which was recently reported by us.[6]



6a : R^1 = H
6b : R^1 = CH_3

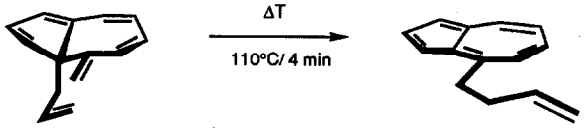
7a : R^1 = H
7b : R^1 = CH_3

LDA = Li N($CH(CH_3)_2$)

8-12	a	b	c	d	e
R^1	H	CH_3	H	H	H
R^2	allyl	allyl	*E*-crotyl	propargyl	benzyl
X	Br	Br	Br	OTos	OTos

Racemic 3a,4-dihydroazulenes **9a-e** are obtained as yellow sensitive oils which should be kept in solution (e.g. *n*-pentane) at temperatures below -20°C. Substituted, shiny purple (R^1 = CH_3) to blue (R^1 = H) azulenes **10** - **12** are side products of the alkylation reaction and can easily be separated from the desired products **9** by column chromatography.

A yellow solution of 3a-allyl substituted dihydroazulene **9a** gradually shows a change in color at room temperature and turns via green to blue. The reason behind this is a [3,3]-sigmatropic rearrangement of the polyolefin **9a** to 4-butenylazulene **10a** which proceeds with regiospecifity in high yield and proved to be irreversible.



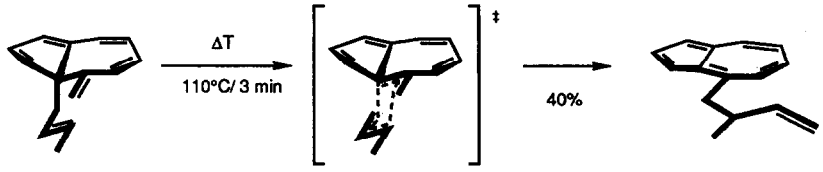
$\Delta H^{\ddagger}$ = 76 ± 4.3 kJ/ mol
$\Delta S^{\ddagger}$ = -90 ± 8.2 J/ mol K

9a *yellow* **10a** *blue*

The reaction can be observed in a nmr spectrometer at temperatures between 40 to 60°C. Analysis of ratios of **9a**:**10a** as a function of time leads via application of Eyring's equation to the enthalpy and entropy of activation of this process.[7] Data were collected at four different temperatures over a range of approximately three halflifetimes. The rate constant for rearrangement **9a** to **10a** at 50°C is $2.56 \cdot 10^{-5}$ s^{-1} and the corresponding mean lifetime of **9a** is calculated to be 65 min. The enthalpy of activation $\Delta H^{\#}$ = 76 kJ/mol is

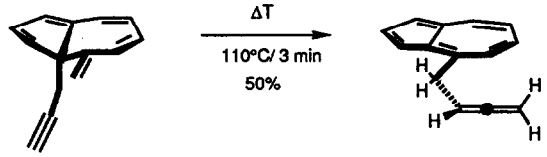
rather low compared to other rearrangement processes and is likely to reflect conjugational effects within the 10π-perimeter which is formed in **10a** during the course of the reaction.[8, 9] The strong negative entropy of activation $\Delta S^{\#}$ = - 90 J/mol K should indicate a rigid, highly structured six-membered transition state of the [3,3]-sigmatropic rearrangement.

3a-*E*-Crotyl substituted dihydroazulene **9c** isomerizes to dark blue 4-(2'-methyl-3'-butenyl)-azulene (**13**). The low yield is presumably due to the restricted thermal stability of **9c** which causes polymeric material besides **13** at 110°C.



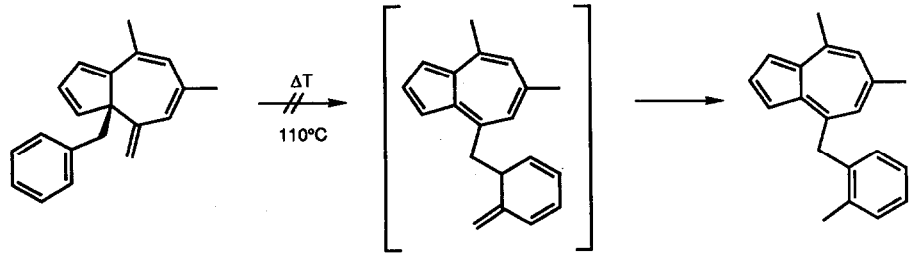
9c **13**

Application of this novel [3,3]-sigmatropic rearrangement enables furthermore the synthesis of previously unknown azulenyl substituted 1,2-propadienes. Thermolysis of 3a-propargyldihydroazulene **9d** leads to 4-(2',3'-butadienyl)-azulene (**14**) within 3 min at 110°C. Typical IR absorbtions at 1950 cm^{-1} (double band) and proton chemical shift values of the butadienyl moiety of **14** allow unambigious characterization of **14**.



