208. Synthesis and Chiroptical Properties of Dimethyl 8,12-Diphenylbenzo[*d*]heptalene-6,7-dicarboxylate

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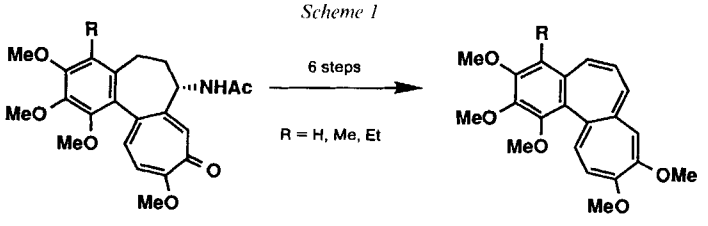
Dedicated to *Arnold Brossi* on the occasion of his 70th birthday

(23.IX.93)

6,10-Diphenylbenz[*a*]azulene (**3**) was reacted with dimethyl acetylenedicarboxylate (ADM) in the presence of 2 mol-% of $[RuH_2(PPh_3)_4]$ in MeCN at 100° to yield a 7:1 mixture of dimethyl 2,6-diphenyl-9,10-benzotricyclo-[6.2.2.0^{1,7}]dodeca-2,4,6,9,11-pentaene-11,12-dicarboxylate (**4**) and dimethyl 8,12-diphenylbenzo[*d*]heptalene-6,7-dicarboxylate (**5**; *Scheme 2*). The tricycle **4**, when heated in DMF at 150° for 1 h led to the formation of 81.5% of the heptalene-6,7-dicarboxylate **5** and 15% of the starting azulene **3**. No rearrangement of tricycle **4** was observed, when it was heated at temperatures up to 180° in pseudocumene. The heptalene-6,7-dicarboxylate **5** was easily separated into its antipodes (*PM*)- and (*MP*)-**5** on a *Chiracel* column (*cf. Fig. 2*). On heating at 150° for 1 h, (*MP*)-**5** showed no racemization at all. The Ru-catalyzed reaction of benz[*a*]azulene (**6**) with ADM led to the formation of dimethyl 9,10-benzotricyclo[6.2.2.0^{1,7}]dodeca-2,4,6,9,11-pentaene-11,12-dicarboxylate (**7**; *Scheme 3*). However, the formation of the corresponding heptalene-6,7-dicarboxylate could not be observed.

Introduction. – Recently, we described the chemical transformation of colchicine (**1**; R=H) and some of its 4-alkyl derivatives into their underlying parent structures **2**, *i.e.* the corresponding 1,2,3,9,10-pentamethoxybenzo[*d*]heptalenes (*Scheme 1*) [1] [2]. Since compounds **2** represent, to the best of our knowledge, the first members of the class of benzo[*d*]heptalenes[2]), we were interested in another synthetic access to this class of compounds, which would also represent the basis of a new and variable approach to colchicinoid-type compounds[3]). Our recent success in the improvement of the synthesis

Scheme 1



1 **2**

[1]) Part of the planned Ph. D. thesis of *A. J. R.*, University of Zurich.

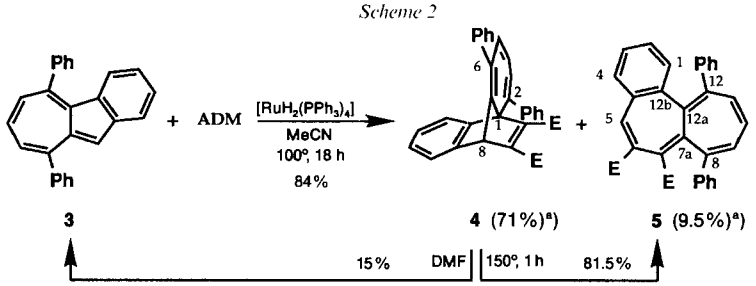
[2]) For the chemistry of heptalenes and their annelated derivatives, see [3–5]. Recently, *Yamamoto et al.* reported the synthesis of [7.7]circulene, the fully benzannelated heptalene [6].

