A Novel Hydrocarbon, 8,10-Dimethylidenetricyclo[7.1.1.$0^{2,7}$]undeca-2,4,6-triene: Synthesis of Benzopinane Skeleton *via* Di-π-methane Rearrangement of Benzonorbornadiene System

by **Aliye Altundaş**[a]), **Nihat Akbulut**[a])*, and **Metin Balcı**[b])*

[a]) Department of Chemistry, Atatürk University, 25240 Erzurum, Turkey

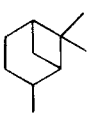
[b]) Department of Chemistry, Middle East Technical University, 06531 Ankara, Turkey

Dedicated to Professor *Özer Bekaroğlu* on the occasion of his 65th birthday

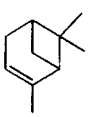
The [4+2] cycloadduct **17** of 2,3-dimethylidene-1,2,3,4-tetrahydro-1,4-methanonaphthalene and 4-phenyl-4*H*-1,2,4-triazole-3,5-dione (PTAD) was subjected to a triplet-sensitized di-π-methane rearrangement. Hydrolysis of the resulting urazol **18** gave the hydrocarbon **7**. Hydrolysis of **18** at lower base concentrations led to isomeric stable semicarbazides **24** and **25**, which were submitted NiO_2 or MnO_2 oxidation, to give the target compound **7**, and oxidation products **26** and **27**.

Introduction. – Monoterpenes possessing the pinane skeleton **1** occur in the wood and leaf oil of many higher plants and can be readily converted into numerous non-natural bicyclo[3.1.1]heptane derivatives [1]. α-Pinene (**2**) and β-pinene (**3**) are the parents of most synthetic pinane derivatives, the former being the most widely distributed natural monoterpene, and both occur as major components of turpentine oil [2][3]. The bicyclo[3.1.1]heptane nucleus is shared in common by the pinene monoterpenes, the bergamotene sesquiterpenes, and highly oxygenated relatives such as paeoniflorin [4].

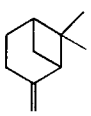
The total synthesis of α-pinene has been carried out starting from ethyl pinonate **4** [5]. *Thomas* and *Fallis* [6] reported a direct total synthesis of racemic α-pinene and



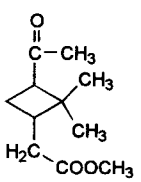
1 pinane



2 α-pinene



3 β-pinene



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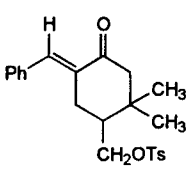

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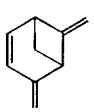

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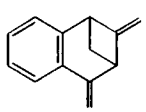
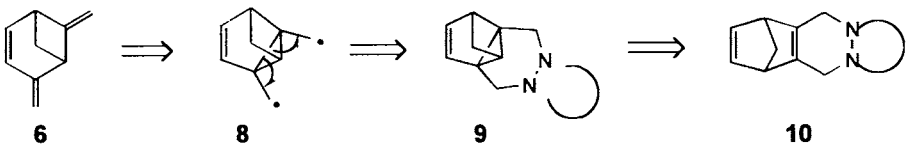


7

β-pinene in which a key step was the intramolecular alkylation of a cyclohexanone derivative **5** to give the required bicyclo[3.1.1]heptane ring system.

Several possible synthetic routes to this interesting natural-product skeleton may be envisaged. These include rearrangement of a related bicyclic systems [7], ring contraction of a suitable diazo ketone [8], or photocyclization of a suitable diene or triene [9]. We wished to develop a general route to the bicyclo[3.1.1]heptane ring which could be used for pinane-skeleton synthesis in the first instance. Especially, we were interested in the synthesis of the compond **6** and its benzo analogue **7**.

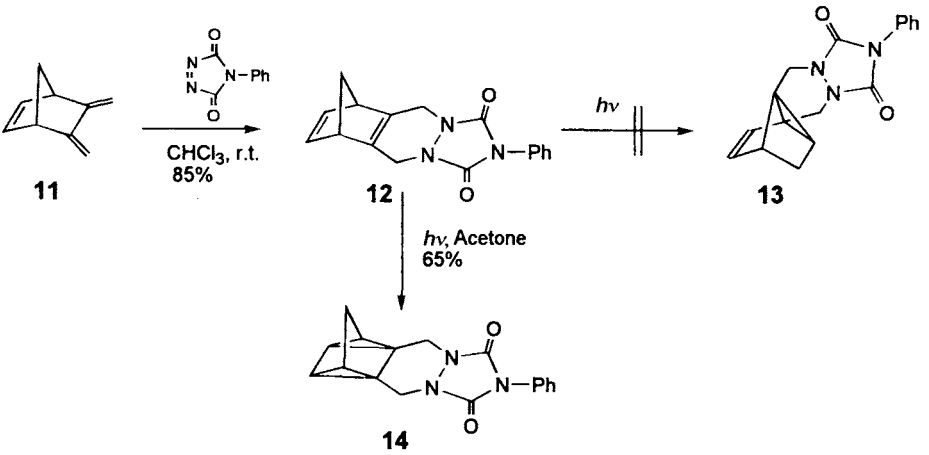
Scheme 1



Results and Discussion. – Our approach to the synthesis of **6** is shown in *Scheme 1*. The connection of the tertiary C-atoms of the exocyclic methylidene groups in **6** leads to the cyclopropyldicarbinyl diradical **8**. It has been shown that this diradical can be efficiently generated by the hydrolysis and oxidation of the corresponding urazols **9** [10]. The urazol **9** could be synthesized starting from the norbornadiene derivative **10** *via* the di-π-methane rearrangement [11].