9d **14**

Attempts to rearrange 3a-benzyl-6,8-dimethyl-3a,4-dihydro-4-methyleneazulene (**9e**) to o-tolyl-methyleneazulene **16** remind of Hurd's experiments to isomerize 4-phenyl-1-butene 1.[4] Parts of the 1,5-hexadiene system in **9e** are incorporated in the benzyl moiety. This seems to give rise to a higher enthalpy of activation for the rearrangement. Thus the energy needed to allow dihydroazulene **9e** to isomerize to the primary rearrangement product **15** obviously surpasses thermal stability of **9e**. Heating **9e** in toluene to 110°C yields only polymers.



9e **15** **16**

Experimental

Typical procedure for synthesis of 3a-alkyl-3a,4-dihydro-4-methyleneazulenes ***rac-9:*** A 100 mL three-necked round bottomed flask equipped with an efficient magnetic stir bar, inert gas in- and outlet and rubber septum is charged with a solution of 2.1 mL (10.0 mmol) diisopropylamine in 20 mL dry diethyl ether and dropwise reacted at 0°C with 7.0 mL (10.0 mmol) of a 1.5M *n*-butyllithium solution in *n*-hexane. 10.0 mmol 4-Methylazulene **6a**[10] or 4,6,8-trimethylazulene **6b** [11] are added in small portions at - 15°C. The brown reaction mixture is allowed to stir for further 15 min at -15°C. A solution of 20.0 mmol alkylation reagent **8** (propargyl tosylate **8d** and benzyl tosylate **8e** were synthesized according to literature procedures,[12] all other products are commercially available) in 20 mL anhydrous diethyl ether are added via syringe at -15°C dropwise to the solution of lithium azulenide **7** in ether (60 min). The reaction mixture is stirred for 14 h at 0°C and hydrolyzed with 25 mL icewater. The organic layer is separated and washed three times with brine. The aqueous phases are collected and extracted twice with diethyl ether. The combined organic layers are dried with magnesiumsulfate and concentrated *in vacuo*. The remaining dark oil is purified by column chromatography (silica gel 60, *n*-pentane; $\underline{R}_f$ **9** = 0.6 - 0.7).

*3a-(2'-Propenyl)-3a,4-dihydro-4-methyleneazulene (**rac-9a**):*

yellow oil; yield: 32%; $C_{14}H_{14}$ (182.3), Calcd.: C 92.26, H 7.74, Found: C 92.13, H 8.03; ^{1}H NMR (300MHz, $CDCl_3$): δ=6.58(d, J=11.2Hz, 1H, 5-H), 6.57(m, 2H, 2-H, 3-H), 6.31(s, 1H, 1-H), 6.03(dd, J=1.0, 12.0Hz, 1H, 8-H), 5.94(dd, J=8.0, 11.2Hz, 1H, 6-H), 5.91(dd, J=8.0, 12.0Hz, 1H, 7-H), 5.76(s, 1H, 9-H_{syn}), 5.48(ddt, J=7.0, 13.4, 16.8Hz, 1H, 2'-H), 4.86(m, 2H, 3'-H), 4.75(s, 1H, 9-H_{anti}), 2.31(ddt, J=1.1, 7.0, 13.4Hz, 1H, 1'-H), 1.78(ddt, J=1.1, 7.0, 13.0Hz, 1H, 1'-H); UV/VIS (*n*-hexane): λ_{max} (lg ε)=389(3.59), 373(3.66), 358(3.60), 258nm(4.14); MS (EI) m/e=182 (20%, M^+), 138(100%, M^+-C_3H_8); IR (CCl_4) ν=3040(=CH_2), 2950(=CH), 2860(C-H), 1680(C=C), 1575cm^{-1}(C=C).