[3]) See [7–9] for classical colchicine syntheses. For newer variants of the synthesis of colchicine-derived compounds, see [9] [10].

of heptalene-1,2-dicarboxylates from azulenes and dimethyl acetylenedicarboxylate (ADM) in polar aprotic solvents such as MeCN in the presence of $[RuH_2(PPh_3)_4]$ [11] as well as of other transition-metal catalysts [12] led us to investigate the reaction of benz[*a*]azulenes with ADM in the presence of transition-metal catalysts in polar aprotic solvents. Here, we report on first results of this synthetic approach to colchicinoid compounds.

Results and Discussion. – The reaction of 6,10-diphenylbenz[*a*]azulene (**3**) [3] with a four-fold molar excess of ADM in the presence of 2 mol-% of $[RuH_2(PPh_3)_4]$ in MeCN at 100° yielded, after 18 h, 71% of the tricycle **4** and 9.5% of the benzo[*d*]heptalene-6,7-dicarboxylate **5** alongside with 16% of recovered azulene **3** (*Scheme 2*). The tricycle **4** could easily be transformed into the benzo[*d*]heptalene **5** by heating in DMF at 150° for 1 h (*Scheme 2*). The starting azulene **3** was formed in this reaction to an extent of 15%. In

Scheme 2

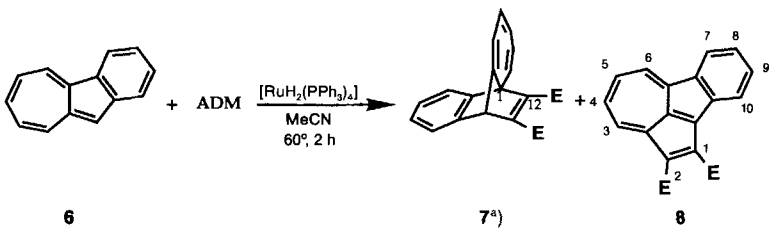


a) 85% and 11.5%, respectively, with regard to reacted **3**.

agreement with our earlier findings that tricycles of type **4** rearrange smoothly into heptalenes in aprotic polar solvents (*cf.* [14] [15]), we observed no rearrangement of **4** into **5** in pseudocumene as solvent, even at 180°. On the other hand, the transformation of **3** and ADM into **5** could also be performed without the catalyst in DMF at 150°. However, no reaction occurred at 100°. The yield of **5** in the purely thermal reaction of **3** and ADM after 18 h amounted to 28% in the presence of 24.5% of recovered **3**. The tricycle **4** could not be detected in this reaction, *i.e.* the rate-determining step in the uncatalyzed reaction at 150° is the *Diels Alder*-type addition of ADM to **3**.

We also investigated the catalyzed addition of ADM to benz[*a*]azulene (**6**) [16]. In this case, a reaction took place already at 60° (*Scheme 3*). From the reaction mixture, which mainly consisted of chromatographically unmoving material, only small amounts of the tricycle **7** and traces of the azulene-1,2-dicarboxylate **8** could be isolated. There was no indication for the presence of the corresponding dimethyl benzo[*d*]heptalene-6,7-dicarboxylate or the formation of the latter compound from the tricycle **7**. Indeed, tricycle **7** decomposed slowly to form **8** as the sole identifiable product. The formation of azulene **8** is best explained by a heterolytic cleavage of the C(1)–C(12) bond in **7** and formation of a new bond between C(6) and C(12). As a rule, this type of intermediates are always formed from tricycles of type **7** which carry no substituent at C(6) and C(8) (*cf.* [11] [14] [15]). The discussed intermediates are stabilized by prototropic shifts to yield correspond-

Scheme 3



a) Tricycle **7** was formed in less than 15%. Azulene **8** was isolated in traces (< 1%).

ing 3,4-ethano-bridged azulene-1,2-dicarboxylates. In the present case, this stabilization is not possible, *i.e.* **8** must be formed from the intermediate by a dehydrogenation reaction. Nevertheless, both addition reactions show that benz[*a*]azulenes easily react with ADM in the presence of $[RuH_2(PPh_3)_4]$ in MeCN to yield tricyclic intermediate of types **4** and **7** which can be rearranged in aprotic polar solvents such as DMF into the corresponding benzo[*d*]heptalenes, at least, when C(6) of the tricycles is substituted.

