189. The Photochemical Synthesis and Denitrogenation of 8,9-Diazadibenzo[*c*,*e*]isobullvalene

by **Ulrich Burger***, **Yves G. Mentha**, **Patricia Millasson**, **Pierre-André Lottaz**, and **Jiri Mareda**

Department of Organic Chemistry, University of Geneva, CH-1211 Geneva 4

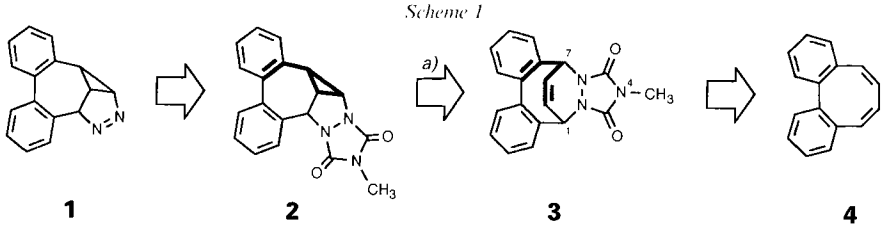
(13.IX.89)

Starting from dibenzo[*a*,*c*]cyclooctene (**4**) and 4-methyl-3*H*-1,2,4-triazol-3,5(4*H*)-dione (MTAD), the strained skeleton of the title azo compound **1** is assembled in a tandem photo-*Diels-Alder* addition/di-π-methane rearrangement sequence. The synthesis is completed by a stepwise hydrolytic oxidation of the ensuing triazolidinedione **2** with nickel peroxide. Thermolysis of **1** in benzene solution is shown to be governed by an initial 1,3-dipolar cycloreversion which leads, *via* an intermediate diazo compound **11**, to cyclobuta[*l*]phenanthrene **8** and two further carbene-derived $C_{16}H_{12}$ products. Photolysis of **1** at 350 nm leads in modest yield (12%), *via* a diazenyl diradical, to an unstable bridged bicyclobutane **10** (dibenzooctavalene). MNDO calculations suggest the latter to have a rapidly inverting, twisted structure of C_2 symmetry.

Introduction. – Bridged azo compounds are well established and attractive precursors for highly strained hydrocarbons and related diradicals [1]. Persistent and transient species including housane [2], prismane [3], and the ground-state triplet 2,4-dimethylcyclobutane-1,3-diyl diradical [4] (to cite but a few) have been prepared *via* azoalkane methodology. Often, the azo compounds of interest issue from the thermal addition (and subsequent oxidative hydrolysis) of triazolediones or related azo dienophiles to suitable π- or σ-systems. Occasionally, the addition process is accompanied by a rearrangement and, thus, gives rise to a skeleton which is essentially different from that of the starting material [1] [5]. More recently, light-induced addition of triazolediones to aromatic compounds and subsequent photorearrangement has opened a new route to complex azo compounds, and quite interesting structures have been assembled by this method [6].

Concentrating on denitrogenation reactions of highly strained systems [7], we were interested in the synthesis of the title diazene **1** and, further, its potential denitrogenation products. In this communication, we wish to report how the target skeleton of **1** can be assembled in a tandem of light-induced reactions; the initial photo-*Diels-Alder* addition being followed immediately by a di-π-methane rearrangement [8]. This crucial transfor-

Scheme 1



a) Di-π-methane rearrangement.

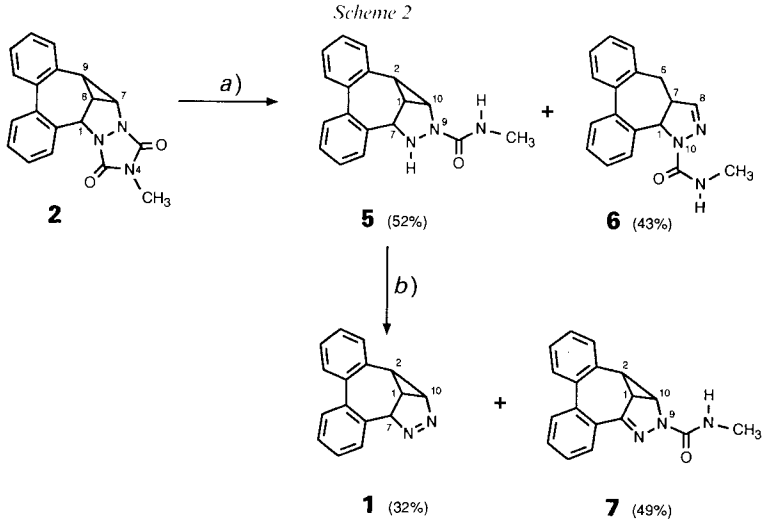
mation is emphasized by bold face in the retrosynthetic *Scheme 1*. After commenting on the rather complex oxidative hydrolysis of the ensuing triazolidinedione **2**, we will report on the thermal behaviour of **1** and, in preliminary terms, on its photolysis.

