

Robert Temme and Rolf Huisgen*

Institut für Organische Chemie der Universität München, Karlstr. 23, D-80333 München, Germany

Received April 1, 1998

Dedicated to the memory of Paul D. Bartlett (1907-1997),
one of the founders of physical organic chemistry

In contrast to common alkenes and enol ethers, the angle-strained double bonds of norbornene, dimethyl norbornadiene-2,3-dicarboxylate, and acenaphthylene undergo [3+2] cycloadditions with isoquinolinium *N*-arylimides. The structures of the crystalline adducts have been elucidated from their ¹H nmr spectra.

J. Heterocyclic Chem., **35**, 643 (1998).

Introduction.

On plotting the electron densities of dipolarophilic C=C bonds versus the rate constants of cycloaddition, nucleophilic-electrophilic 1,3-dipoles show a pronounced minimum for common alkenes [2a]. Sustmann [3] discovered the high explanatory power of perturbation MO theory for these rate phenomena which had hitherto proved puzzling [4].

Isoquinolinium *N*-arylimides **1** add rapidly to the electron-deficient C=C bonds of acrylic esters [5] as well as to electron-rich enamines [6]. However, no reaction of **1** with ethylene, 1-hexene, cyclopentene, 3,4-dihydro-2H-pyran, or 1-ethoxycyclohexene was observed.

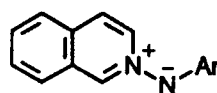
Diels-Alder reactions of cyclopentadiene with dienophiles furnish derivatives of bicyclo[2.2.1]hept-2-ene (norbornene). Alder and Stein used the addition of phenyl azide as a diagnostic tool for this type of double bond [7]. The relative rate constants for the cycloadditions of phenyl azide (carbon tetrachloride, 25°) to norbornene, cyclopentene, and cyclohexene are found to be in the ratio 5700:56:1 [8]. Other 1,3-dipoles of the propargyl-allenyl type [2b], such as diazomethane, diphenylnitrilimine, benzonitrile oxide, *etc.*, also show such high reactivity towards the strained double bond of norbornene [9].

Heats of hydrogenation reflect the difference in ring strain of cycloalkenes and cycloalkanes. The hydrogenation enthalpy of norbornene exceeds that of cyclohexene by 6 kcal mol⁻¹ [10,11]. Strain release in the dipolarophile also increases the heat of cycloaddition. However, it is an oversimplification to ascribe the *high reaction rate* of the bicyclo[2.2.1]heptene double bond to this thermodynamic quantity. In fact, strain release and log *k*₂ of cycloadditions to highly strained cycloalkenes are not strictly proportional; other phenomena contribute to the kinetics as well [12].

Results and Discussion.

Isoquinolinium *N*-phenylimide (**1**) is not isolable and has a modest lifetime in solution. However, the mobile equilibrium of the carbon disulfide adduct **2** with **1a** + CS₂

offers a convenient neutral source of this 1,3-dipole [13]. More stable is the *N*-(2-pyridyl) compound **1b**, which is found in equilibrium with the dimer **3**.

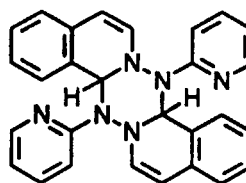


1a Ar = C₆H₅

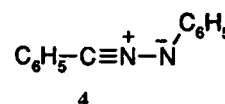
1b Ar = C₅H₄N-(2)



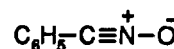
2



3



4



5

In contrast to the inertness seen with cyclohexene and cyclopentene, **1a** and **1b** were found to combine with norbornene upon treatment with an excess of the dipolarophile in dichloromethane at room temperature. The additions were neither fast nor clean. The red colors of **1a** and **1b** faded over a period of 1-2 days, and subsequent chromatography furnished the colorless crystals of the 1:1 adducts in 38% and 48% yield, respectively. The presence of diastereoisomers in the mother liquor cannot be excluded, although the ¹H nmr spectra of the isolated adducts leave no doubt that **6a** and **6b** correspond in stereochemistry.