For this purpose, the structurally simpler 2,3-dimethylidenebicyclo[2.2.1]hept-5-ene (**11**) [12] was studied first. When **11** was allowed to react with 4-phenyl-4*H*-1,2,4-triazoline-3,5-dione (PTAD) at ambient temperature in $CHCl_3$, the [2 + 4] cycloadduct **12** was obtained in 85% yield (*Scheme 2*).

Scheme 2

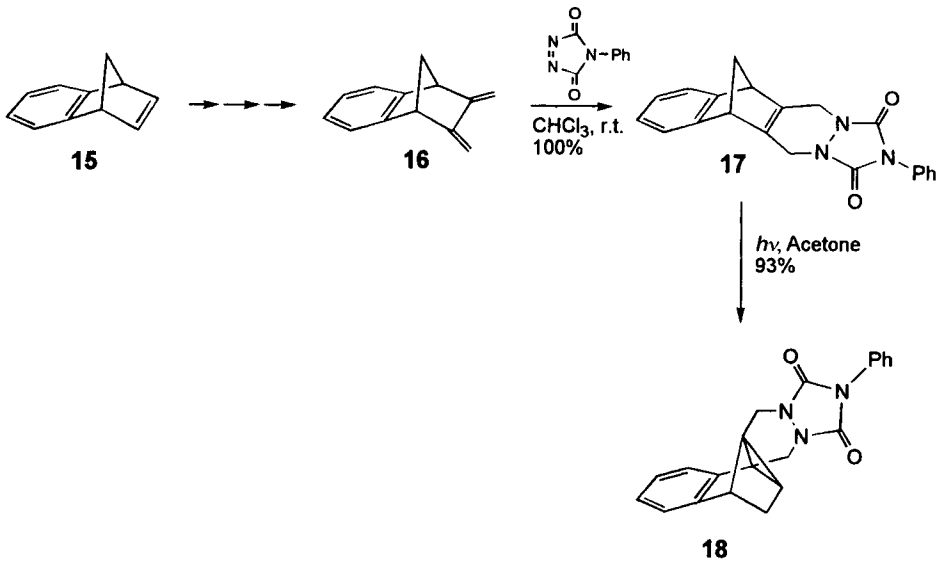


Although we were aware of the fact that di-π-methane rearrangement in norbornadiene is suppressed in favor of the intramolecular [2 + 2] cycloaddition [13], we have studied the photolysis of **12**. This norbornadiene derivative **12** gave quadricyclene **14** on either

direct or sensitized irradiation in solution. After this unsuccessful attempt, we have turned our attention to the synthesis of the corresponding benzo derivative **7**.

2,3-Dimethylidene-1,2,3,4-tetrahydro-1,4-methanonaphthalene (**16**) was prepared as reported recently in the literature [14]. Pd-Catalyzed methoxycarbonylation of benzonorbornadiene **15** gave the corresponding dicarboxylate which was transformed, in three steps, to **16** (*Scheme 3*). Treatment of **16** with PTAD at ambient temperature in $CHCl_3$ gave, in quantitative yield, the urazole **17**, which was characterized by means of NMR spectra. The structure elucidation was straightforward in view of its C_s symmetry. Photochemical reaction of **17** conducted in acetone at room temperature[1]) led to a single product. Isomerization was very rapid, high-yield conversion to the pentacyclo[5.4.$0^{2,4}$.$0^{3,6}$] system **18** being complete within 2h.

Scheme 3



The aliphatic region of the 200-MHz ^{1}H-NMR spectrum of the photo product **18** in $CDCl_3$ displays eight distinct regions which uniquely characterize each relevant H-atom (*Fig.*). That the triazole moiety must be positioned at C(2) and C(8) follows unequivocally from the extensive double-resonance experiments. Both CH_2N protons give rise to two distinct *AB* systems with the coupling constants 12.8 and 11.9 Hz, respectively. The H_{endo}–C(17) atom, which is heavily shielded because of its proximity to the arene π cloud, appears at 0.88 ppm as *d* (9.4 Hz) due to its large spin interaction with H_{exo}–C(17). H_{exo}–C(17) resonates at 2.85 ppm as *ddd*. Bridgehead atom H–C(10) gives rise to a *dd* (J = 7.4 and 2.5 Hz) due to the coupling with H_{exo}–C(18) and cyclopropane H–C(17) as a result of their *W*-arrangement. The ^{13}C-NMR spectrum also confirms the proposed structure.