Results. – In aprotic solution and up to *ca.* 150°, dibenzo[*a*,*c*]cyclooctene (**4**) is astonishingly unreactive towards 4-methyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione (MTAD), a renowned and powerful dienophile [9]. This stands in marked contrast to the behaviour of the parent cyclooctatetraene [10] and is due to the rigid twisted conformation of **4**. According to recent studies, this compound exists at room temperature in separable enantiomeric forms protected by a racemization barrier ($\Delta G^{\neq}$) of 29.5 kcal/mol [11]. Clearly, the diene moiety of **4** cannot adopt properly the transition-state geometry of a thermal *Diels-Alder* reaction. However, when a mixture of **4** and MTAD is photolyzed at 350 nm in MeCN with benzophenone present as triplet sensitizer ($hc/E_T = 413$ nm), the desired cycloaddition occurs readily. Additionally, it gives access to the di-π-methane rearrangement, *i.e.* adduct **2** is obtained directly. From a preparative-scale experiment performed in a *Rayonet* reactor and run to *ca.* 90% completion, we obtain **2** in 36% yield, with a small amount of intermediate **3** (3.5%). Both adducts are isolated by column chromatography as colourless crystals and fully characterized by standard spectroscopic means. In a control experiment, we have established that **3** gives **2** under the above mentioned photochemical conditions.

In absence of the triplet sensitizer, **4** reacts at 350 nm in a sluggish fashion with MTAD giving small amounts of **3**, together with polymers. Moreover, the known electrocyclization of **4** [12] occurs as an undesired competing reaction.

In the triazolidinedione **2**, we have, in principle, assembled the skeleton of our target diazene **1**. However, the oxidative hydrolysis necessary to complete the synthesis turned out to be much more difficult to perform than we had anticipated. Standard methods, including $CuCl_2$ oxidation or, simply, hydrazinolysis, give an intractable mixture of products, together with starting material. We reverted, therefore, to a stepwise procedure

Scheme 2



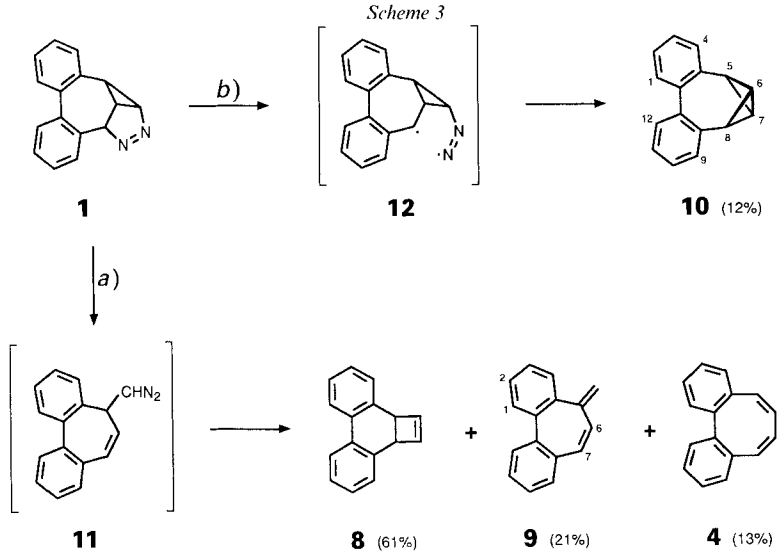
a) KOH, EtOH/$HOCH_2CH_2OH$/H_2O,100°, 2 h. *b*) $(NiO_2)_x$, CH_2Cl_2, –20°.

that had met with success in related work [4] [7] [13]. It entails first cleaving the triazolidinedione and then oxidizing the resulting semicarbazide with nickel peroxide [4]. Hydrolysis of **2** with KOH in H_2O/EtOH/ethylene glycol 1:2:1, indeed, gives the semicarbazide **5** in 52% yield. However, in competition, nearly half of the precious triazolidinedione undergoes opening of the three-membered ring to give the semicarbazone **6** in 43% yield. Both products of this hydrolysis are isolated by column chromatography as crystalline compounds.

