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ISOMERIZATIONS OF BENZANNELATED C_9H_{10} BICYCLIC SYSTEMS INTO CYCLONONATETRAENES. INSIGHT INTO THE BEHAVIOUR OF MEDIUM-SIZED CONJUGATED RINGS[1]

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Abstract—Dibenzobicyclo[5.2.0]non-8-ene **9** was prepared from 2,3:6,7-dibenzocycloheptatriene as starting material. The bicyclic system **9** isomerized thermally to give *cis,trans*- and *cis,cis*-1,2:7,8-dibenzocyclononatetraene. The formation of *cis,trans*-1,2:7,8-dibenzocyclononatetraene occurs in an allowed concerted electrocyclic process of general interest.

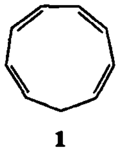
Medium-sized conjugated ring systems are sensitive to valence bond isomerizations.[2,3] This characteristic has been attributed to the relief of the steric interactions between the hydrogen atoms at the ring juncture. Cyclononatetraene (CNT) **1** manifests this property by its isomerization to a bicyclic system.[4] This behaviour is attributed to *peri* H–H repulsions, predicted theoretically to be significant.[5] However, bicyclic systems were converted into the monocyclic cyclononatetraenide anion **2**, despite the steric interactions present in the latter.[6] This phenomenon is assigned to the aromatic stabilization of **2**, being a 10π-electron Huckeloid system.

Benzene annelation of **1** has been shown[7,8] to inhibit the double bond isomerization since this process involves the disruption of aromaticity in the fused benzene rings. On the other hand steric effects have been shown to be significant in the formation of aromaticity of benzene annelated cyclononatetraenide anions.[7a,8a,9] We wish to report on the application of benzene annelation to the investigation of the chemistry of the cyclononatetraene system.

Cyclononatetraene **1** has been shown[10] to be very unstable and to undergo a thermal disrotatory electrocyclic process to *cis*-8,9-dihydroindene **3**. Vogel[11] suggested that the thermal isomerization of bicyclo[6.1.0]nonatriene **4** into **3** proceeds via the intermediacy of **1**. Since then, it has been established[12] that in the thermolysis of **4**, **3** is followed by its structural isomer *trans*-8,9-dihydroindene **5**. Such bond reorganizations have been observed in a variety of bicyclic systems, where the intermediacy of a medium-sized conjugated monocyclic system was suggested.[2–4] While the formation of **3** is suggested[10,13] to originate from *cis*^{4}-CNT **1**, the formation of the *trans* fused system *viz.* **5** has to be accounted for. Its formation can be rationalized[14] by the intermediacy of a mono-*trans* cyclononatetraene (CNT) system **6** or **7**. A number of pathways were considered[13,15,16] for the transformation of **4** into **3** and **5**, and their heteroanalogs.

Several attempts to trap the monocyclic isomers and their stereochemistry were claimed.[17,18] However, objections regarding these conclusions were reported.[19] Furthermore, the stepwise transformations suggested could not be verified and remain an enigma. Only one pathway, i.e. **4**→ (bicyclo[5.2.0]nonatriene) **8**[16]→(*cis,trans,cis*^{2}-CNT) **7**→**5**, includes all the intermediates which account for all the products in a single stepwise process.