The structure of the tricycles **4** and **7** follows unequivocally from their ^{1}H-NMR spectra. Quite characteristic is the low-field position of the signal of H–C(8) which appears in $CDCl_3$ as well as in C_6D_6 around 4.5 ppm (*cf. Exper. Part* and [14] [15]). The neighboring H-atoms at the completely planar seven-membered ring (*cf.* [14] [15]) show vicinal coupling constants of *ca.* 12 Hz across C=C bonds and *ca.* 7.4 to 8.7 Hz across C–C bonds (*cf. Exper. Part* as well as [14] [15]).

The rearrangement of **4** into **5** is characterized by a tremendous low-field shift of the *s* for H–C(8) in **4** (4.51 ppm). It appears in **5** as *s* at 8.41 ppm (*cf. Fig. 1*) due to its new

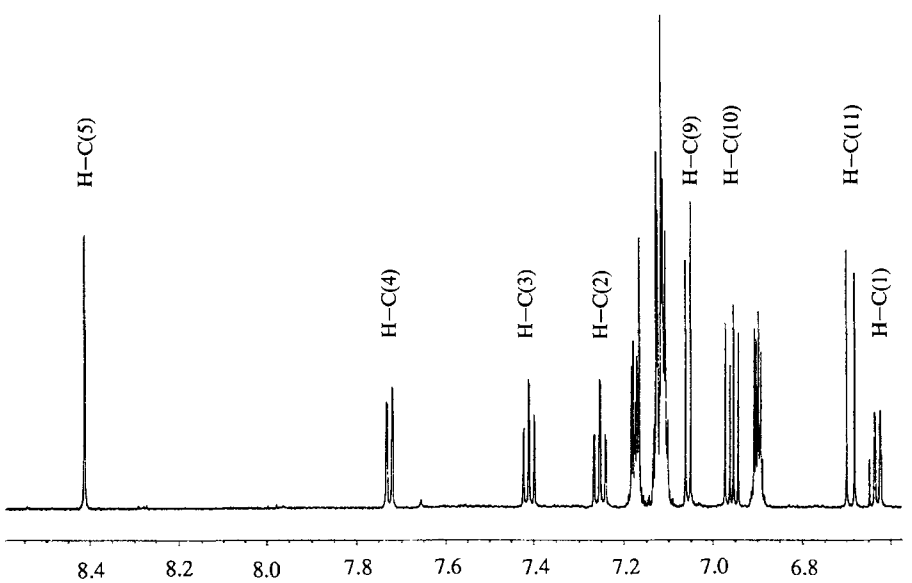


Fig. 1. *^{1}H-NMR Spectrum* (600 MHz, (D_6)acetone) *of dimethyl 8,12-diphenylbenzo[*d*]heptalene-6,7-dicarboxylate* (**5**; region of the olefinic and aromatic H-atoms)

position at C(5) in conjugation to the ester group at C(6). Quite typical for the heptalene structure of **5** is also $^3J(9,10) = 6.5$ Hz (*cf.* [17]) which indicates a torsion angle Θ between the two neighboring H-atoms of 30–35° as it is found for most of the heptalenes with at least two substituents in their *peri*-positions (*cf.* [17] [18]). One also observes a pronounced shift difference between H–C(4) (7.73 ppm) and H–C(1) (6.63 ppm) which indicates that H–C(1) must immerse in the π-cloud of the Ph substituent at C(12). The spatial relation of H–C(4) and H–C(5) was secured by an observed strong reciprocal ^{1}H-NOE between these two H-atoms. Therefore, there is no doubt about the benzo-[*d*]heptalene structure of **5**.