The reaction of semicarbazide **5** with nickel peroxide in CH_2Cl_2 results, after prep. TLC, in the isolation of the crystalline azo compound **1**. Once again, in this concluding oxidation, a competing reaction producing the semicarbazone **7** (49%) accounts for the modest yield (32%) of the desired product **1**. Conditions to convert **7** into **1** have not yet been found.

Heating a sealed deoxygenated solution of **1** in C_6D_6 gives, cleanly, three isomeric hydrocarbons: cyclobuta[*l*]phenanthrene **8** (61%), the methylidene derivative **9** (21%), and dibenzo[*a,c*]cyclooctene (**4**; 13%). The kinetics of this relatively slow reaction follow a first-order rate law with k_1 (108°) = $2 \cdot 10^{-6}\,s^{-1}$. All products are isolated and identified by comparison with authentic material. A sample of the previously unknown methylidene compound **9** is synthesized independently by *Wittig* reaction of the corresponding ketone [14]. Photolysis of azo compound **1** in benzene or MeOH at 350 nm produces a fourth isomer of the $C_{16}H_{12}$ series to which we assign the structure of dibenzooctavalene **10** [15]. This sensitive hydrocarbon is obtained in *ca.* 12% yield (determined by NMR) and is accompanied by small amounts of **4** (*ca.* 1%) and **9** (*ca.* 1%). Unfortunately, the photolysis also gives much polymerisation. Filtration through basic alumina effectively frees the hydrocarbons from polymers. Use of light of shorter wavelength or of benzophenone as sensitizer does not improve the yield of **10**. Upon heating, **10** gives **4** with a half life of *ca.* 10 h in C_6D_6 at 108°.

Scheme 3



a) C_6D_6, 108°, $k_1 = 2 \times 10^{-6}\,s^{-1}$. *b*) C_6D_6, *hv* (350 nm).

So far, we have not found conditions that allow us to obtain analytically pure samples of **10**. Our structural assignment relies essentially upon a careful ^{1}H-NMR study of the crude compound in C_6D_6 solution.

The bicyclobutane moiety is readily recognised from an A_2M_2 spin pattern at 1.62 and 3.27 ppm, respectively, with a coupling constant $J_{AM} = 3.3$ Hz. Spin saturation of the low-field bicyclobutane resonance (H–C(5) and H–C(8)) results in a positive NOE for the two equivalent aromatic protons (H–C(4) and H–C(9)) at 7.07 ppm. *Vice versa*, a positive NOE is observed for H–C(5) and H–C(8) at 3.27 ppm upon spin saturation of H–C(4) and H–C(9). A further resonance appearing at low field (δ 7.76 ppm) and assigned to the equivalent protons H–C(1) and H–C(12) supports the overall structure of **10** as an *ortho*-disubstituted biphenyl.

We have performed MNDO semiempirical calculations [16] to optimize the geometry of **10**. It reaches its energy minimum at a twisted conformation belonging to point group C_2. A lateral view [17] of this computed ground state conformation of **10** is shown in the *Figure*. This structure, if rigid, would suggest an $AA'MM'$ spin pattern for the resonances of the bicyclobutane protons. However, when C_{2v}-symmetry is imposed on **10**, the computed heat of formation rises only by 2.9 kcal/mol. This low barrier of inversion of **10**, as determined by MNDO, finds corroboration in the A_2M_2 spin pattern observed in the NMR spectrum.

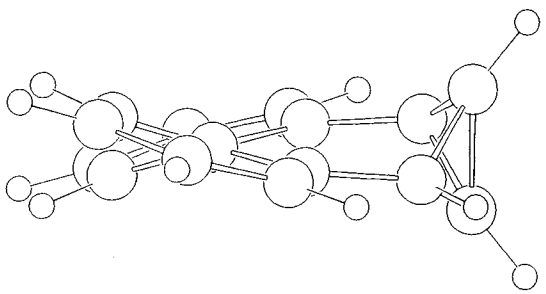
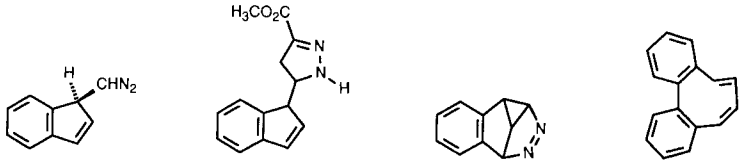


Figure. *Lateral view* [17] *of the computed ground-state structure of compound* **10** (MNDO [16])