The thermal and photochemical extrusion of N_2 from appropriate azo alkanes has served as a particularly convenient and effective method for the generation of authentic diradicals which have been postulated in photo-rearrangements [15].

[1]) The apparatus consisted of a 254-nm Hg arc lamp surrounded by a water-cooled quarz immersion vessel.

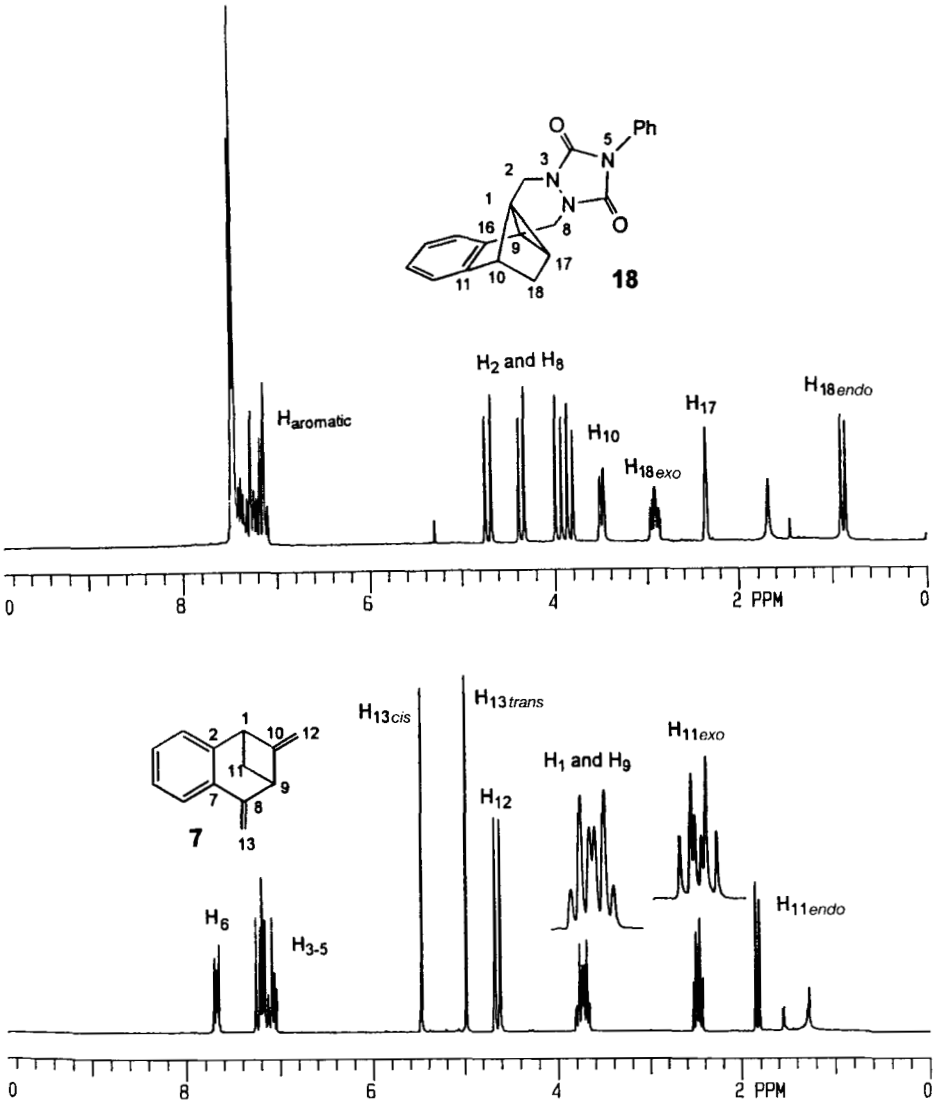
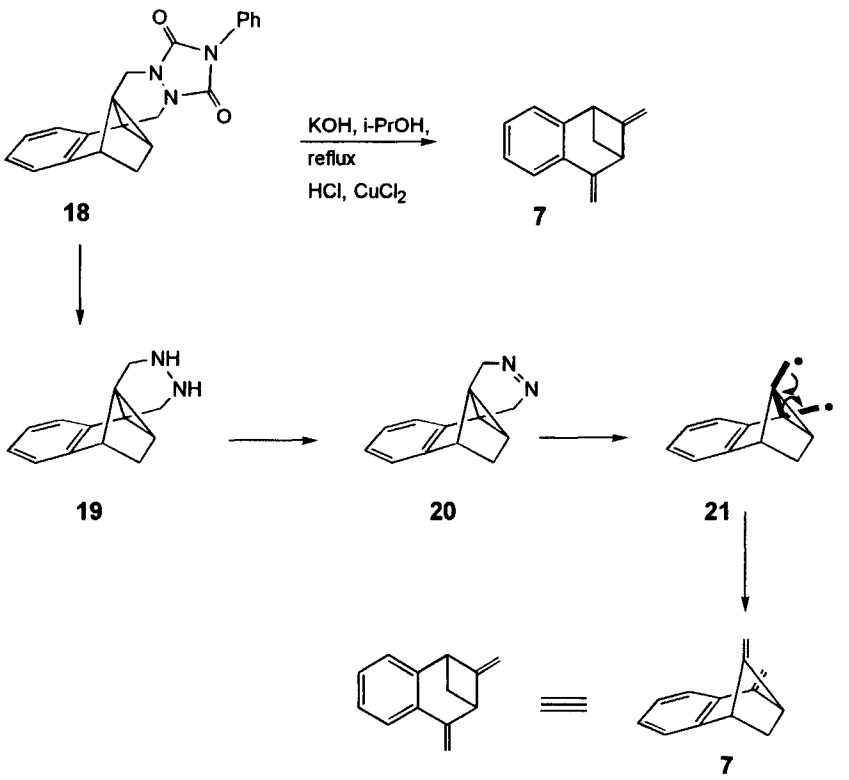