The heptalene structure of **5** is further secured by the CD spectra of its two antipodes (*cf. Fig. 2*), which were easily separated on a *Chiracel OD* column. The antipodes turned out to be optically very stable. We were not able to racemize them by heating up to 150°,

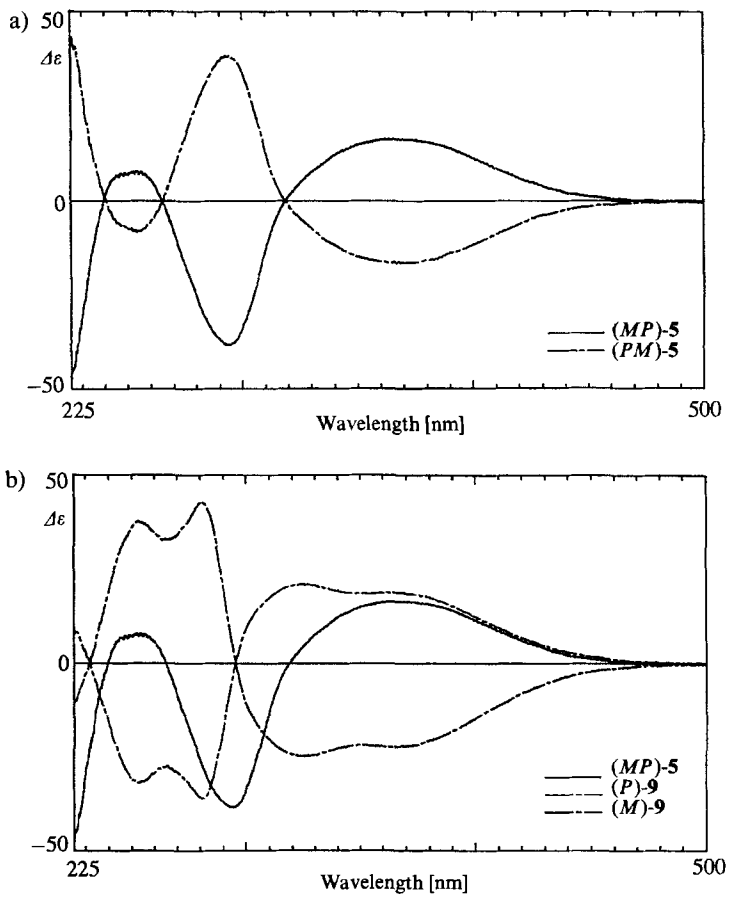


Fig. 2. a) *CD Spectra* (hexane/i-PrOH 93:7) *of* (PM)- *and* (MP)-**5**; b) *Comparison of the CD spectra* (hexane/i-PrOH 93:7) *of dimethyl* (M)- *and* (P)-*5,6,8,10-tetramethylheptalene-1,2-dicarboxylate* ((M)- *and* (P)-**9**) [19] *with those of* (MP)-**5**

at least during 1 h. We assign the (*MP*)-configuration[4]) to the antipode of **5** which shows a nearly perfect agreement of its longest-wavelength +CE at 363–367 nm with that of the (*M*)-configurated antipode of dimethyl 5,6,8,10-tetramethylheptalene-1,2-dicarboxylate ((*M*)-**9**; *cf. Fig. 2, b*) [19][5]). We suppose that the strong −CE at 293 nm is mainly determined by the spatial (*M*)-helical arrangement of the benzo ring and the Ph substituent at C(12) (*cf.* [22]). The work is continued.

We thank Prof. *M. Hesse* and his coworkers for mass spectra, Prof. *W. von Philipsborn* and his coworkers for NMR support, and *H. Frohofer* for elemental analyses. The financial support of this work by the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung* is gratefully acknowledged.

Experimental Part

General. See [11] [18]. M.p. on a *Büchi* apparatus (model *FP5*); values are not corrected. UV spectra on an *Otsuka* spectrophotometer (model *MCPD 1100*). IR spectra on a *Perkin-Elmer* spectrophotometer (model *FT-IR 1600*). ^{1}H-NMR spectra on *Bruker* instruments (models *AC 300* and *AMX 600*). CD spectra were measured on a *Jasco* spectropolarimeter (model *J-500A*). HPLC separations on a *Chiracel OD* column (25.0 × 0.46 cm) from *Daicel Chemical Industries*, equipped with a corresponding pre-column (5.0 × 0.46 cm).

1. Benz[*a*]azulenes. – 1.1. *Benz[*a*]azulene* (**6**). It was synthesized from anthranilic acid and 1,1-dichloroethene following the procedure of *Wege* and coworkers [16][6]). M.p. 187.2–188.3° (EtOH; [16]: 189–190°).