Discussion. – The most prominent feature of diazene **1** is the presence of a strained 4,5-dihydro-3*H*-pyrazole subunit. This allows for thermal 1,3-dipolar cycloreversion [18] as an alternative to the direct loss of N_2 *via* a diradical pathway. Indeed, a cycloreversion of **1** with intermediate formation of a diazo compound **11** can account perfectly well for the three hydrocarbons **8**, **9**, and **4** formed by the thermal decay reaction. Although the diazo intermediate **11** was not directly observed in our experiments, its formation has ample precedent [6b] [7] [18] [19]. In particular, we have intercepted (indenyl)diazomethane **13** as adduct **14** to methylacrylate during the thermolysis of 1,2-diazabenzo[*e*]semibullvalene **15** [20]. The latter shares the 4,5-dihydro-3*H*-pyrazole subunit with **1**. Intermediate **13**, moreover, has also been detected by IR in the matrix isolation photolysis of **15** [6b].



13 **14** **15** **16**

The diazo compound **11** and the corresponding carbene can, in principle, exist in two discrete conformations with the side chain being pseudoaxial and pseudoequatorial, respectively. This is suggested by the relatively high activation barrier we observe by ^{1}H-NMR for the ring inversion of the parent 5*H*-dibenzo[*a,c*]cycloheptene ($\Delta G^{\neq} = 13.4$ kcal/mol). At least one of these conformations must lead by ring enlargement to the (*E,Z*)-dibenzocyclooctene **16** which, by subsequent electrocyclization, gives the main product of the thermolysis, *i.e.* the cyclobutene derivative **8**. Obviously, compounds **9** and **4** have their respective origins in conventional H- and C-shifts.

The highly-strained bicyclobutane **10**, striking in its unusually large bridging [15], clearly has its origin in a homolytic process, triggered by the $n \rightarrow \pi^*$ excitation of **1**. This electronic transition of diazene **1** has a very low extinction coefficient ($\varepsilon = 470$ cm^2/mol at 334 nm in MeOH) which, at least in part, accounts for the modest chemical yield of **10**. Theoretical work [21], *cf.* [19c], suggests a diazenyl diradical **12** to be an intermediate on the pathway **1** → **10**.

Our continuing efforts to overcome difficulties due to the high reactivity of **10** to further study its physical properties are encouraged by the obvious thermal stability of this unusual hydrocarbon.

The authors wish to express their gratitude to Mr. *J. P. Saulnier* and *P. Edder* (NMR), Mrs. *D. Clément* (MS), and *H.-J. Eder* (elemental analysis). Financial support was provided by the *Swiss National Science Foundation* (grant No. 2000-5.376).

Experimental Part

General. Photolyses: *Srinivasan-Griffin* reactor *(Rayonet-RPR-100)* with *RPR* lamps, 2537 Å; quartz vessels; *RPR* lamps, 3500 Å; *Pyrex* vessels. GC: *Perkin-Elmer-900;* glass columns. UV spectra (λ [nm] (log ε)): *Kontron-Uvikon-860.* IR spectra [cm^{-1}]: *Polaris-Mattson* FT-IR spectrometer. NMR spectra: *Bruker WM-360* (8.46 Tesla) or *Varian XL-200* (4.7 Tesla); chemical shifts in δ [ppm] relative to internal TMS; apparent scalar coupling constants J in Hz; multiplicities for ^{13}C under off-resonance decoupling or according to attached proton test (APT). Explicit ^{13}C assignment is based on heteronuclear shift correlation. MS: (*m/z* (% relative to base peak)): *Finnigan-4023* with INCOS data system; electron impact, 70 eV.

10,11,12,13-Dibenzo-4-methyl-2,4,6-triazatetracyclo[6.5.0.0^{2,6}.0^{7,9}]trideca-10,12-diene-3,5-dione (= *4b,4c,5,6,6a,6b-Hexahydro-*N^{im}*-methyldibenzo[4,5:6,7]cyclopropa[1′,3′:2,3;1′,2′-*d*]cyclohepta[1,2-*c*]pyrazole-5,6-dicarboximide;* **2**) *and 8,9,10,11-Dibenzo-4-methyl-2,4,6-triazatricyclo[5.4.2.0^{2,6}]trideca-8,10,12-triene-3,5-dione* (= *5,6,7,8-Tetrahydro-*N^{im}*-methyl-5,8-ethenodibenzo[*d,f*][1,2]diazocine-6,7-dicarboximide;* **3**). A deoxygenated soln. of 4 [22] (482 mg, 2.36 mmol), MTAD [9] (532 mg, 4.71 mmol), and benzophenone (360 mg, 1.98 mmol) in 22 ml of CH_3CN was irradiated at 350 nm for 5.25 h in a thin-walled *Pyrex* vessel with internal H_2O cooling. Removal of the solvent, followed by CC over silica gel (CH_2Cl_2/acetone 19:1) gave **2** (245 mg, 36%) with R_f 0.09, **3** (24 mg, 3.5%) with R_f 0.16, and recovered **4** 48 mg (10%).