Figure. *200-MHz ^{1}H-NMR Spectra of urazol* **18** *and hydrocarbon* **7**

Hydrolysis of **18** and subsequent loss of N_2 were successfully realized by initial saponifacation with 20% KOH in i-PrOH (100°, 15 h), acidification to pH 3 with 0.1N HCl (0°, 5 min), and oxidation with $CuCl_2$. After chromatography, we isolated the hydrocarbon **7** as the sole product in 26% yield (*Scheme 4*). The structure of **7** has been elucidated on the basis of its ^{1}H- (200 MHz) and ^{13}C-NMR, and by NOE measurements.

The ^{1}H-NMR spectrum (*Fig.*) of **7** contains four *s* at 5.40, 4.99, 4.67, and 4.61 ppm attributed to the exocyclic olefinic H-atoms. NOE Experiments have revealed that *s* resonating at lower fields (5.40 and 4.99) belong to H_{cis}–C(13) and H_{trans}–C(13) because of the proximity to the benzene ring. The atoms H–C(1) and H–C(9)

Scheme 4

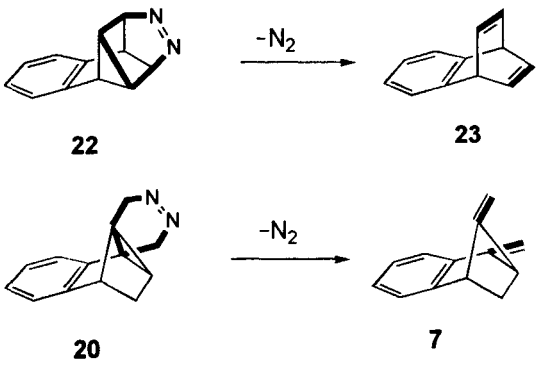


appear at 3.69 and 3.77 ppm as an *AB* system. This assignment was established unambiguously from the HETCOR spectrum. Both parts of the *AB* systems show further coupling with one of the $CH_2(11)$ atoms (J = 5.7 Hz). There is no further measurable coupling between H_{endo}–C(11), and H–C(1) and C(9) due to nearly 90° dihedral angles between H_{endo}–C(11), and H–C(1) and H–C(9). The large long-range coupling (^4J = 5.9 Hz) between H–C(1) and H–C(9) has the expected value [16] and indicates clearly the presence of a strained cyclobutyl ring. Furthermore, 13-line ^{13}C-NMR and DEPT spectra are completely in agreement with the proposed structure.

From a mechanistic viewpoint, the formation of the hydrocarbon **7** is the result of hydrolysis of the urazol ring in **18** followed by dehydrogenation to give the labile diazo compound **20**, which, in turn, can easily undergo denitrogenation reaction under the given reaction conditions. The resulting diradical easily leads to the final product **7** by undergoing a *Grob*-type fragmentation reaction.

Zimmerman et al. [15] have studied the thermal and photochemical behavior of the compound **22**. The azo compound **22** was found to lose easily N_2 at 50–80°. The reaction proceeded essentially quantitatively to afford barrelene **23** (*Scheme 5*). In the case of **20**, the reaction follows a similar mechanism and gives the fragmentation product **7**. The fact that this reaction proceeds at lower temperature can be attributed to the highly strained C-skeleton of **20** which can release some part of the strain energy upon dinitrogenation.