*3a-(2'-Propenyl)-3a,4-dihydro-4-methylene-6,8-dimethylazulene (**rac-9b**):*

yellow oil; yield: 28%; $C_{16}H_{18}$ (210.1), Calcd.: 210.1402 Found: 210.1402; ^{1}H NMR (300MHz, $CDCl_3$): δ=6.62(dd, J=1.4, 5.5Hz, 1H, 3-H), 6.58(dd, J=2.4, 5.5Hz, 1H, 2-H), 6.37(s, 1H, 1-H), 5.87(s, 1H, 5-H), 5.84(s, 1H, 7-H), 5.56(s, 1H, 9-H_{syn}), 5.42(dddd, J=7.6, 10.5, 14.4, 18.3Hz, 1H, 2'-H), 4.84(m, 2H, 3'-H), 4.61(s, 1H, 9-H_{anti}), 2.31(m, 1H, 1'-H), 2.10(s, 3H, CH_3), 1.98(s, 3H, CH_3), 1.89(m, 1H, 1'-H); UV/VIS (*n*-hexane): λ_{max} (lg ε)= 368(3.71), 260nm(4.27); MS (EI) m/e=210 (86%, M^+) 195(100%, M^+-CH_3); IR (CCl_4) ν=3050(=CH_2), 2910(=CH), 2850(C-H), 1625(C=C), 1580cm^{-1}(C=C).

*3a-(2'-Butenyl)-3a,4-dihydro-4-methyleneazulene (**rac-9c**):*

yellow oil; yield: 12%; $C_{15}H_{16}$ (196.3), Calcd.: C 91.78, H 8.22, Found: C 90.86, H 8.45; ^{1}H NMR (300MHz, $CDCl_3$): δ=6.58(d, J=11.2Hz, 1H, 5-H), 6.57(m, 2H, 2-H, 3-H), 6.30(s, 1H, 1-H), 5.99(dd, J=1.0, 12.0Hz, 1H, 8-H), 5.94(dd, J=7.5, 11.2Hz, 1H, 6-H), 5.88(dd, J=7.5, 12.0Hz, 1H, 7-H), 5.75(s, 1H, 9-H_{syn}), 5.27(dqt, J=1.3, 6.0, 15.0Hz, 1H, 3'-H), 5.15(dqt, J=1.8, 7.0, 15.0Hz, 1H, 2'-H), 4.75(s, 1H, 9-H_{anti}), 2.16(ddd, J=1.3, 7.0, 13.6Hz, 1H, 1'-H), 1.67(ddd, J=1.3, 7.0, 13.6Hz, 1H, 1'-H), 1.57(ddt, J=1.3, 1.8, 6.0Hz, 3H, CH_3); UV/VIS (*n*-hexane): λ_{max} =372, 356sh, 352sh, 345sh, 320sh, 299sh, 284sh, 257nm; MS (EI) m/e=196 (63%, M^+), 115(100%); IR (CCl_4) ν=3010(=CH_2), 2910(=CH), 2850(C-H), 1690cm^{-1}(C=C).

*3a-(2'-Propinyl)-3a,4-dihydro-4-methyleneazulene (**rac-9d**):*

yellow oil; yield: 16%; $C_{14}H_{12}$ (180.3), Calcd.: C 93.29, H 6.71, Found: C 92.83, H 7.09 ^{1}H NMR (300MHz, $CDCl_3$): δ=6.73(dd, J=1.2, 5.5Hz, 1H, 3-H), 6.63(dd, J=2.3, 5.5Hz, 1H, 2-H), 6.57(d, J=10.9Hz, 1H, 5-H), 6.34, s, 1H, 1-H), 6.08(dd, J=0.8, 11.4Hz, 1H, 8-H), 5.96(dd, J=7.7, 10.9Hz, 1H, 6-H), 5.90(dd, J=7.7, 11.4Hz, 1H, 7-H), 5.91(s, 1H, 9-H_{syn}), 4.88(s, 1H, 9-H_{anti}), 2.52(dd, J=2.7, 16.3Hz, 1H, 1'-H), 1.93(t, J=2.7Hz, 1H, 2'-H); 1.79(dd, J=2.7, 16.3Hz, 1H, 1'-H). UV/VIS (*n*-hexane): λ_{max} (lg ε)=368(2.69)sh, 371(3.74), 3.55(3.69)sh, 258(4.23), 226nm(3.86)sh. MS (EI) m/e=180(100%, M^+); IR (CCl_4) ν=3300(≡CH), 2950cm^{-1} (=CH).