Data for **2**: colourless crystals. M.p. 269–271°. IR ($CDCl_3$): 1760*s*, 1705*s*, 1461*s*, 1450*s*, 1395*m*, 1295*m*, 1267*m*. ^{1}H-NMR ($CDCl_3$, 200 MHz): 2.40 (*s*, CH_3); 2.62 (*dd*, J = 8.6, 5.9, H–C(9)); 2.93 (*ddd*, J = 8.6, 6.6, 4.9, H–C(8)); 3.85 (*dd*, J = 6.6, 5.9, H–C(7)); 5.26 (*d*, J = 4.9, H–C(1)); 7.24–7.54 (*m*, 8 arom. H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 24.85 (CH_3); 25.17 (C(9)); 32.83 (C(7)); 33.28 (C(8)); 60.93 (C(1)); 127.4 (CH); 128.0 (CH); 128.1 (CH); 128.9 (C); 129.3 (CH); 130.0 (CH); 131.4 (CH); 131.6 (CH); 132.0 (C); 133.7 (CH); 138.1 (C); 138.9 (C); 148.5 (CO); 155.5 (CO). MS: 318 (22), 317 (100), 260 (8), 218 (51), 217 (49), 216 (15), 204 (25), 203 (73), 202 (88). HR-MS: 317.1175 ($C_{19}H_{15}N_3O_2$, calc. 317.1164).

Data for **3**: colourless crystals. M.p. 244–246°. IR ($CDCl_3$): 1800*s*, 1766*s*, 1705*s*, 1470*s*, 1445*m*, 1400*m*, 1371*m*, 1291*m*, 1280*m*, 1250*m*. ^{1}H-NMR ($CDCl_3$, 200 MHz): 2.85 (*s*, CH_3); 5.63, 6.21 (*AA′BB′*, H–C(1)/H–C(7), H–C(12)/H–C(13)); 7.30–7.60 (*m*, 8 arom. H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 25.05 (CH_3); 59.06 (CH); 125.3 (CH); 128.3 (CH); 128.7 (CH); 129.0 (CH); 136.3 (CH); 136.7 (C); 137.2 (C); 150.3 (CO). MS: 318 (14), 317 (60), 260 (6), 231 (7), 218 (51), 217 (44), 204 (30), 203 (100), 202 (100). HR-MS: 317.1150 ($C_{19}H_{15}N_3O_2$, calc. 317.1164).

N-Methyl-8,9-diaza-3,4,5,6-dibenzotricyclo[5.3.0.0^{2,10}]deca-3,5-diene-9-carboxamide (= *4b,4c,5,6,6a,6b-Hexahydro-N^{an}-methyldibenzo[4,5:6,7]cyclopropa[1',3':2,3;1',2'-d]cyclohepta[1,2-c]pyrazole-6-carboxamide*; **5**) *and N-Methyl-9,10-diaza-2,3,4,5-dibenzobicyclo[5.3.0]deca-2,4,8-triene-10-carboxamide* (*4b,5,7a,8-Tetrahydro-N^{an}-methyldibenzo[4,5:6,7]cycloheptа[1,2-c]pyrazole-5-carboxamide*; **6**) *by Hydrolysis of* **2**. A soln. of KOH (430 mg, 7.6 mmol) and **2** (326 mg, 1.03 mmol) in 15 ml of H_2O/EtOH/ethylene glycol 1:2:1 was kept at 100° for 2 h with stirring. The cold mixture was extracted with 3 × 15 ml of Et_2O, washed with H_2O and sat. brine, and dried ($MgSO_4$). Removal of the solvent, followed by CC over silica gel (CH_2Cl_2/acetone 19:1) gave **5** (156 mg, 52%) with R_f 0.11 and **6** (129 mg, 43%) with R_f 0.24.