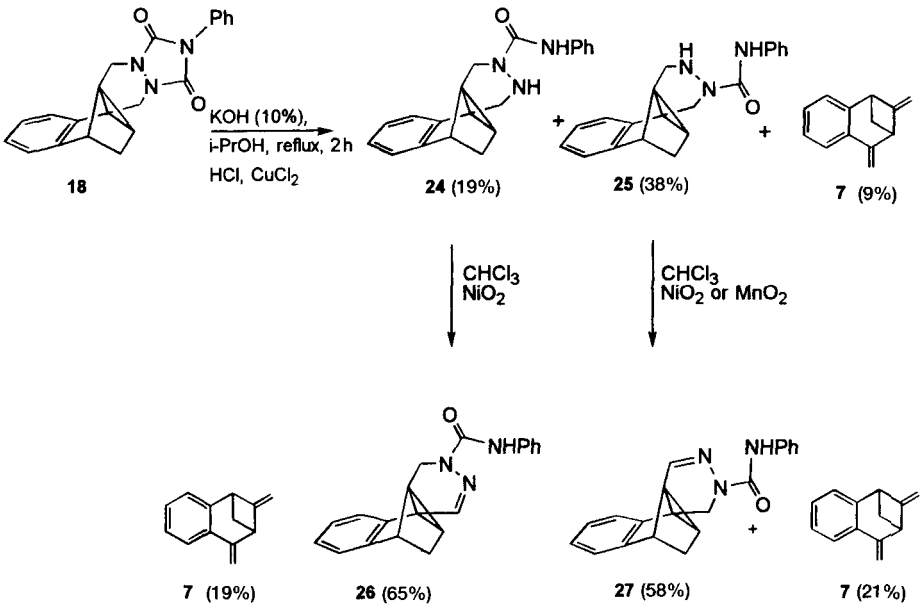
Scheme 5



However, when the hydrolysis of **18** was run at lower base concentrations (*ca.* 10%), we isolated mainly the partial-hydrolysis [17] products **24** and **25** beside the hydrocarbon **7** (*Scheme 6*). The hydrolysis products were separated by column chromatography. We were not able to distinguish between the isomers **24** and **25** even by NOE experiments. Oxidation of **24** and **25** either with MnO_2 or NiO_2 resulted in the formation of hydrocarbon **7** (19 and 21%, resp.) and the corresponding dehydrogenation products **26** and **27** in a yield of 65 and 58%, respectively. We assume that some part of the partial-hydrolysis products **24** and **25** undergoes oxidative fragmentation, followed by N_2 extrusion, to give the hydrocarbon **7**.

The methodology described in this paper opens up a new entry to the synthesis of hitherto unknown benzo-annelated pinane skeleton. Further work in this field is in progress.

Scheme 6



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Experimental Part

General. M.p.: determined on a *Thomas Hoover* cap. melting-point apparatus. Infrared IR Spectra: from KBr pellets, on a *Perkin-Elmer 377* spectrophotometer. ^{1}H-NMR Spectra: on a 200-MHz *Varian* spectrometer; δ in ppm, $SiMe_4$ as internal standard. Column chromatography (CC): on silica gel (60 mesh) and Al_2O_3 (*Merck*).

6-Phenyl-4,6,8-triazatetracyclo[9.2.1.0^{2,10},0^{4,8}]tetradeca-2(10),12-diene-5,7-dione (**12**). To a magnetically stirred soln. of 260 mg (2.2 mmol) of **11** in 20 ml of $CHCl_3$, 4-phenyl-4*H*-1,2,4-triazole-3,5-dione (500 mg, 2.85 mmol) was added in small portions at r.t. The mixture was stirred for 30 min at r.t. After evaporation of solvent, the residue was purified by CC (Al_2O_3, $CHCl_3$): **12** (550 mg, 85%). Colorless crystals from CH_2Cl_2/hexane. M.p. 160–162°. IR (KBr): 3115*m*, 2970*m*, 2860*w*, 1770*s*, 1716*m*, 1693*m*, 1594*m*, 1497*s*, 1422*m*, 1356*m*, 1288*m*, 1239*m*, 1136*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.54–7.31 (*m* 5 arom. H); 6.86 (*t*, H–C(12), H–C(13)); 4.51 (br. *d*, ^2J = 13.5, 1 H–C(3), 1 H–C(9)); 4.09 (br. *d*, ^2J = 13.5, 1 H–C(3), 1 H–C(9)); 3.56 (br. *s*, H–C(1), H–C(11)); 2.17 (*d*, *A* part of *AB* system, ^2J = 6.5, H_{endo}–C(14) or H_{exo}–C(14)); 2.13 (*d*, *B* part of *AB* system, ^2J = 6.5, H_{endo}–C(14) or H_{exo}–C(14)). ^{13}C-NMR (50 MHz, $CDCl_3$): 154.02 (C(5), C(7)); 144.56, 144.30, 133.35, 131.09, 130.00, 127.39 (arom. and olef. C); 74.31 (C(3), C(9)); 52.95 (C(1), C(11)); 47.03 (C(14)).