The problematic behaviour of **4** during the thermolysis seems to be a key problem in the isomerizations of bicyclic systems via intermediates of medium-sized conjugated rings. The fact that bicyclo[6.1.0]nonatriene **4** rearranges to **8** encouraged us to explore the thermolysis of the dibenzene annelated intermediate i.e. dibenzobicyclo[5.2.0]non-8-ene **9**. This compound seems to be an adequate substrate in the establishment of a pathway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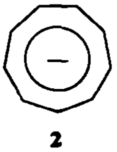
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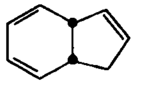
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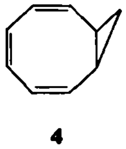
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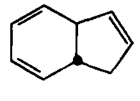
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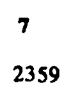
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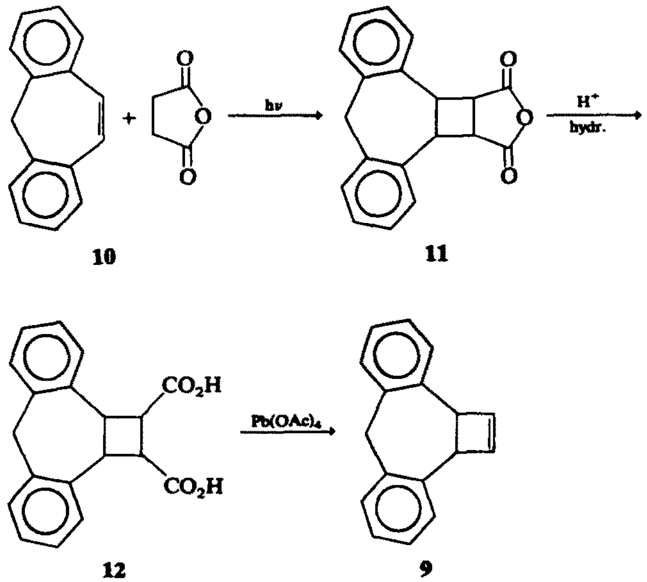
8

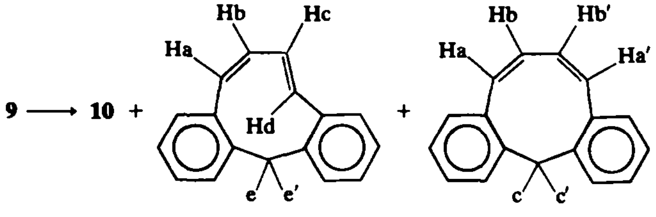


Scheme 1.

similar to that of **8**→**7**→**5** due to the expected stabilization of the corresponding intermediary dibenzocyclononatetraene isomers.[7,8]

Dibenzobicyclo[5.2.0]non-8-ene **9** was prepared as outlined in Scheme 1. 2,3:6,7-Dibenzocycloheptatriene **10**, obtained by an improved process by the reduction of dibenztropone with $LiAlH_4$-$AlCl_3$, was irradiated with maleic anhydride, benzil was added as a sensitizer. The resulting cycloadduct **11** was hydrolyzed with base to form the diacid **12**. In the mass spectrum the expected molecular ion ($m/e = 308$) appears. The successive loss of water, carbon dioxide, carbon monoxide and acetylene occurred to form the stable cycloheptatrienyl ion ($m/e = 192$, 100%). The infra-red spectrum of **12** shows the carbonyl frequency at $1700\,cm^{-1}$ while a broad hydroxyl band is observed at $3100\,cm^{-1}$. Oxidative bisdecarboxylation of **12** applying Grob's method[20] ($Pb(OAc)_4$) led to the formation of **9** (m.p. 70°). The structure of **9** was confirmed by its spectral properties. The mass spectrum reveals the molecular ion ($m/e = 218$, 100%), and fragmentation of acetylene (192, $M-C_2H_2$) thus indicating the presence of a fused cyclobutene ring. The NMR spectrum is rather peculiar and consists of an aromatic multiplet, two broad bands at 4.02 and 6.45 ppm and a singlet at 4.54 ppm. This NMR spectrum is temperature dependent and will be discussed elsewhere. The low yield (25%) of the bis-decarboxylation process encouraged us to look for alternate routes. Bisdecarboxylation with lead tetraacetate in presence of oxygen[20d] resulted in a slight increase (31%) of **9**. However, electrochemical bisdecarboxylation[21] resulted in a decrease in the yield of **9**. Applying Paquett's recently published method[22] for bisdecarboxylation of *vic.*-dicarboxylic acids on **12** we isolated only 1,2:5,6-dibenzocycloheptatriene **10** in 45% yield. We assume that the formation of **10** originates from a cyclo-reversion reaction of the intermediary **9**. These results indicate the facile fragmentation of an acetylenic component from **9**.