Data for **5**: colourless crystals. M.p. 202–203°. IR ($CDCl_3$): 3422*m*, 3332*w*, 1665*s*, 1525*s*, 1488*m*, 1454*m*, 1442*m*, 1419*m*, 1334*m*, 1309*m*, 1256*m*, 1154*w*. ^{1}H-NMR ($CDCl_3$, 200 MHz): 2.33 (*m*, H–C(2)); 2.46 (*ddd*, *J* = 8.3, 5.8, 4.0, H–C(1)); 2.74 (*d*, *J* = 5, CH_3); 3.70 (*d*, *J* = 10.5, H–N(8)); 4.36 (*dd*, *J* = 7.5, 5.8, H–C(10)); 4.50 (*ddd*, *J* = 10.5, 4.0, 1.6, H–C(7)); 6.26 (br. *q*, *J* = 5.0, MeN*H*); 7.2–7.7 (*m*, 8 arom. H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 22.17 (CH, CH_3); 26.58 (CH, CH_3); 30.11 (CH, CH_3); 39.03 (CH); 65.09 (CH); 127.4 (CH); 127.8 (CH); 127.9 (CH); 129.2 (CH); 129.4 (CH); 131.1 (CH); 131.6 (CH); 132.5 (CH); 134.9 (C); 136.3 (C); 137.4 (C); 137.8 (C); 162.2 (CO). MS: 292 (6), 291 (23), 235 (18), 234 (100), 233 (56), 219 (47), 218 (53), 217 (67), 216 (18), 208 (29), 207 (55), 205 (39), 191 (35), 189 (22), 182 (32), 165 (27). HR-MS: 291.1381 ($C_{18}H_{17}N_3O$, calc. 291.1372).

Data for **6**: colourless crystals. M.p. 175–177°. IR ($CDCl_3$): 3455*m*, 1670*s*, 1605*m*, 1535*s*, 1487*m*, 1453*m*, 1444*m*, 1420*m*, 1370*m*, 1337*m*, 1299*m*, 1259*m*, 1222*w*, 1198*m*, 1180*m*. ^{1}H-NMR ($CDCl_3$, 200 MHz; 2 rotamers in a 5:4 ratio): 2.57, 2.90 (2*d* each *J* = 5 CH_3N; spin-saturation transfer [23] at 100° upon irradiation of either CH_3N resonance); 2.4–2.9 (*m*, CH_2(6)); 3.9, 4.0 (2*m*, H–C(7)); 5.08, 5.22 (2*d*, *J* = 11.5, 10.8, H–C(1)); 5.40, 5.95 (2 br. *m*, NH); 6.69, 6.70 (2 narrow *m*, H–C(8)); 7.0–7.6 (*m*, all arom. H). MS: 291 (6), 234 (10), 219 (44), 217 (11), 178 (16), 165 (20), 58 (100).

8,9-Diaza-3,4,5,6-dibenzotricyclo[5.3.0.0^{2,10}]deca-3,5,8-triene (= *8,9-Diazadibenzo[c,e]isobullvalene* = *4b,4c,6a,6b-Tetrahydrodibenzo[4,5:6,7]cyclopropa[1',3':2,3;1',2'-d]cyclohepta[1,2-c]pyrazole*; **1**), *and N-Methyl-8,9-diaza-3,4,5,6-dibenzotricyclo[5.3.0.0^{2,10}]deca-3,5,7-triene-9-carboxamide* (= *4c,6,6a,6b-Tetrahydro-N^{an}-methyldibenzo[4,5:6,7]cyclopropa[1',3':2,3;1',2'-d]cyclohepta[1,2-c]pyrazole-6-carboxamide*; **7**) *by Oxidation of* **5**. Freshly prepared nickel peroxide (380 mg, $1.8 \cdot 10^{-3}$ mol 'O') was added with stirring to a cold (–20°) soln. of **5** (109 mg, 0.37 mmol) in 25 ml of CH_2Cl_2. After 15 h, a second portion of nickel peroxide (240 mg, $1.14 \cdot 10^{-3}$ mol 'O') was added and stirring was continued for 3 h. The soln. was filtered over *Celite* and the solvent removed. Prep. TLC (silica gel, CH_2Cl_2/acetone 19:1) gave **1** (27.8 mg, 32%) with R_f 0.48, and **7** (52.4 mg, 49%) with R_f 0.16.