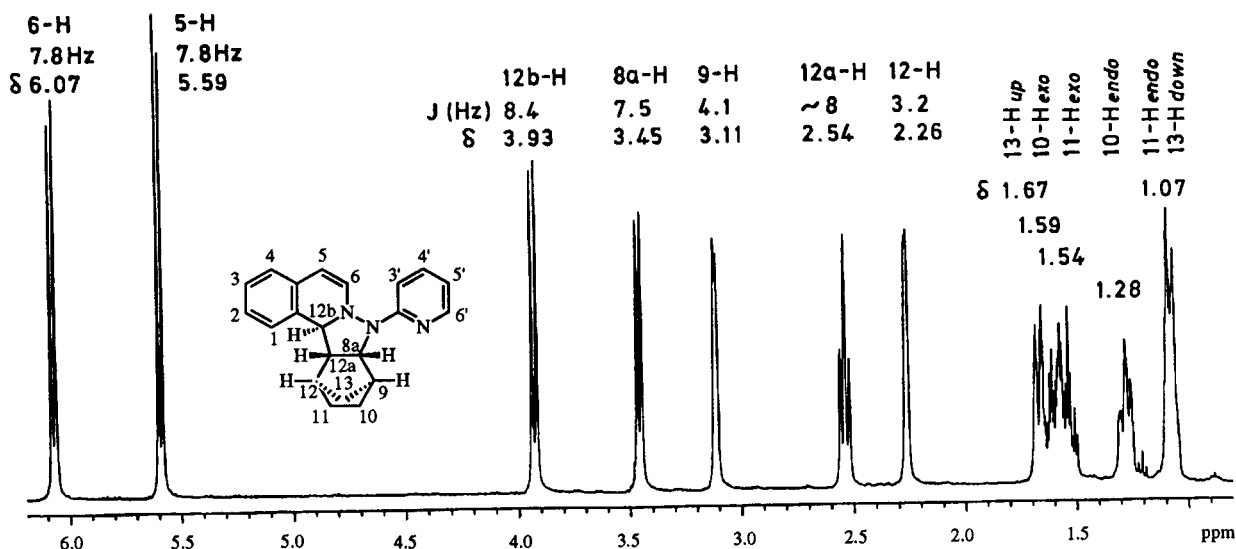
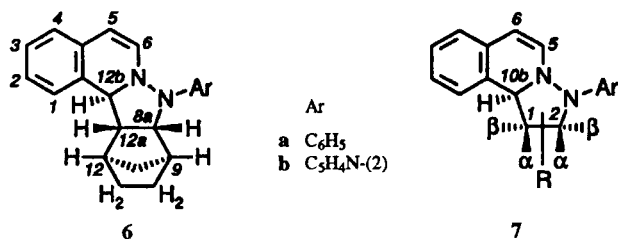


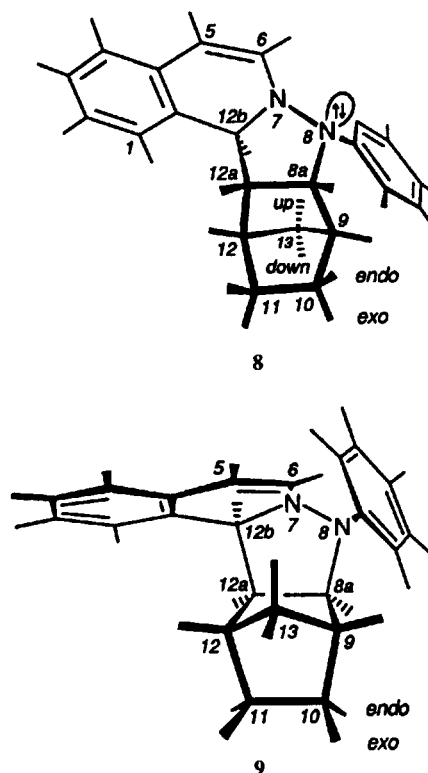
Figure 1. ^1H nmr spectrum (400 MHz) of cycloadduct **6b** in deuteriochloroform (Section).