Thermolysis of **9** at 290°C in order to obtain the isomerization reaction resulted in a mixture of three products which were separated. One product was identified as 1,2:3,4-dibenzocycloheptatriene **10** (NMR, TLC, and mixed m.p. with an authentic sample). This compound originates from the formerly discussed cycloreversion reaction which further emphasizes the tendency of this system to lose acetylene. The two other products showed the same molecular ion and a closely related mass spectrum. The elemental analysis established a similar composition ($C_{17}H_{14}$). The fact that the molecular ions of the these products did not lose acetylene indicates that they are isomers of the parent hydrocarbon *viz.* **9**. The structure of these isomers was fully confirmed by their proton NMR spectra. The spectrum of one isomer is attributed to *cis,trans*-1,2:7,8-dibenzocyclononatetraene **13**. The vinylic proton appears as an ABCD spectrum. Proton H_a appears at 6.60 ppm (double doublet). Proton H_b appears as a triplet of doublets at 6.46 ppm. The triplet of doublets at 5.95 ppm is assigned to proton H_c while the double doublet at 6.15 ppm is assigned to proton H_d. The nine-membered benzylic protons H_e and $H_{e'}$ appear as an AB pattern ($\delta_A = 4.24$, $\delta_B = 3.46$ ppm, $J = 14$ Hz). This assignment was confirmed by double resonance experiments. For example, irradiation at 6.46 ppm converted the pattern of H_c into a doublet ($J = 16$ Hz) split further by proton H_a ($J = 1$ Hz), H_a appears as a narrow doublet as a result of allylic splitting by H_c and the allylic coupling of H_d disappears. Irradiation at 3.46 ppm converted the doublet at 4.24 ppm into a singlet. The vinylic ABCD pattern of **13** clearly shows two vinylic coupling constants $J_{ab} = 11$ Hz and $J_{cd} = 16$ Hz. The appearance of two vinylic coupling constants (^3J) and their magnitude strictly confirm the existence of a *cis,trans* double bond configuration in **13**. Similar coupling constants were obtained in a series of *cis* and *trans* benzannelated [11][23] and [13][24] annulenes. The appearance of an AB pattern for



13 **14**

protons H_e and $H_{e'}$ suggests a rigid asymmetric configuration for **13**. Drieding models similarly suggest a non-flexible configuration of **13**. The other isomer was identified as *cis,cis*-1,2:7,8-dibenzycyclononatetraene **14**. Its simple NMR spectrum consists of a singlet at 4.38 ppm assigned to protons H_c and $H_{c'}$ and a single AB pattern of the four vinylic protons ($\delta_A = 5.89$, $\delta_B = 6.23$ ppm, $J = 12$ Hz). The benzene ring protons appear as an unresolved multiplet at 6.95–7.15 ppm. The coupling constant of the vinylic AB spectrum of **14** ($J = 12$ Hz) is in agreement with an all-*cis* configuration. This assignment is further supported by the similar coupling constants found in other benzene annelated cyclononatetraene with a *cis* configuration.[8,9] Dreiding model of **14** indicated a flexible nonplanar molecule. The appearance of protons H_c and $H_{c'}$ as a singlet suggests a fast dynamic exchange which averages the shifts of these protons. However, experiments at low temperatures (up to −90°C) did not show any significant change, suggesting a low barrier for this ring inversion process.

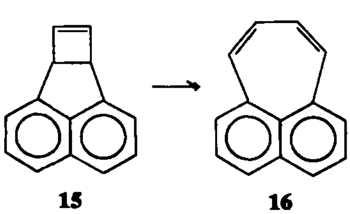
A gradual increase in temperature of the thermolysis of **9** affected a concomitant disappearance of **13** and enrichment of isomer **14** in the reaction mixture. When **9** was thermolysed at 300–320° the ratio of the isomers **14**/**13** gradually increased. The thermolysis of **13** itself at 310° resulted in the sole formation of **14**. These results are rationalized by the mechanism suggested previously for the thermal isomerization of **4**.