*3a-Benzyl-3a,4-dihydro-4-methylene-6,8-dimethyl-azulene (**rac-9e**):*

yellow oil; yield: 18%; $C_{20}H_{20}$ (260.4), Calcd.: C 92.26, H 7.74, Found: C 92.05, H 7.60; ^{1}H NMR (300MHz, $CDCl_3$): δ=7.13(m, 3H, C_6H_5), 6.94(m, 2H, C_6H_5), 6.57(dd, J=1.3, 5.5Hz, 1H, 3-H), 6.46(dd, J=2.5, 5.5Hz, 1H, 2-H), 6.26(s, 1H, 1-H), 5.95(s, 1H, 5-H), 5.93(s, 1H, 7-H), 5.34(s, 1H, 9-H_{syn}), 4.55(s, 1H, 9-H_{anti}), 2.81(d, J=12.7Hz, 1H, 1'-H), 2.36(d, J=12.7Hz, 1H, 1'-H), 2.10(s, 3H, CH_3), 2.04(s, 3H, CH_3); UV/VIS (*n*-hexane): λ_{max} (lg ε)=366(3.66), 262nm(4.22); MS (EI) m/e=260 (41%, M^+), 254(100%, M^+-CH_3); IR (CCl_4) ν=3060(=CH_2), 2940(=CH), 2860(C-H), 1620(C=C), 1580cm^{-1}(C=C).

*General procedure for [3,3]-sigmatropic rearrangements of dihydroazulenes **rac-9a-d** to substituted azulenes **10a, 10b, 13 and 14**:* 1.0 mmol Dihydroazulene **9** are dissolved in 10 mL toluene. The reaction mixture is refluxed for 4 min and thereafter concentrated *in vacuo*. The blue to purple oily residue is purified by column chromatography (Al_2O_3 BII-III, *n*-pentane, R_f=0.4-0.5):

*4-(3'-Butenyl)-azulene (**10a**):*

blue oil; yield: quantitative; $C_{14}H_{14}$ (182.3), Calcd.: C 92.26, H 7.74, Found: C 92.45, H 7.55; ^{1}H NMR (300MHz, $CDCl_3$): δ=8.26(d, J=9.5Hz, 1H, 8-H), 7.80(t, J=3.9Hz, 1H, 2-H), 7.46(d, J=3.9, 1H, 3-H), 7.45(dt, J=1.1, 10.2Hz, 1H, 6-H), 7.35(dd, J=1.4, 3.9Hz, 1H, 1-H), 7.07(d, J=10.2Hz, 1H, 5-H), 7.01(t, J=9.5Hz, 1H, 7-H), 5.91(ddt, J=6.7, 10.2, 17.0Hz, 1H, 3'-H), 5.07(dq, J=1.4, 17.0Hz, 1H, 4'-H), 4.97(dq, J=1.4, 10.2Hz, 1H, 4'-H), 3.26(m, 2H, 1'-H), 2.56(m, 2H, 2'-H); UV/VIS (*n*-hexane): λ_{max} (lg ε)=680(2.20), 644(2.31)sh, 618(2.57), 591(2.58), 569(2.62), 550(2.54)sh, 534(2.46)sh, 513(2.32)sh, 387(2.14)sh, 356(3.21), 343(3.68), 339(3.64)sh, 330(3.54), 325(3.47)sh, 318(3.35)sh, 300(3.77), 283(4.71), 278(4.71), 274(4.71)sh, 270(4.56)sh, 241nm(4.43); MS (EI) m/e=182 (6%, M^+), 142(100%, M^+-C_3H_4); IR (CCl_4) ν=3020(=CH_2), 2950(=CH), 2810(C-H), 1570cm^{-1}(C=C).

*4-(3'-Butenyl)-6,8-dimethylazulene (**10b**):*

purple oil; yield: 95%; $C_{16}H_{18}$ (210.2), Calcd.: 210.1610 Found: 210.1590; ^{1}H NMR (300MHz, $CDCl_3$): δ= 7.66(t, J=3.8Hz, 1H, 2-H), 7.40(d, J=3.8Hz, 1H, 1-H), 7.35(d, J=3.8Hz, 1H, 3-H), 7.05(s, 1H, 5-H), 7.04(s, 1H, 7-H), 5.95(ddt, J=6.6, 10.3, 17.0Hz, 1H, 3'-H), 5.10(dq, J=1.7, 17.0Hz, 1H, 4'-H), 5.01(m, 1H, 4'-H), 3.26(m, 2H, 1'-H), 2.87(s, 3H, CH_3), 2.62(s, 3H, CH_3), 2.58(m, 2H, 2'-H). UV/VIS (*n*-hexane): λ_{max} (lgε)= 643(2.16), 616(2.35)sh, 592(2.59), 565(2.63), 550(2.66), 538(2.62), 360(2.99), 350(3.69), 345(3.63), 335(3.56), 330(3.47), 325(3.39), 306(3.79), 296(4.54), 291(4.67), 286(4.67), 282(4.61), 247nm(4.47); MS (EI) m/e=210 (100%, M^+); IR (CCl_4) ν=3015(=CH_2), 2910(=CH), 2840(C-H), 1630(C=C), 1570cm^{-1}(C=C).