Comparison with the ^1H nmr spectra of the norbornene adducts of diphenylnitrilimine (**4**) [9,14] and benzonitrile *N*-oxide (**5**) [9] establishes the *exo* addition of **1a** and **1b** to norbornene. It is well-known that the bridgehead protons of bicyclo[2.2.1]heptenes couple only with the vicinal *exo*-protons; the coupling with the *endo*-H is suppressed by dihedral angles of $80\text{--}85^\circ$.



As illustrated in Figure 1 for **6b**, the bridgehead protons, 9-H and 12-H, appear as doublets with $J_{9,exo-10} = 4.1$ Hz and $J_{12,exo-11} = 3.2$ Hz; a data collection quotes a range of 3–4 Hz for such couplings [15]. The *endo*-8a-H (δ 3.45) couples only with 12a-H ($J = 7.5$ Hz), and the pseudo triplet of 12a-H resonates at δ 2.54. The doublet of 12b-H is observed at higher frequency (δ 3.93) because it is deshielded by N-7 and the benzo ring. The AX pattern of the vinylic 5-H and 6-H is characteristic for 1,2-dihydroisoquinolines of type **7**; the shift of δ 6.07 for 5-H reflects the electron release by N-7. The ^1H nmr data of **6a** were assigned analogously.

The *exo* addition of **1** to norbornene is no surprise. However, there are two different steric pathways of combining the *exo*-norbornene unit with **1**. The 12a-H and



12b-H are *trans*-*vic* oriented in the *exo,exo*-adduct **8** and *cis*-*vic* arranged in the *endo,exo*-adduct **9**. Their differentiation by ^1H nmr arguments requires molecular models; the illustrations **8** and **9** are based on photographs of Dreiding models. The stereochemistry at N-7 and N-8 simulates the structures of two related cycloadducts established by X-ray analyses [16]. The nitrogen bonds are pyramidalized, and the torsion angle between their lone-pair orbitals is close to 90° , the optimal value for

hydrazines [17]. The *n*-orbital at N-8 bisects the plane of the *N*-aryl at an angle of $\sim 80^\circ$, close to the orthogonality favored by the aniline-type resonance.

The cycloadducts are chiral. The configuration, arbitrarily chosen in the formulae, has 12b-H (10b-H of **7**) on the β -side. Circumstantial evidence favors the ring annellation shown by *exo,exo*-structure **8** for the cycloadducts **6a** and **6b**.

The bridgehead protons of norbornane resonate at δ 2.19. In the cycloadducts **6**, 9-H and 12-H are in different environments; one of them appears at δ 2.18 in **6a** and 2.26 in **6b**, in accordance with the parent norbornane. The second bridgehead-H, however, is shifted to δ 2.54 in the *N*-phenyl compound **6a** and to δ 3.11 in the *N*-(2-pyridyl) derivative **6b**. The *exo,exo* model **8** reveals that 9-H is deshielded by the *N*8-aryl moiety; due to the pyridine nitrogen, the effect is stronger in **6b** than in **6a**. In the *endo,exo* structure **9** the 9-H cannot be influenced by the *N*-aryl substituent.

The coupling constant $J_{12a,12b}$ is 8.4 Hz for **6a** and 8.5 Hz for **6b**; unfortunately, they fall in the overlap region of J_{trans} and J_{cis} values observed for more than 30 compounds of type **7** [5].

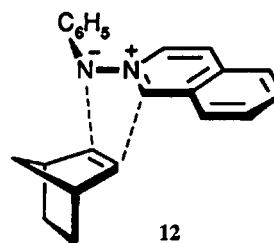
A possible argument in favor of structure **9** is as follows: $\delta(8a-H)$ 2.98 of **6a** is shifted to higher frequencies in **6b** (3.45 ppm). An even larger $\Delta\delta$ (0.6-1.3 ppm) between *N*-(2-pyridyl) and *N*-phenyl cycloadducts was observed for compounds **7**, but was strictly confined to the 2β -H as a consequence of an intramolecular hydrogen bond with the 2-pyridyl nitrogen [5,6,16]. Only in the *endo,exo* structure **9** is the 8a-H located on the β -side.