Data for **1**: colourless crystals. M.p. 154° (dec.). UV (MeOH): 214 (33800), 258 (15200), 334 (470). IR ($CDCl_3$): 3070*m*, 2963*m*, 1509*m*, 1498*m*, 1446*m*, 1438*m*, 1317*m*, 1261*s*, 1095*s*, 1017*s*. ^{1}H-NMR ($CDCl_3$, 200 MHz): 2.42 (*ddd*, *J* = 8.0, 7.0, 4.1, H–C(1)); 2.83 (*t*, *J* = 8.0, H–C(2)); 5.15 (*ddd*, *J* = 8.0, 4.1, 1.2, H–C(10)); 5.50 (*dd*, *J* = 7.0, 1.2, H–C(7)); 7.15–7.55 (*m*, 8 arom. H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 23.98 (C(1)); 26.42 (C(2)); 67.11 (C(10)); 92.36 (C(7)); 127.2 (CH); 127.6 (CH); 127.7 (CH); 129.1 (CH); 130.7 (CH); 131.0 (C); 131.2 (CH); 131.4 (CH); 131.9 (CH); 133.8 (C); 138.1 (C); 139.4 (C). MS: 232 (1), 231 (1), 204 (46), 203 (100), 202 (67), 178 (49), 176 (12), 101 (35), 100 (10), 89 (22), 88 (19), 76 (31), 75 (21). HR-MS: 232.0983 ($C_{16}H_{12}N_2$, calc. 232.1000).

Data for **7**: colourless crystals. M.p. 160–161°. IR ($CDCl_3$): 3450*m*, 1672*s*, 1535*s*, 1478*m*, 1448*m*, 1420*m*, 1392*m*, 1332*m*, 1298*m*, 820*m*, 790*m*. ^{1}H-NMR ($CDCl_3$, 200 MHz): 2.32 (*dd*, *J* = 8.8, 6.5, H–C(1)); 2.76 (*d*, *J* = 5.0, CH_3); 3.27 (*dd*, *J* = 8.8, 5.5, H–C(2)); 4.65 (*dd*, *J* = 6.5, 5.5, H–C(10)); 5.60 (br. *q*, *J* = 5.0, NH); 7.2–7.8 (*m*, 8 arom. H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 16.11 (CH); 26.52 (CH, CH_3); 33.91 (CH, CH_3); 40.05 (CH, CH_3); 123.3 (CH); 127.3 (CH); 127.6 (CH); 128.0 (CH); 128.7 (CH); 129.9 (CH); 132.5 (C); 132.7 (CH); 133.1 (C); 133.3 (CH); 139.4 (C); 139.6 (C); 155.3 (C); 155.6 (C).

Thermolysis of **1**. A soln. of **1** (7.6 mg, 0.03 mmol) in C_6D_6 (0.8 ml) was filtered over Na_2CO_3, deoxygenated (Ar), sealed in a *Pyrex* NMR tube, and heated in a vertical *Büchi* furnace at 108° for 2.5 d. The formation of **8** [12], **9**, and **4**, in a time-independent ratio of 64:22:14, was followed by periodic ^{1}H-NMR monitoring. The material balance at completion of the thermolysis was 95% by NMR integration.

5-Methylidene-5H-dibenzo[a,c]cycloheptene (**9**). An anal. sample of **9** was obtained analogously to [14b] from the corresponding dibenzotropone [14a] and purified by prep. TLC on silica gel (CH_2Cl_2/acetone 19:1).

Data for **9**: yellow oil. ^{1}H-NMR (C_6D_6, 200 MHz): 4.95 (*m*, 1 H, CH_2=C(5)); 5.16 (*m*, 1 H, CH_2=C(5)); 6.32 (*d*, *J* = 11.5, H–C(7)); 6.50 (*dt*, *J* = 11.5, 1.4, H–C(6)); 6.95–7.60 (*m*, 8 arom. H). ^{13}C-NMR (C_6D_6, 50 MHz): 117.12 (CH_2); 9 or 10 CH at 127.49, 127.52, 128.37, 128.90, 130.14, 130.68, 130.87, 131.10, 135.21; 5 C at 136.46, 137.95, 139.76, 144.47, 146.76. MS: 204 (100), 178 (10), 165 (11), 152 (8), 102 (18), 101 (58), 89 (20), 88 (25), 76 (23).

Photolysis of **1**. For preliminary experiments and tentative assignment of **10**, see text.

REFERENCES

[1] Reviews: a) W. Adam, O. De Lucchi, *Angew. Chem.* **1980,** *92,* 815; *ibid. Int. Ed.* **1980,** *19,* 762; b) P. S. Engel, *Chem. Rev.* **1980,** *80,* 99.

[2] R. Criegee, A. Rimmelin, *Chem. Ber.* **1957,** *90,* 414.