These results reveal that **9** undergoes, in line with the Woodward–Hoffmann rules,[25] a preliminary conrotatory thermal electrocyclic isomerization into the *cis,trans* isomer **13**. In turn this isomer undergoes a configuruation isomerization of the *trans* double bond into the all *cis* isomer **14**. It can be seen that these conclusions confirm the mechanism proposed for the isomerization of **4** to **3** and **5** via **8**. These results therefore advocate that benzene annelation is an efficient tool for investigating the stepwise isomerization of bicyclo[5.2.0]nonatriene **8** skeleton into a cis^4-cyclononatetraene **1**.

In view of the inability to detect the intermediary monocyclic medium size conjugated ring systems during the isomerization of the related bicyclic systems, it seems that benzene annelation may serve as a stabilizer of the diverse configurations of its monocyclic counterpart. The formation of a *cis,trans* configuration of the "butadiene" part of **13** upon thermal ring opening of the fused polycyclic system **9** should be noted. Thermolysis of dibenzo-annelated bicyclo[3.2.0] and bicyclo[4.2.0] skeletons into their benzene annelated monocyclic derivatives always furnished the butadiene "bridge" in a *cis,cis* configuration.[26,27] For example the thermolysis of **15** and **17** afforded pleadiene **16**[26] and 1,2:3,4-dibenzocyclooctatetraene **18**[27a] respectively. At first glance it seems that these isomerizations proceed *via* a disallowed or a stepwise mechanism. A biradical mechanism has been put forward to account for these results.[28] However, the results presented here suggest an allowed concerted electrocyclic pathway viz. a preliminary conrotatory process into a *cis,trans* "butadiene bridge" followed by the *trans* double bond isomerization into the respective *cis* configuration. This suggestion takes into account the high temperatures (ca. 400°) in which these transformations are conducted.

In view of the suggestion that bicyclo[5.2.0]nonatriene **8** is an intermediate in the thermal rearrangement of bicyclo[6.1.0]nonatriene **4** to cyclononatetraenes, we studied the possible isomerization of dibenzobicyclo[6.1.0]nonatriene **19** into cis^2-1,2:5,6-dibenzocyclononatetraene **20**. While bicyclic C_9H_{10} systems with one benzene annelation are known to undergo thermal and photochemical isomerizations,[29] the isomerization of **19** would become impossible since the preliminary [3.3]sigmatropic shift may be avoided.

The synthetic approach to **19** was based on a carbene addition to 1,2:5,6-dibenzocyclooctatetraene **21**. Experiments to add dihalocarbenes to **21** in diverse methods, including phase transfer catalysis[30] and crown ethers[30] failed. Furthermore, experiments to add methylene to **21** by the Simmons–Smith reaction[31] failed as well. On the



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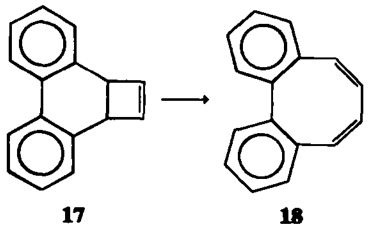
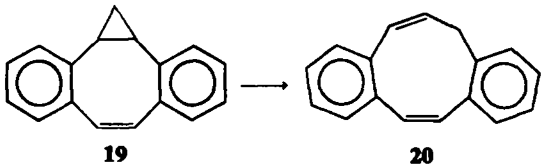