However, structure **8** was finally established with the aid of DQF-COSY [18] and NOESY [19] experiments which provided definitive assignments of all protons of **6b**, including the aromatic H. The observed NOE effects indicate the proximity of 8a-H/9-H and 12-H/12a-H without coupling being involved. The deshielded bridgehead proton is 9-H; the *exo,exo* structure **8** shows the short distance between 9-H and the edge of the *N*-phenyl or *N*-(2-pyridyl) moiety. The NOESY experiment also reveals the proximity of 12-H (bridgehead) to 12b-H (2.5 Å) and 1-H (2.7 Å); the distances were estimated using the Dreiding model. A small NOE effect links even 8a-H with the vinylic 6-H (3.2 Å) in **6a**, which is in accordance with model **8**, but is inconceivable in **9**.

Further evidence for the *exo,exo* structure **8** comes from the cycloadduct of **1a** to dimethyl norbornadiene-2,3-dicarboxylate (**10**). The reaction was complete after 30 minutes at room temperature and furnished 61% of the crystalline **11**. In the 1H nmr spectrum, the singlet attributable to 12b-H indicates that C-12a is quaternary; $\delta(12b-H)$ 4.86 reveals a shift to higher frequency, compared with **6a** (δ 3.86), as a result of the anisotropy of the *trans-vic*-CO₂CH₃ group. Thus, it can be concluded that addition of the 1,3-dipole occurred at the ester-bearing double bond of **10**.

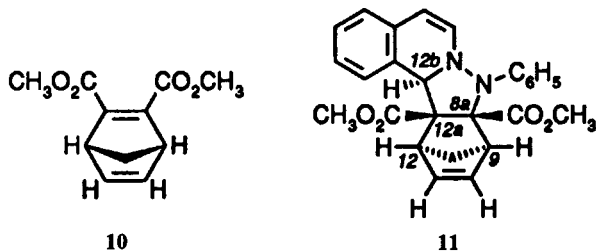
Our previous nmr study involved numerous derivatives of **7** bearing methyl ester groups at all four positions of C-1 and C-2 [5]. It is only the 1α -CO₂CH₃ that is located within the shielding cone of the benzo ring and thus shows low $\delta(OCH_3)$ values. This reliable criterion can also be applied to **11**: One ester methyl resonates normally at δ 3.70; the second at δ 3.00 exhibits the *low-frequency shift* and establishes the α -position (front side) of the 12a-CO₂CH₃ group. A diester derived from **9** should display two "normal" OCH₃ shifts.

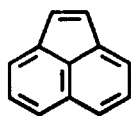
Of course, **11** is not amenable to the test for *exo* addition to **10** because it no longer contains H-atoms in positions 8a and 12a. Nevertheless, although minor contributions from *endo* attacks of 1,3-dipoles to norbornadiene and derivatives have been observed [20], the validity of structure **11** can safely be assumed. The bridgehead protons, 9-H and 12-H, are in allylic positions and appear at δ 3.64 and 3.20, respectively.



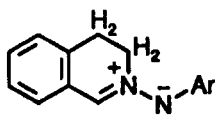
The cycloaddition pathways leading to the *exo,exo* adducts **6** and **11** start with the π overlap in the orientation complex **12**. This approach is the sterically less demanding of the two possibilities.

The mass spectrum of **6b** features the molecular peak (57%). The main fragmentation of M^+ is a cycloreversion which affords the base peak m/z 220 corresponding to $[C_{14}H_{10}N_3^+] = [M^{++} - \text{norbornene} - H]$. This fragment has appeared in many mass spectra of adducts of **1b**, and a triazolium structure has been proposed [5]. [Isoquinoline $^{+}$] and [isoquinolinium $^{+}$] were observed to a minor extent.