1.2. *6,10-Diphenylbenz[*a*]azulene* (**3**). It was synthesized according to the procedure developed by *Kapicak* and *Battiste* [13]. M.p. 135.2–135.9° (EtOH; [13]: 136–137°).

2. Reaction of the Benz[*a*]azulenes with Dimethyl Acetylenedicarboxylate (ADM). – All reactions were performed under Ar in oven-dried *Schlenk* vessels. MeCN (*Fluka, puriss.*) and ADM (*Fluka, puriss.*) were distilled before use. DMF (*Fluka, puriss.*) and 1,2,4-trimethylbenzene (*Fluka, puriss.*) were used without further purification.

2.1. *6,10-Diphenylbenz[*a*]azulene* (**3**) *and ADM.* Azulene **3** (0.270 g, 0.82 mmol) was dissolved in MeCN (5 ml) and ADM (0.44 ml, 3.23 mmol) and $[RuH_2(PPh_3)_4]$ (0.022 g; 2 mol-%) added. The *Schlenk* vessel was closed and the mixture heated at 100° for 18 h. The solvent was distilled off and the residue separated by CC (silica gel; hexane/Et_2O 1:1) to yield in a first fraction **3** (0.043 g, 15.9%), followed by *dimethyl (1*RS,*8*SR*)-2,6-diphenyl-9,10-benzotricyclo[6.2.2.0^{1,7}]dodeca-2,4,6,9,11-pentaene-11,12-dicarboxylate* (**4**; 0.272 g, 71.2%), and, finally, by *dimethyl (7a*PM,*12a*MP*)-8,12-diphenylbenzo[*d*]heptalene-6,7-dicarboxylate* (**5**; 0.037 g, 9.6%).

Data of **4**. M.p. 111° (dec.; hexane). R_f (hexane/Et_2O 1:1) 0.49. UV (hexane): λ_{max} 370 (sh, 3.76), 350 (sh, 3.90), 282 (sh, 4.43), 250 (4.60); λ_{min} 240 (4.58). IR (KBr): 3059*w*, 3024*w*, 2948*w*, 2925*w*, 2850*w*, 1718*s*, 1436*m*, 1264*m*, 1206*m*, 1127*m*, 1068*w*, 1024*w*, 757*m*, 701*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.70–7.67 (*m*, 2 arom. H); 7.48 (*d*, with f.s., J_{ortho} = 7.5, H–C(3′)); 7.38–7.28 (*m*, 8 arom. H); 7.12–7.04 (*m*, 3 arom. H); 6.06 (*d*, ^3J(4,3) = 8.73, H–C(3)); 5.78 (*dd*, ^3J(3,4) = 8.71, ^3J(5,4) = 11.99, H–C(4)); 5.60 (*d*, ^3J(4,5) = 11.94, H–C(5)); 4.51 (*s*, H–C(8)); 3.69 (*s*, MeOCO–C(12)); 3.13 (*s*, MeOCO–C(11)).

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[4]) The two descriptors of absolute helicity refer to the two twisted π-systems around the central C(7a)–C(12a) heptalene bond and the peripheral C(12a)–C(12b) bond between the benzo ring and the non-benzo-annelated ring of the heptalene system. This means that the second stereochemical descriptors describes the helicity that is also found in colchicine and colchinoids (*cf.* [20] and lit. cited there) as tetrahydrobenzo[*a*]heptalene derivatives.

[5]) Racemic **9** was separated on the *Chiracel OD* column (hexane/i-PrOH 93:7). The configuration of (*M*)- and (*P*)-**9** had been determined by chemical correlation and confirmed by an X-ray crystal structure analysis [19] (*cf.* also [21]). We recognized that the antipodes of **5** and **9** showed just an inverse elution behavior, *i.e.* (*MP*)-**5** und (*P*)-**9** possess the shorter t_R as compared with their antipodes. It should also be mentioned that colchicine and deacetamidocolchicine as well as deacetamidoisocolchicine with the same (*P*)-configuration around the C(12a)–C(12b) bond as in (*MP*)-**5** show qualitatively opposite CE to those of (*MP*)-**5** (*cf.* [20]). However, we have to take into account that the tropolone ring in colchicine and its derivatives is nearly planar (*cf.* [1] [2] [20]), whereas its counterpart in the benzo[*d*]heptalenes is strongly twisted (*cf.* ^3J(9,10) = 6.5 in **5** as well as [17] [18]).