17 **18**



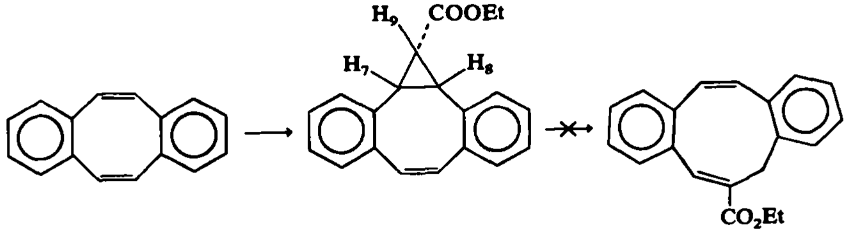
19 20

other hand by applying ethyldiazoacetate in the presence of copper-bronze on **21** the adduct ethyl-*exo*-1,2:5,6-dibenzobicyclo[6.1.0]nonatriene-9-carboxylate **22** was formed,[32] whose structure elucidation was based on its spectral characteristics. The mass spectrum reveals the molecular ion ($m/e = 290$) and the product of fragmentation of the cyclopropane component ($m/e = 203$). The infrared spectrum of **22** reveals the carbonyl stretching at 1720 cm^{-1} while the ultraviolet spectrum shows a *cis*-stilbene chromophore. The NMR spectrum confirms the proposed stereochemistry for **22**. Protons H_7, H_8 and H_9 show an AX_2 pattern: protons H_7 and H_8 appear at 2.93 ppm and H_9 appears at 2.27 ppm. The coupling constant of the cyclopropane protons ($J_{AX} = 5$ Hz) confirms the *exo* configuration and is in good agreement with other *exo*-ethoxycarbonylcarbene adducts.[33] An additional product isolated from the reaction mixture was identified as diethylfumarate (12%). This product probably arises from a dimerization of the carbenoid species.[32] Compound **22** showed high stability upon heating. Thermolysis of **22** at 220° fully recovered the starting material despite the fact that polycyclic ethoxy-carbonylcarbene adducts of naphthalene or acenaphthene were isomerized under similar conditions.[34] At higher temperatures compound **22** was decomposed. The application of rhodium complexes[35] in order to isomerize **22** to **23** failed as well. These failures to isomerize **22** as attributed to the effect of the benzannelation which avoids a primary [3.3]sigmatropic rearrangement of the bicyclo[6.1.0]nonatriene skeleton.

Another attempt to isomerize **22** was based on its deprotonation. The formed anion may in principle[25] undergo a conrotatory ring opening (cyclopropyl to allyl anion), into *cis,trans*-1,2:5,6-dibenzocyclononatetraenyl anion analogous to the parent system which undergoes this process with great ease.[36] It should also be noted that the *cis,trans* anion can isomerize into the all-*cis* anion similarly to the monocyclic aromatic anion.[36] Treatment of **22** with lithium isopropylcyclohexyl amide[37] in THF-d_8 resulted in the formation of the anion derived from **22** and no isomerized anionic species could be detected. Upon its quenching with water only a mixture of **22** and its *endo* isomer was obtained. The assignment of the stereochemistry of the *endo* isomer of **22** was deduced from the proton NMR of this compound. The AX_2 pattern of the cyclopropyl protons exhibited a coupling constant ($J_{AX} = 8.5$ Hz) characteristic of an *endo* configuration and in agreement with other ethoxycarbonylcarbene adducts to which an *endo* configuration has been assigned,[33] thus epimerization at C_9 took place. This epimerization is explicable by a nonstereoselective protonation process of the anion. The expected isomerization of the anion of **22** into the dibenzocyclononatetraenyl anions did not take place although these anions are expected to be aromatic due to 10π-electron delocalization of the anionic component. The failure of this isomerization may be attributed to steric interactions. The *peri* H–H repulsions have been previously shown to be significant in medium size rings, especially in the cyclononatetraenyl anion.[5,9] While isomerization into *trans*-cyclononatetraenyl anion is favoured as *peri* H–H *trans* repulsions are removed, the conrotatory isomerization of the anion of **22** into the *trans* dibenzocyclononatetraenyl anion does not remove *peri* H–H repulsions and simultaneously forms an unfavoured *trans* configuration.[9] Moreover, this trans configuration forces the bulky ethoxycarbonyl group into the inner part of the framework thus forming additional repulsion interactions.

CONCLUSIONS

Benzannelation of bicyclic C_9H_{10} systems has been shown here to be an efficient tool in the study of the isomerization pathway of these systems. The thermolysis of dibenzobicyclo[5.2.0]nonatriene **9** in a conrotatory reaction to the *cis,trans*-dibenzocyclononatetraene **13** and the configurational isomerization of **13** to **14** proved that the thermolytic behaviour of the parent hydrocaron **8** could be followed. The observation that the *cis,trans* double bonds of **13** are isomerized to the all-*cis* isomer **14** shows that the Woodward–Hoffmann rules are obeyed in the isomerization of **9** thus shedding light on the thermolytic pathway of polycyclic systems including a bicylobutene component.