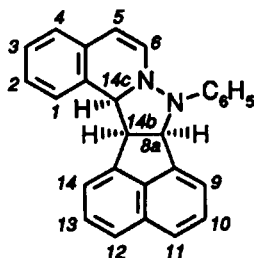




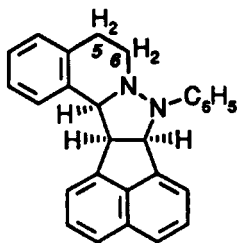
13



14



15



16

Acenaphthylene (13) contains only sp^2 -hybridized centers in the 5-membered ring. The reduction of the angle sum from 600° to 540° in the 5-membered ring creates angle strain. In the course of our efforts to assess the limits of the cycloaddition capacity of **1**, we reacted **1a** with **13** in dichloromethane at room temperature. The ^1H nmr spectrum of the cycloadduct, isolated in 29% yield [21], suggests the endo structure **15**. The doublets of the vinylic 5-H and 6-H appear as far upfield as δ 4.46 and 5.52; the corresponding protons in the parent system of **7** resonate at δ 5.26 and 5.99. The 5-H and 6-H of **15** are thus located in the shielding region of the naphthalene ring. Even one doublet of an aromatic proton (probably 14a-H) is shifted to δ 6.11.

Refluxing with Raney nickel in butanol converts **15** into the 5,6-dihydro compound **16**, which was found to be identical to the cycloadduct of 3,4-dihydroisoquinolinium *N*-phenylimide (**14**) with acenaphthylene [20]. The addition capacity of **14**, which has been systematically studied by Grashey [20], far exceeds that of **1a** since no sacrifice of aromatic resonance is required in its cycloadditions.

EXPERIMENTAL

Instruments and Techniques: See reference [6].

(rel-12b- β H)-(±)-8,8a,9,10,11,12,12a,12b-Octahydro-8-phenyl-9,12-methanoindazolo[3,2-*a*]isoquinoline (**6a**).

The carbon disulfide adduct **2** (1.48 g, 5.00 mmoles) was reacted with 5.00 g (53 mmoles) of norbornene in 5 ml of dichloromethane. After 24 hours at room temperature, the volatiles were distilled *in vacuo* from the dark-brown solution. Column chromatography of the residue on basic alumina with benzene as eluent afforded 0.66 g (42%) of **6a** as a pale yellow oil; colorless crystals (0.59 g, 38%), mp 153 – 154° , were

obtained from diethyl ether/petroleum ether; ir: ν 695, 737, 750, 773, 797 (aromatic CH out-of-plane deformations), 1498, 1599 st (aromatic ring vibrations), 1623 cm^{-1} (C=C of enamine); ^1H nmr (60 MHz): δ 0.76–1.83 (m, 6H), 2.18 (s br, 12-H), 2.46 (t, J \sim 8.2 Hz, 12a-H), 2.54 (s br, 9-H), 2.98 (d, $J_{8a,12a} = 7.6$ Hz, 8a-H), 3.86 (d, $J_{12a,12b} = 8.4$ Hz, 12b-H), 5.45 and 6.07 (AB, $J_{5,6} = 8.0$ Hz, 5-H and 6-H), 6.7–7.8 (m, 9 aromatic H).

Anal. Calcd. for $\text{C}_{22}\text{H}_{22}\text{N}_2$ (314.4): C, 84.04; H, 7.05; N, 8.91. Found: C, 84.25; H, 7.05; N, 8.86.

8,8a,9,10,11,12,12a,12b-Octahydro-8-(2-pyridyl)-9,12-methanoindazolo[3,2-*a*]isoquinoline (**6b**).