Photolysis of **12**: *6-Phenyl-4,6,8-triazahexacyclo[9.2.1.0^{2,10},0^{4,8},0^{2,13},0^{10,12}]tetradecane-5,7-dione* (**14**). A soln. of 550 mg (1.88 mmol) of **12** in 150 ml of acetone was placed into quartz phototube. The magnetically stirred soln. was flushed with N_2 and irradiated at 254 nm for 2.5 h. After evaporation of acetone, the residue was purified by CC (Al_2O_3 $CHCl_3$): **14** (356 mg, 65%). Colorless crystals from CH_2Cl_2/hexane. M.p. 185–186°. IR (KBr): 3010*m*, 2855*m*, 1765*s*, 1699*m*, 1582*m*, 1488*s*, 1425*s*, 1317*m*, 1270*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.58–7.37 (*m*, 5 arom. H); 4.06 (*d*, *A* part of *AB* system, ^2J = 12.8, 1 H–C(3), 1 H–C(9)); 3.89 (*d*, *B* part of *AB* system ^2J = 12.8, 1 H–C(3), 1 H–C(9)); 2.06–1.83 (*AB* system, ^2J = 11.4, H_{endo}–C(14), H_{exo}–C(14)); 1.83–1.73 (*AB* system, ^3J = 4.4, H–C(1), H–C(11), H–(12), H–C(13)). ^{13}C-NMR (50 MHz, $CDCl_3$): 154.26 (C(5), C(7)); 133.54, 131.09, 129.99, 127.47, (arom. C); 45.65; 34.71; 29.84; 25.62; 21.47.

6-Phenyl-4,6,8-triazapentacyclo[9.6.1.0^{2,10}.0^{4,8}.0^{12,17}]octadeca-2(10),12(17),13,15-tetraene-5,7-dione (**17**). To a magnetically stirred soln. of 1 g (5.95 mmol) of **16** in 20 ml of $CHCl_3$, 4-phenyl-4*H*-1,2,4-triazole-3,5-dione (1.1 g, 6.3 mmol) was added in small portions at r.t. The mixture was stirred for 30 min at r.t. $CHCl_3$ was removed at reduced pressure. The residue was purified by CC (Al_2O_3 $CHCl_3$): **17** (quant. yield, 2.04 g). Crystallization from CH_2Cl_2/hexane afforded colorless crystals. M. p. 195–197°. IR (KBr): 3080*w*, 3000*m*, 2980*m*, 2910*m*, 2880*m*, 1795*s*, 1600*m*, 1500*s*, 1450*m*, 1410*m*, 1350*m*, 1290*m*, 1240*m*, 1150*m*, 1140*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.49–7.33 (*m*, 5 arom. H), 7.32–6.98 (*AA'BB'* system, 4 arom. H), 4.54 (*d*, *A* part of *AB* system, ^2J = 13.6, 1 H–C(3), 1 H–C(9)); 4.08 (*d*, *B* part of *AB* system, ^2J = 13.6, 1 H–C(3), 1 H–C(9)); 3.89 (*t*, ^3J = 1.5, H–C(1), 1 H–C(11)); 2.49 (*dt*, *A* part of *AB* system, ^2J = 7.4, ^3J = 1.5, 1 H–C(18)); 2.39 (*dt*, *B* part of *AB* system, ^2J = 7.4, ^3J = 1.5, 1 H–(18)). ^{13}C-NMR (50 MHz, $CDCl_3$): 152.51 (C(5), C(7)); 150.37, 142.73, 131.67, 129.61, 128.56, 125.90, 125.52, 122.09 (arom. and olef. CH); 62.72 (C(3), C(9)); 51.61 (C(1), C(11)); 44.55 (C(18)). Anal. calc. for $C_{21}H_{17}O_2N_3$: C 73.45, H 4.99; found: C 73.01, H 5.12.

5-Phenyl-3,5,7-triazahexacyclo[8.6.2.0^{1,9}.0^{3,7}.0^{9,17}0^{11,16}]octadeca-11(16),12,14-triene-4,6-dione (**18**). A soln. of 2 g (5.83 mmol) of **17** in 150 ml of acetone was placed into quartz phototube. The magnetically stirred soln. was flushed with N_2 and irradiated at 254 nm for 2 h. Evaporation of acetone gave **18**. Colorless crystals (1.85 g, 93%) from Et_2O/CH_2Cl_2. M.p. 152–153°. IR (KBr): 3040*m*, 3000*m*, 2940*m*, 2900*m*, 2880*m*, 1765*s*, 1700*s*, 1600, 1490, 1460, 1440, 1400, 1350. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.48–7.09 (*m*, 9 arom. H); 4.70 (*d*, *A* part of *AB* system, ^2J = 12.8, 1 H–C(2) or 1 H–C(8)); 4.45 (*d*, *A* part of *AB* system, ^2J = 11.9, 1 H–C(2) or 1 H–C(8)); 3.95 (*d*, *B* part of *AB* system, ^2J = 12.8, 1 H–C(2) or 1 H–C(8)); 3.83 (*d*, *B* part of *AB* system, ^2J = 11.9, 1 H–C(2) or 1 H–C(8)); 3.50 (*dd*, ^3J = 7.5, ^4J = 2.4, 1 H–C(10)); 2.85 (*dt*, ^2J = 9.4, ^3J = 2.4 Hz, 1 H_{exo}–C(18)); 2.35 (*t*, ^2J = ^4J = 2.4, H–C(17)); 0.88 (*d*, ^2J = 9.4, 1 H_{endo}–C(18)). ^{13}C-NMR (50 MHz, $CDCl_3$) 153.72, 153.45 (C(4), C(6)); 145.36, 140.86, 131.62, 129.62, 128.62, 127.10, 126.54, 125.86, 123.04, 121.21 (arom. C); 54.06; 45.67; 45.38; 41.82; 35.15; 30.69; 29.87. Anal. calc. for $C_{21}H_{17}O_2N_3$: C 73.45, H 4.99; found: C 73.76, H 4.89.