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EXPERIMENTAL

Melting points were taken on a Fisher-Johns apparatus (uncorrected). UV spectra were recorded with the aid of Unicam S.P. 800 spectrometer. Infrared spectra were recorded with a Perkin-Elmer Model 337 spectrometer. ^1H NMR spectra were recorded on a Varian HA-100D spectrometer at 100 MHz, and on a Varian SC-300 at 300 MHz, the reported chemical shifts (δ) are downfield relative to TMS. Mass spectra were recorded with an Atlas MAT CH 4 spectrometer at 70 eV

1,2:5,6-*Dibenzobicyclo*[5.2.0]*nonadiene*-8,9-*dicarboxilic acid* **12**.

Into 1 litre irradiation flask equipped with a condenser, stirrer and a gas inlet were placed 5 g (26 mmol) of dibenzo[a,e]cycloheptadiene **10** 2.25 g (26 mmol) of recrystallized maleic anhydride, 400 mg benzil (sensitizer), and 800 ml of dry hexane. N_2 was bubbled into the solution and the solution was irradiated with a Hanovia 450 W lamp during 5 h. The precipitate was filtered and transferred into a solution of 85 ml of 1.46 M KOH. This solution was refluxed for 3 hours. After treating the solution with charcoal it was filtered, and acidified with dilute HCl. The white precipitate, 5.2 g, was filtered, dried and used without further purification (yield 64%). A sample was recrystallized from acetone-water (1:1); m.p. 189°; (Analysis calc. for $C_{19}H_4O_4$: C, 74.02; H, 5.19%; found: C, 73.70; H, 5.43); IR^{Nujol}: 3200 (broad), 1700, 1380, 1260, 1230, 765, 740, 615 cm^{-1}; MS *m/e*: 308(M), 290, 262, 255, 193, 192 (100%), 188.

1,2:5,6-*Dibenzobicyclo*[5.2.0] *non*-8-*ene* **9**

(a) *Decarboxylation with lead tetraacetate*. A mixture of 1.25 g (4 mmol) of the diacid in 40 ml of dry benzene and 0.8 ml of pyridine was heated under nitrogen to 50°C. To the stirred solution was added portionwise 2.1 g (4.6 mmol) of lead tetraacetate. After the evolution of CO_2 ceased, the solution was refluxed for an additional 2 hours. The dark mixture was poured over dilute nitric acid (5%) and extracted with dichloromethane. The organic layer was separated, washed with dilute nitric acid (5%) and water, dried and evaporated. The oil obtained after evaporation was chromatographed over 100 g Florisil. Elution with hexane resulted in a yellow oil which was crystallized from methanol; 230 mg of **9** were obtained; m.p. 72° (yield 25%); (Analysis calc. for $C_{17}H_{14}$: C, 93.58; H, 6.42. Found: C, 92.75; H, 6.30); IR ν_{max}^{KBr}: 2970, 1620, 1300, 1220, 750, 690 cm^{-1}; UV $\lambda_{max}^{C_6H_{12}}$: 255 ($\varepsilon$ = 17.500), 295^s nm(2400); MS *m/e* = 218(100%), 217, 215, 202, 201, 192, 190.

(b) *Decarboxylation with lead tetraacetate under oxygen*. A mixture of 4 g (13 mmol) of the diacid **12** in 40 ml dry pyridine (distilled over KOH) was heated to 67°C. Oxygen was bubbled for 15 minutes and 14.7 g (33 mmol) of lead tetraacetate was added portionwise. After similar treatment to that described in (a) 900 mg of **9** were obtained. (yield 31%).