Isoquinolinium *N*-(2-pyridyl)imide (**1b**, 500 mg, 2.26 mmoles) and 2.00 g (21.3 mmoles) of norbornene were dissolved in 2 ml of dichloromethane. After 2 days at 20° , the solvent and excess of dipolarophile were removed. The dark-brown residue was purified on a column of basic alumina. Elution with diethyl ether/petroleum ether (1:1) furnished **6b** (0.34 g, 48%), colorless cubes, mp 142 – 143° , crystallized at -10° ; ir: ν 736, 747, 772, 787, 1278, 1332, 1440, 1470, 1476, 1562, 1595; 1624 cm^{-1} (C=C of enehydrazine); ^1H nmr (400 MHz, DQF-COSY, NOESY): δ 1.07 (d, J \sim 9 Hz, further split, 2H, 11-*Hendo* + 13-*Hdown*), 1.28 (tdd, 10-*Hendo*), 1.54 and 1.59 (m, 11-*Hexo* and 10-*Hexo*), 1.67 (dd, 13-*Hup*), 2.26 (d, $J_{exo-11,12} = 3.2$ Hz, 12-H), 2.54 (t, $J_{8a,12a} \sim J_{12a,12b} \sim 8.0$ Hz, 12a-H), 3.11 (d, $J_{9,10exo} = 4.1$ Hz, 9-H), 3.45 (d, $J_{8a,12a} = 7.5$ Hz, 8a-H), 3.93 (d, $J_{12a,12b} = 8.5$ Hz, 12b-H), 5.59 and 6.07 (AX, $J_{5,6} = 7.8$ Hz, 5-H and 6-H), 6.64 (ddd, 8 lines, 5'-H), 6.93 (d, 3'-H), 6.99 (2 d, 4-H), 7.12 (m, 2-H), 7.15 (m, 1-H), 7.20 (m, 3-H), 7.45 (ddd, 7 lines, 4'-H), 8.22 (ddd, 8 lines, 6'-H); ms: (70 eV, 100°): m/z (%): 315 (57) [M^+ , ^{13}C calcd 13%/found 12%], 220 (100) [M^+ - C_7H_{11} , $\text{C}_{14}\text{H}_{10}\text{N}_3^+$], 169 (10), 168 (10), 130 (5) [isoquinolinium $^+$], 129 (9) [isoquinoline $^+$].

Anal. Calcd. for $\text{C}_{21}\text{H}_{21}\text{N}_3$ (315.4): C, 79.96; H, 6.71; N, 13.32. Found: C, 79.69; H, 6.76; N, 13.12.

Dimethyl 8,8a,9,12,12a,12b-Hexahydro-8-phenyl-9,12-methanoindazolo[3,2-*a*]isoquinoline-8a,12a-dicarboxylate (**11**).

Dimethyl norbornadiene-2,3-dicarboxylate (**10**, 520 mg, 2.50 mmoles) was allowed to react with 740 mg (2.50 mmoles) of **2** in 5 ml of dichloromethane. The red color of **1a** disappeared more rapidly than in the reaction with norbornene. After 30 minutes, the solvent was removed in a rotary evaporator, and the residue was crystallized from chloroform/diethyl ether; after 2 days, 650 mg (61%) of **11** was deposited in the form of colorless cubes; ir: ν 700, 722, 745, 768; 1228, 1240, 1248 st (C=O); 1436, 1465 m, 1501, 1600 st (aromatic ring modes), 1627 (C=C), 1735 cm^{-1} vst (C=O); ^1H nmr (400 MHz): δ 1.59 (dt, $J_{13a,13b} = 9.8$ Hz, $J_{9,13a} \sim J_{12,13a} \sim 1.6$ Hz, 13a-H), 2.01 (d br, $J_{13a,13b} = 9.8$ Hz, 13b-H), 3.00 (s, OCH₃), 3.20 (s br, 12-H), 3.64 (dt, $J_{9,10} = 3.1$ Hz, $J_{9,13} = 1.5$ Hz, 9-H), 3.70 (s, OCH₃), 4.86 (s, 12b-H), 5.33, 6.49 (2 d, $J_{5,6} = 7.9$ Hz, 5-H and 6-H), 6.28 (dd, $J_{10,11} = 5.5$ Hz, $J_{11,12} = 3.1$ Hz, 11-H), 6.53 (dd, $J_{10,11} = 5.5$ Hz, $J_{9,10} = 3.4$ Hz, 10-H), 6.80 (t, 4'-H), 6.88 (dt, 2'/6'-H), 6.92 (dd, 4-H), 7.05 (td, 2-H), 7.10 (d br, 1-H), 7.16 (td, 3-H), 7.24 (dd, 3'/5'-H); ^{13}C nmr (100 MHz, DEPT): δ 44.7 (C-13), 48.7, 50.0 (C-9, C-12), 51.1, 52.3 (2 OCH₃), 67.7 (C-12b), 81.2 (C-12a), 87.7 (C-8a), 100.4 (C-5), 115.3 (C-2'/6'), 118.9 (C-4'); 124.6, 124.8, 127.7, 128.6 (C-1 to C-4); 127.4 (C-12c) 129.0 (C-3'/5'), 131.8 (C-4a); 135.6, 138.4 (C-10, C-11), 137.1 (C-6), 142.6 (C-1'); 171.7, 172.4 (2 C=O). The assignments of δ_{H} and

δ_C are based on two-dimensional analyses of several adducts of **1a** [16] and the data for norbornene.