8,10-Dimethylidenetricyclo[7.1.1.0^{2,7}]undeca-2,4,6-triene (**7**). A soln. of **18** (2 g, 5.8 mmol) and KOH (5.7 g, 100 mmol) in 28 ml of i-PrOH was refluxed for 15 h. Then, the mixture was cooled to −20° and added to 20 ml of H_2O. After the mixture was acidified with 0.1N HCl to pH 3, the sat. soln. of 7.3 g of $CuCl_2$ in pure H_2O was added to the mixture and extracted with $CHCl_3$. The org. phase was washed with H_2O, dried ($MgSO_4$), and

evaporated. The oily residue was chromatographed (Al_2O_3, $CHCl_3$/hexane 1:2) to give **7** (254 mg, 26%). IR (film): 3060*m*, 2980*m*, 2910*m*, 1680*w*, 1480*w*, 1440*w*, 1260*w*, 1090*m*, 1060*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.71 (*m*, H–C(6)); 7.26–7.05 (*m*, 3 arom. H); 5.48 (*s*, H–C(13)); 4.99 (*s*, H–C(13)), 4.67 (*s*, 1 H–C(12_a) or 1 H–C(12_b)), 4.62 (*s*, 1 H_a–C(12), or 1 H_b–C(12)); 3.77 (*dd*, *A* part of *AB* system, ^4J = 5.9, ^3J = 5.7, H–C(1)); 3.69 (*dd*, *B* part of *AB* system, ^4J = 5.9, ^3J = 5.7, H–C(9)); 2.48 (*dt*, *A* part of *AB* system, ^3J = 8.0, ^3J = 5.7, H_{exo}–C(11)); 1.83 (*d*, *J* = 8.0, *B* part of *AB* system, H_{endo}–C(11)). ^{13}C-NMR (50 MHz, $CDCl_3$): 154.58, 148.38, 145.87, 131.14, 128.46, 127.03, 125.58, 123.77 (arom. C); 103.81 (C(13)); 96.87 (C(12); 55.15 (C(1)); 51.24 (C(9)); 36.97 (C(11)); 36.97 (C(11)). Anal. calc. for $C_{13}H_{12}$: C 90.11, H 8.89; found: C 89.74, H 9.02.

Hydrolysis of **18** *at Lower Base Concentration.* A soln. of **18** (2 g, 5.8 mmol) and KOH (2.8 g, 50 mmol) in 28 ml of i-ProH was refluxed for 5 h, and the reaction mixture was worked up as described above. The oily residue was chromatographed (Al_2O_3, $CHCl_3$/hexane 1:2). The first fraction gave **7** (90 mg, 9%). Second fraction was a mixture consisting of partial-hydrolysis products **24** and **25**. The isomer mixture was rechromatographed (Al_2O_3 column, $CHCl_3$/hexane 2:3). The first fraction was **24** or **25**.

N-*Phenyl-11,12-diazapentacyclo[6.5.2.0^{1,9}.0^{2,7}.0^{9,14}]pentadeca-2(7),3,5-triene-12-carboxamide* (**24**; 350 mg, 19%). Colorless crystals from CH_2Cl_2/hexane. M.p. 165–166°. IR (KBr): 3220*s*, 3210*s*, 3090*m*, 2920*m*, 1660*s*, 1610*s*, 1590*s*, 1500*s*, 1430*m*, 1350*m*, 1310*m*, 1240*s*, 1120*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 8.49 (br. *s*, NHPh); 7.49–6.67 (*m*, 9 arom. H); 4.73–4.63 (br. *s*, NH); 4.02 (*d*, *A* part of *AB* system, ^2J = 14.4, 1 H–C(10)); 3.40 (*dd*, *A* part of *AB* system, ^3J = 7.4, ^4J = 2.5, H–C(8)); 3.25 (*m*, 1 H–C(10), 2 H–C(13)); 2.80 (*ddd*, ^2J = 9.2, ^3J = 7.4, ^3J = 3.2, H_{exo}–C(15)); 2.12 (*m*, H–C(14)); 0.77 (*d*, ^2J = 9.2, H_{endo}–C(15)). ^{13}C-NMR (50 MHz, $CDCl_3$), 155.51 (CO); 149.42, 142.25, 129.42, 129.38, 126.67, 126.07, 123.01, 122.88, 121.26, 119.01 (arom. C); 53.97; 48.08; 45.91; 38.72; 34.88; 29.56. Anal. calc. for $C_{20}H_{19}N_2O$: C 79.18, H 6.31; found: C 79.56, H 6.09.