[6]) We thank cand. chem. *Peter Nuesch* for his cooperation in this synthesis.

Data of **5**. M.p. 162° (hexane/acetone). R_f (hexane/Et_2O 1:1) 0.28. UV (hexane): λ_{max} 358 (sh, 3.56), 284.4 (4.40), 245 (sh, 4.41), 223.5 (4.51); λ_{min} 268.2 (4.37), 219.3 (4.50). IR (KBr): 3018*w*, 2947*w*, 1716*s*, 1434*m*, 1271*s*, 1237*s*, 1202*m*, 1129*m*, 1105*m*, 1070*w*, 1032*w*. ^{1}H-NMR (600 MHz, (D_6)acetone; *cf. Fig. 1*): 8.413 (*s*, H–C(5)); 7.727 (*dt*, $^3J(3,4) = 7.81$, $^4J(2,4) = 1.25$, $^5J(1,4) = 0.63$, H–C(4)); 7.411 (*td*, $^3J(4,3) = 7.81$, $^3J(2,3) = 7.39$, $^4J(1,3) = 1.26$, H–C(3)); 7.253 (*td*, $^3J(1,2) = 7.72$, $^3J(3,2) = 7.38$, $^4J(4,2) = 1.28$, H–C(2)); 7.18–7.16 (*m*, 2 arom. H); 7.13–7.10 (*m*, 6 arom. H); 7.056 (*d*, $^3J(10,9) = 6.52$, H–C(9)); 6.958 (*dd*, $^3J(11,10) = 11.44$, $^3J(9,10) = 6.55$, H–C(10)); 6.91–6.89 (*m*, 2 arom. H); 6.687 (*d*, $^3J(10,11) = 11.40$, H–C(11)); 6.628 (*dt*, $^3J(2,1) = 7.72$, $^4J(3,1) = 1.25$, $^5J(4,1) = 0.63$, H–C(1)); 3.728 (*s*, MeOCO–C(6)); 3.171 (*s*, MeOCO–C(7)). ^{1}H-NOE (400 MHz, (D_6)acetone): 8.413 (H–C(5))→7.727 (*s*); 7.727 (H–C(4))→8.413 (*s*), 7.411 (*s*); 6.628 (H–C(1))→7.253 (*s*), 6.91–6.89 (*s*). EI-MS: 472.2 (37, $M^{+\cdot}$), 440.2 (12, $[M - MeOH]^+$), 412.2 (100, $[M - MeOH - CH_2O]^+$), 352.2 (23). CI-MS (NH_3): 490.2 (100, $[M + NH_4]^+$). Anal. calc. for $C_{32}H_{24}O_4$ (472.54): C 81.34, H 5.19; found: C 81.40, H 5.18.

2.1.1. *Thermal Reaction of* **4**. Tricycle **4** (0.190 g, 0.40 mmol) was dissolved in DMF (5 ml) and heated at 150° for 1 h. After this time, the starting material had been vanished, and workup of the residue by CC (silica gel; hexane/Et_2O 1:1) yielded **4** (0.020 g, 15%) and **5** (0.155 g, 81.5%).

In control experiments, **4** was heated for 1 h in 1,2,4-trimethylbenzene at 150° as well as at 180°. No change of **4** could be observed.

2.1.2. *Purely Thermal Reaction of* **3** *with ADM*. Benz[*a*]azulene **3** (0.020 g, 0.06 mmol) and ADM (0.025 ml, 0.2 mmol) were dissolved in DMF (1 ml) and heated at 100° for 2 h. No reaction at all could be observed. When the temp. was raised to 150°, a slow reaction occurred. Workup (*vide supra*) after 18 h yielded 24.5% of starting azulene **3** (0.005 g) and 28% of **5** (0.008 g).

2.1.3. *Optical Resolution of* (PM,MP)-**5**. Racemic **5** was completely separated in anal. amounts on the *Chiracel OD* column with hexane/i-PrOH (93:7; flow rate 0.8 ml/min) into its antipodes which showed t_R 12.4 ((*MP*)-isomer) and 18.9 min ((*PM*)-isomer).