Anal. Calcd. for $C_{26}H_{24}N_2O_4$ (428.5): C, 72.88; H, 5.65; N, 6.54. Found: C, 72.62; H, 5.39; N, 6.68.

8,8a,14b,14c-Tetrahydro-7-phenylacenaphtho[1,2-*c*]pyrazolo[5,1-*a*]isoquinoline (**15**) [21].

N-Anilinoisoquinolinium bromide [13] (1.51 g, 5.01 mmoles) was dissolved in 75 ml of water. The red precipitate formed on basifying with 25 ml of saturated aqueous sodium carbonate solution was extracted with diethyl ether (total volume 125 ml). After briefly drying the organic phase over sodium sulfate, 912 mg (5.99 mmoles) of acenaphthylene (**13**) was added to the ethereal solution of **1a**. Two days later, 10 ml of acetonitrile was added, and the ether was distilled off. Colorless crystals of **11** (515 mg, 28%) were deposited from the black-brown acetonitrile solution. Recrystallization from the same solvent gave a pure sample, mp 214-215° dec. A second experiment, performed with 2 equivalents of acenaphthylene, furnished **11** in 29% yield; ir: ν 664, 697 m, 771 st, 791 m (aromatic CH out-of-plane deformations), 1453 m, 1488, 1568 m, 1599 st (aromatic ring vibrations), 1627 cm^{-1} st (C=C of enehydrazine); 1H nmr (400 MHz): δ 4.46 (d, $J_{5,6} = 7.8$ Hz, 5-H), 4.49 (pseudo t, $J \sim 6.9$ Hz, 14b-H), 4.87 (d, $J_{8a,14b} = 7.6$ Hz, 8a-H), 5.52 (d, $J_{5,6} = 7.8$ Hz, 6-H), 5.77 (d, $J_{14b,14c} = 6.7$ Hz, 14c-H), 6.11 (d, $J = 7.0$ Hz, 1 aromatic H), 6.70 (ddd, 1 aromatic H), 6.96-7.72 (13 aromatic H).

Anal. Calcd. for $C_{27}H_{20}N_2$ (372.4): C, 87.06; H, 5.41; N, 7.52. Found: C, 86.74; H, 5.54; N, 7.64.

5,6,8,8a,14b,14c-Hexahydro-7-phenylacenaphtho[1,2-*c*]pyrazolo[5,1-*a*]isoquinoline (**16**).

Cycloadduct **11** (300 mg, 0.81 mmole) and 1 g of Raney nickel were refluxed in 30 ml of butanol for 3 hours. After hot filtration, the catalyst was repeatedly extracted with dichloromethane. The combined organic phases were concentrated *in vacuo*; the residue crystallized on trituration with diethyl ether. Repeated recrystallizations from dichloromethane/methanol furnished 124 mg (41%) of **16** as fine colorless needles, mp 216-218° dec; that this product was identical to a specimen prepared from **14** and acenaphthylene [22] was verified by mixed mp determination and comparison of ir spectra [23].

Anal. Calcd. for $C_{27}H_{22}N_2$ (374.5): N, 7.48. Found: N, 7.63.

Acknowledgments.

We are very grateful to the *Fonds der Chemischen Industrie*, Frankfurt, for the support of the research program. We thank *Helmut Huber* for the nmr service, *Helmut Schulz* for the micro-

analyses, and *Dr. David S. Stephenson* for a two-dimensional nmr analysis.

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- [23] We thank Professor R. Grashey, Munich, for a comparison specimen.