As the second fraction we isolated the isomer N-*phenyl-11,12-diazapentacyclo[6.5.2.0^{1,9}.0^{2,7}.0^{8,14}]pentadeca-2(7),3,5-triene-11-carboxamide* (**25**; 700 mg, 38%). Colorless crystals from CH_2Cl_2/hexane. M.p. 175–176°. IR (KBr): 3310*s*, 3200*s*, 3020*m*, 2820*m*, 1650*s*, 1590*s*, 1500*s*, 1460*s*, 1430*m*, 1330*m*, 1310*m*, 1260*s*, 1210*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 8.40 (br. *s*, NHPh); 6.94–7.51 (*m*, 9 arom. H); 4.95 (br. *s*, NH); 3.33–3.10 (*m*, H–C(8), 2 H–C(10), 2 H–C(13)); 2.77 (*m*, H_{exo}–C(15)); 2.16 (*m*, H–C(14)); 0.82 (*d*, ^2J = 9.2, H_{endo}–C(15)). ^{13}C-NMR (50 MHz, $CDCl_3$): 155.22 (CO); 148.69, 142.71, 139.42, 129.29, 126.86, 125.90, 123.46, 123.26, 122.95, 120.81, 119.68, 119.13 (arom. C); 53.81; 46.10; 44.19; 42.87; 35.41; 30.54; 29.78. Anal. calc. for $C_{20}H_{19}N_2O$: C 79.18, H 6.31; found: C 79.03, H 6.34.

N-*Phenyl-11,12-diazapentacyclo[6.5.2.0^{1,9}.0^{2,7}.0^{9,14}]pentadeca-2(7),3,5,10-tetraene-12-carboxamide* (**26**). Compound **24** (300 mg, 0.96 mmol) was dissolved in 20 ml of CH_2Cl_2. NiO_2 [18] (550 mg, 6.09 mmol) was added in portions during 15 min. The mixture was stirred for 12 h at r.t. The mixture filtered through a short column (silica gel) eluting with $CHCl_3$/hexane 2:3. The first fraction gave **7** (30 mg, 19%). Second fraction yielded **26** (195 mg, 65%). Colorless crystals from Et_2O/hexane. M.p. 169–170°. IR (KBr): 3320*s*, 3040*m*, 2960*m*, 1660*s*, 1580*s*, 1520*s*, 1430*s*, 1360*m*, 1330*m*, 1300*m*, 1220*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 8.50 (br. *s*, NHPh); 7.00–7.68 (*m*, 9 arom. H, 1 olef. H); 4.79 (*d*, ^2J = 12, 1 H–C(10)); 3.59 (*dd*, ^3J = 7.3, ^4J = 2.7, H–C(8)); 3.33 (*d*, ^2J = 12, 1 H–C(10)); 2.92 (*ddd*, ^2J = 9.8, ^3J = 7.3, ^3J = 2.7, H_{exo}–C(15)); 2.57 (*t*, ^3J = ^4J = 2.6, H–C(14)); 0.85 (*d*, ^2J = 9.8, H_{endo}–C(15)). ^{13}C-NMR (50 MHz, $CDCl_3$): 154.10 (CO); 147.69, 140.18, 138.95, 138.79, 129.38, 126.94, 126.52, 123.48, 121.72, 119.64 (arom. and olef. C); 59.81; 45.73; 37.46; 36.16; 34.77; 30.02. Anal. calc. for $C_{20}H_{17}N_2O$: C 79.71, H 5.68; found: C 79.53, H 5.54.

N-*Phenyl-11,12-diazapentacyclo[6.5.2.0^{1,9}.0^{2,7}.0^{9,14}]pentadeca-2(7),3,5,12-tetraene-11-carboxamide* (**27**). Isomer **27** was synthesized from **25** as described above and recrystallized from Et_2O/hexane: 168 mg (56%). M.p. 104–105°. IR (KBr): 3350*s*, 3030*m*, 2970*m*, 2930*m*, 2850*m*, 1684*s*, 1620*s*, 1580*s*, 1500*s*, 1440*s*, 1370*m*, 1240*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 8.50 (br. *s*, NHPh); 7.00–7.60 (*m*, 9 arom. H, 1 olef. H); 5.02 (*d*, ^2J = 12, 1 H–C(13)); 3.72 (*dd*, ^3J = 7.5, ^4J = 2.3, H–C(8)); 3.67 (*d*, ^2J = 12, 1 H–C(13)); 3.23 (*dd*, ^3J = 3.7, ^4J = 2.3, H–C(14)); 2.86 (*ddd*, ^2J = 10.2, ^3J = 7.5, ^3J = 3.7, H_{endo}–C(15)); 0.97 (*d*, ^2J = 10.2, H_{exo}–C(15)). ^{13}C-NMR (50 MHz, $CDCl_3$): 156.25 (CO); 150.18, 145.47, 142.15, 140.48, 136.09, 130.80, 128.54, 128.25, 124.00, 124.93, 122.08, 121.09 (arom. and olef. C); 54.53; 49.34; 46.61; 42.64; 38.90; 32.27. Anal. calc. for $C_{20}H_{17}N_2O$: C 79.71, H 5.68; found: C 79.43, H 5.48.

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