(c) *Electrolytic decarboxylation*[21]. Into the electrolytic cell equipped with a condenser, magnetic stirrer and two platinum electrodes were placed 1.47 g (4.7 mmol) of the diacid **12**, 100 ml of a pyridine-water solution (15:85) and 1.25 ml triethylamine. The solution was stirred for 15 minutes and the electrodes were connected to the power. The cell was cooled with an ice bath and electrolysis was conducted at 150 V and 0.5 A, while stirring. The resulting mixture was poured over dilute hydrochloric acid (10%). After extraction with dichloromethane and similar treatment to that described in part (a), 120 mg of **9**, were obtained. (yield 12%).

Thermolysis of **9**: *Preparation of cis,trans*-1,2:7,8-*dibenzocyclononatetraene* **13** *and cis,cis*-1,2:7,8-*dibenzocyclononatetraene* **14**

The thermolysis oven was equipped with 20 cm glass tube (diameter 1.5 cm) filled with glass chips (1–2 mm diameter). One of the tube ends was connected to the receiving flask, inseted in a cooling bath, while the other end was connected to a capillary T-shaped tube closed at the top with a sleeve stopper. The capillary sidearm was connected to N_2 through a reduction valve. The injector contains the solution to be pyrolyzed and was fixed to a plate which moved horizontally by a mechanical preadjusted constant speed system. Thus, a constant injection rate of the solution into the glass tube in the oven was achieved. The oven has an inside thermocouple which enabled temperature regulation within ±1°C.

.The oven was heated prior to the pyrolysis to 290°C for 40 minutes in order to achieve constant temperature, while the system was flushed with nitrogen. Into the injector was placed a soluton of 150 mg (0.5 mmol) of 1,2:5,6-dibenzobicyclo[5.2.0]non-8-ene **9** in 15 ml dry benzene. The solution was injected into the oven at a rate of 1 ml/min followed by a nitrogen steam through the sidearm and the thermolysis was conducted for 15 min. The oven was then cooled to room temperature and the glass tube and glass chips were washed with dichloromethane which was combined with the benzene solution which condensed in the receiving flask. The brown suspension was filtered and the solution was evaporated to give a brown oil, 450 mg of the oil were column chromatographed over SiO_2 (150 cm height diameter 2 cm), elution with hexane. The eluents were transferred through a UV detector (λ = 280 nm).

Evaporation of the first fraction yielded 58 mg of **10** (12%); m.p. 106°; ^1H NMR ($CDCl_3$): 7.3 (m, 8H), 6.99 (s, 2H), 3.70 ppm (s, 2H).

Evaporation of the second fraction afforded 75 mg of *cis,cis*-1,2:7,8-dibenzocyclononatetraene **14** an oil which did not crystallized (16% yield); (Analysis calculated for $C_{17}H_{14}$: C, 93.58; H, 6.42. Found: C, 92.10; H, 6.75); IR ν_{max}^{neat}: 2920, 1630, 1490, 1030, 780, 745 cm^{-1}. UV $\lambda_{max}^{C_6H_{12}}$:255($\varepsilon$ = 12,000), 290^s(8,500). MS *m/e* = 219, 219(M, 100%), 217, 215, 201, 202. ^1H NMR ($CDCl_3$):6.95–7.15(m, 8H), 6.25(d, 2H, J = 12 Hz), 5.89(d, 2H, J = 12Hz), 4.38 ppm (s, 2H).

Evaporation of the third fraction yielded 68 mg of *cis,trans*-1,2:7,8-dibenzocyclononatetraene **13** (oil, 15% yield); (Analysis calc. for $C_{17}H_{14}$: C, 93.58; H, 6.42. Found: C, 91.70; H, 6.88); IR ν_{max}^{neat}: 2960, 1600, 1520, 1060, 960, 930, 790, 770; UV $\lambda_{max}^{C_6H_{12}}$:258(11,000), 280^s(6,500), 335(1,800); MS *m/e*: 219, 218(M, 100%), 217, 215, 202, 201; ^1H NMR ($CDCl_3$): 7.0–7.8 ppm (m, 8H), 6.60(dd, 1H, J_1 = 11 Hz; J_2 = 1 Hz), 6.46(ddd, 1H, J_1 = 11 Hz; J_2 = 2.5 Hz; J_3 = 1 Hz), 6.15(dd, 1H, J_1 = 16 Hz; J_2 = 1 Hz), 5.95(ddd, 1H, J_1 = 16 Hz; J_2 = 2.5 Hz; J_3 = 1 Hz), 4.24(d, 1H, J = 14 Hz), 3.46 ppm (d, 1H, J = 14 Hz).