4-(2'-Methyl-3'-butenyl)-azulene (13):

blue oil; yield: 40%; $C_{15}H_{16}$ (196.3), Calcd.: C 91.78, H 8.22, Found: C 91.58, H 8.67; ^{1}H NMR (300MHz, $CDCl_3$): δ=8.35(d, J=9.6Hz, 1H, 8-H), 7.84(t, J=3.8Hz, 1H, 2-H), 7.53(dt, J=1.0, 10.4Hz, 1H, 6-H), 7.45(d, J=3.8Hz, 1H, 3-H), 7.38(d, J=3.9Hz, 1H, 1-H), 7.13(d, J=10.4Hz, 1H, 5-H), 7.10(t, J=9.6Hz, 1H, 7-H), 5.90(ddd, J=7.1, 10.3, 17.3Hz, 1H, 3'-H), 4.97(dd, J=1.0, 17.3Hz, 1H, 4'-H), 4.92(dd, J=1.0, 10.3Hz, 1H, 4'-H)3.30(dd, J=6.9, 12.8Hz, 1H, 1'-H), 3.12(dd, J=8.0, 12.8Hz, 1H, 1'-H), 2.81(dddq, J=6.7, 6.9, 7.1, 8.0Hz, 1H, 2'-H), 1.07(d, J=6.7Hz, 3H, CH_3); UV/VIS (*n*-hexane): λ_{max} =680, 644sh, 618, 590, 570, 551sh, 531sh, 512sh, 395sh, 355, 344, 340, 329, 325sh, 316sh, 300, 284, 279, 275, 270sh, 265sh, 243nm; MS (EI) m/e=169 (87%, M^+), 167(100%, M^+-C_2H_5); IR (CCl_4) ν=3010(=CH_2), 2920(=CH), 2840(C-H) 1560cm^{-1}(C=C).

4-(2',3'-Butadienyl)-azulene (14):

blue oil; yield: 50%; $C_{14}H_{12}$ (180.3), Calcd.: C 93.29, H 6.71, Found: C 93.11, H 6.75; ^{1}H NMR (300MHz, $CDCl_3$): δ=8.35(d, J=9.6Hz, 1H, 8-H), 7.86(t, J=3.8Hz, 1H, 2-H), 7.56(dd, J=9.6, 9.8Hz, 1H, 6-H), 7.49(d, J=3.8Hz, 1H, 3-H), 7.39(dd, J=1.3, 3.8Hz, 1H, 1-H), 7.22(d, J=9.8Hz, 1H, 5-H), 7.12(t, J=9.6Hz, 1H, 7-H), 5.44(tt, J=6.6, 7.4Hz, 1H, 2'-H), 4.75(dt, J=2.9, 6.6Hz, 2H, 3'-H), 3.93(dt, J=2.9, 7.4Hz, 2H, 1'-H); UV/VIS (*n*-hexane): λ_{max} (lg ε)=680(2.15), 645(2.29)sh, 619(2.55), 591(2.57), 570(2.61), 552(2.53)sh, 534(2.45)sh, 513(2.31)sh, 356(3.09), 343(3.61), 340(3.59)sh, 330(3.49), 326(3.43)sh, 319(3.30)sh, 300(3.63), 284(4.64), 279(4.64), 275(4.61)sh, 270(4.47)sh, 265(4.28)sh, 242nm(4.36) MS (EI) m/e=180 (100%, M^+); IR (CCl_4) ν= 2950(=CH), 1950cm^{-1}(C=C=C).

References and Notes

1. Dedicated to Professor Gábor Fodor on the occasion of his 75th birthday.
2. This work was generously supported by the Deutsche Forschungsgemeinschaft and the Fond der Chemischen Industrie.
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