CD (hexane/i-PrOH 93:7; $c = 2.714 \cdot 10^{-5}$ mol/l; *cf. Fig. 2*) *of* (MP)-**5**: 240 (0), 254 (7,0, pos. max.), 276 (0), 294 (−34.4, neg. max.), 319 (0), 363 (14.8, pos. max.), 490 (0).

CD (hexane/i-PrOH 93:7; $c = 2.714 \cdot 10^{-5}$ mol/l; *cf. Fig. 2*) *of* (PM)-**5**: 240 (0), 254 (−7.6, neg. max.), 276 (0), 293 (34.5, pos. max.), 319 (0), 367 (−14.9, neg. max.), 490 (0).

Control Experiment. The (*MP*)-isomer, when heated in a sealed ampoule in hexane/i-PrOH (93:7) at 150° for 1 h, showed no racemization at all according to its completely unchanged CD.

2.2. *Benz[a]azulene* (**6**) *and ADM*. Azulene **6** (0.110 g, 0.618 mmol), ADM (0.2 ml, 1.6 mmol), and [$RuH_2(PPh_3)_4$] (0.015 g, 2 mol-%) were dissolved in MeCN (5 ml) and heated at 60° for 2 h. All starting material had been consumed after this time. CC (silica gel; hexane/Et_2O 3:2) of the residue yielded mostly non-moving brownish material at the start of the column and a fraction (*ca.* 0.03 g, 15%) which mainly contained *dimethyl 9,10-benzotricyclo[6.2.2.0^{1,7}]dodeca-2,4,6,9,11-pentaene-11,12-dicarboxylate* (7) and small amounts of *dimethyl benzo[a]cyclopent[cd]azulene-1,2-dicarboxylate* (**8**). The tricycle **7** decomposed on the column as well as in solution to form **8** as the sole identifiable product. Therefore, both products could only be characterized by their ^{1}H-NMR.

^{1}H-NMR (300 MHz, C_6D_6; C_6D_5H at 7.157) *of* **7**: 7.20–7.10 (2 *dd*, partly covered by the signal of C_6D_5H, H–C(3′,6′)); 6.88–6.74 (2 *td*, H–C(4′,5′)); 6.285 (*d*, $^3J(3,2) = 12.07$, H–C(2)); 5.807 (*dd*, $^3J(2,3) = 12.19$, $^3J(4,3) = 7.69$, H–C(3)); 5.454 (*dd*, $^3J(5,4) = 11.79$, $^3J(3,4) = 7.71$, H–C(4)); 5.250 (*dd*, $^3J(4,5) = 11.86$, $^3J(6,5) = 7.43$, H–C(5)); 4.787 (*d*, $^3J(5,6) = 7.40$, H–C(6)); 4.498 (*s*, H–C(8)); 3.390, 3.210 (2*s*, 2 MeOCO).

^{1}H-NMR (300 MHz, $CDCl_3$; $CHCl_3$ at 7.260) *of* **8**: 9.391 (*d*, $^3J(3,4) = 9.50$, H–C(3)); 8.397 (*d*, $^3J(6,5) = 9.16$, H–C(6)); 8.319 (*t*, $\Sigma\,^3J(5,6) + {}^3J(4,5) = 19.59$, $^3J(4,5) = 10.43$, H–C(5)); 8.068 (*td*-like, $^3J(4,5) = 10.42$, $^3J(3,4) = 9.58$, $^4J(4,6) = 0.85$, H–C(4)); 7.992 (*dt*-like, $^3J(9,10) = 7.48$, $^4J(8,10) \approx 2 \cdot {}^5J(7,10)$, $^4J + {}^5J = 1.7$, H–C(10)); 7.645 (*dt*-like, $^3J(7,8) = 7.52$, $^4J(7,9) \approx 2 \cdot {}^5J(7,10)$, $^4J(7,9) \approx 0.8$, H–C(7)); 7.456 (*td*, $^3J(9,10) = 7.51$, $^3J(8,9) = 7.57$, $^4J(7,9) = 1.11$, H–C(9)); 7.26 (*td*?, partly covered by the signal of $CHCl_3$, H–C(8)); 4.112, 3.975 (2*s*, 2 MeOCO).

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