Thermolysis of a solution of 70 mg (0.32 mmol) of *cis,trans*-1,2:7,8-dibenzocyclononatetraene in 5 ml of dry benzene **13** conducted under similar conditions as described above afforded a mixture of **13** and **14** (identified by ^1H NMR), no 1,2:5,6-dibenzocycloheptatriene (**10**) was detected.

Pyrolysis of 180 mg (0.8 mmol) of **13** in 10 ml of dry benzene at 365° in a similar way to that described above yielded 40 mg of 1,2:5,6-dibenzocycloheptatriene **10** (yield 26%) and 30 mg of *cis,cis*-dibenzocyclononatetraene **14**, yield 14%.

Ethyl-exo-*1,2:5,6-dibenzobicyclo*[6.2.0]*nonatrien-9-carboxylate* **22**.

A mixture of 900 mg (4.4 mmol) of 1,2:5,6-dibenzocyclooctatetraene **21** and 75 mg of copper-bronze were heated under nitrogen to 150–155°C. Into the stirred melt were injected 0.7 ml (6.7 mmol) ethyldiazoacetate during 2 h. The mixture was stirred for an additional 1 h and afterwards cooled to room temperature. The resulting oil was extracted with dichloromethane, filtered and evaporated. The residue was chromatographed on 60 g SiO_2. Elution with 200 ml of benzene afforded 250 mg recovered **22** (28%). Further elutions with benzene afforded 40 mg of **22** as an oil (34% yield); (Analysis calculated for $C_{20}H_{18}O_2$: C, 82.75; H, 6.20. Found: C, 82.37; H, 6.15); IR ν_{max}^{neat}: 2980, 1730, 1490, 1380, 1300, 750 cm^{-1}; ^1H NMR ($CDCl_3$): 7.10 (m, 8H), 6.80 (s, 2H), 4.28 (q, 2H, J = 8Hz), 2.93 (d, 2H, J = 5.0 Hz), 2.27 (t, 1H, J = 8.0 Hz), 1.3 ppm (t, 3H, J = 5.0 Hz); MS *m/e*: 290, 218, 217, 203, 202, 148, 142 (100%), 141. Elution with chloroform afforded 96 mg of diethylfumarate (yield 12%) identified by comparison with an authentic sample.

Basic isomerization of ethyl-exo-*1,2:5,6-dibenzobicyclo*[6.1.0]*nonatriene-9-carboxylate* **22**. *An attempt to prepare* cis,trans-*dibenzocyclononatetraenyl anion*

A solution (under nitrogen) of 0.46 ml (2.5 mmol) of *N*-isopropylcyclohexylamine (distilled from CaH_2) in 10 ml dry THF was cooled to −65°C and to it was added 1.11 ml (2.5 mmol) of a 2.1 M solution of *n*-butyl lithium in cyclohexane and stirred for another 15 minutes. Into the solution was added with stirring a solution of 300 mg of **22** (0.1 mmol) in 2 ml dry THF. The solution temperature was raised to −40°C and stirred for an additional 1 h, and then quenched with 15 ml of water. The layers were separated and the organic phase was washed with water, dried and evaporated. The residue consisted of a mixture of the two isomers *endo* and *exo* **22**. ^1H NMR of the *endo* isomer of **22** ($CDCl_3$): 7.1 (m, 8H), 6,65 (s, 2H), 4.20 (q, 2H, J = 5.0 Hz), 3.10 (d, 2H, J = 8.5 Hz), 1.90 (t, 1H, J = 8.5 Hz), 1.42 ppm (t, 3H, J = 5.0 Hz).

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