[3] T. J. Katz, N. Acton, *J. Am. Chem. Soc.* **1973,** *95,* 2738.

[4] G. J. Snyder, D. A. Dougherty, *J. Am. Chem. Soc.* **1989,** *111,* 3927.

[5] F. Jensen, C. S. Foote, *J. Am. Chem. Soc.* **1987,** *109,* 6376.

[6] a) S. J. Hamrock, R. S. Sheridan, *Tetrahedron Lett.* **1988,** *29,* 5509; b) D. P. Kjell, R. S. Sheridan, *J. Am. Chem. Soc.* **1986,** *108,* 4111; c) D. P. Kjell, R. S. Sheridan, *J. Photochem.* **1985,** *28,* 205.

[7] U. Burger, Y. Mentha, P. J. Thorel, *Helv. Chim. Acta* **1986,** *69,* 670.

[8] Review: H. E. Zimmerman, in 'Rearrangements in Ground and Excited States', Ed. P. de Mayo, Academic Press, New York, 1980, Vol. 3. p. 131.

[9] a) M. E. Burrage, R. C. Cookson, S. S. Gupte, I. D. R. Stevens, *J. Chem. Soc., Perkin Trans. 2* **1975,** 1325; b) R. C. Cookson, S. S. Gupte, I. D. R. Stevens, C. T. Watts, *Org. Synth.* **1971,** *51,* 121.

[10] a) J. P. Snyder, H. Isaksen, *Tetrahedron Lett.* **1977,** 889; b) R. Huisgen, W. E. Konz, U. Schnegg, *Angew. Chem.* **1972,** *84,* 765; *ibid. Int. Ed.* **1972,** *11,* 715; c) A. B. Evnin, R. D. Miller, G. R. Evanega, *Tetrahedron Lett.* **1968,** 5863.

[11] a) P. Rashidi-Ranjbar, J. Sandström, *Tetrahedron Lett.* **1987,** *28,* 1537; b) N. Z. Huang, T. C. W. Mak, *J. Mol. Struct.* **1983,** *101,* 135.

[12] E. Vogel, *Tetrahedron Lett.* **1963,** 673.

[13] R. Jösel, G. Schröder, *Liebigs Ann. Chem.* **1980,** 1428.

[14] a) J. W. Cook, G. T. Dickson, J. D. Loudon, *J. Chem. Soc.* **1947,** 746; b) G. Wittig, U. Schöllkopf, *Org. Synth.* **1960,** *40,* 66.

[15] For the parent octavalene see: a) M. Christl, R. Lang, C. Herzog, *Tetrahedron* **1986,** *42,* 1585; b) R. Gleiter, P. Bischof, M. Christl, *J. Org. Chem.* **1986,** *51,* 2895; c) M. Christl, R. Lang, *J. Am. Chem. Soc.* **1982,** *104,* 4494.

[16] a) J. J. P. Stewart, QCPE 455; b) M. J. S. Dewar, W. Thiel, *J. Am. Chem. Soc.* **1977,** *99,* 4899.

[17] 'XTAL Program Version 2.6', Eds. S. R. Hall and J. M. Stewart, Universities of Western Australia and Maryland.

[18] For review on 1,3-dipolar cycloreversions, see *e.g.* G. Bianchi, R. Candolfi, in '1,3-Dipolar Cycloaddition Chemistry', Ed. A. Padwa, John Wiley, New York, 1984, Vol. 2, p. 451.

[19] a) A. Padwa, T. Kumagai, M. Tohidi, *J. Org. Chem.* **1983,** *48,* 1834; b) W. Adam, W. D. Gillaspey, E. M. Peters, K. Peters, R. Rosenthal, H. G. v. Schnering, *ibid.* **1985,** *50,* 580; c) W. Adam, M. Dörr, K. Hill, E. M. Peters, Karl Peters, H. G. v. Schnering, *ibid.* **1985,** *50,* 587; d) W. Adam, O. De Lucchi, M. Dörr, *J. Am. Chem. Soc.* **1989,** *111,* 5209.

[20] U. Burger, P. J. Thorel, Y. Mentha, *Chimia* **1987,** *41,* 26.

[21] B. Bigot, A. Sevin, A. Davaquet, *J. Am. Chem. Soc.* **1978,** *100,* 2639.

[22] H. N. C. Wong, F. Sondheimer, *J. Org. Chem.* **1980,** *45,* 2438.

[23] M. L. Martin, J. J. Delpuech, G. J. Martin, 'Pratical NMR Spectroscopy', Heyden, London, 1980, p. 315.