Tetrahedron Vol. 45, No. 10, pp. 3115 to 3130, 1989
Printed in Great Britain.

0040-4020/89 $3.00 + .00

ANTIAROMATIC COMPOUNDS — 24.[1] STERIC EFFECTS ON VALENCE ISOMERIZATIONS IN THE DEWAR PYRIDINE/AZAPRISMANE/PYRIDINE SYSTEM

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(*Received in Belgium* 8 *May* 1988)

Abstract — The alkynes **5a-c** undergo addition to the azete **4** with formation of the 1-Dewar pyridines **6a-c** which, in turn, are isomerized to the 4,5,6-tri-tert-butylpyridines **8**, **14**, or **19**, respectively, under trifluoroacetic acid catalysis (**6a, b**) or in the presence of silver tetrafluoroborate (**6b, c**). In the case of **6a**, the process also proceeds under thermal conditions (to give **8**). The pyridines **8**, **14**, and **19** can be transformed to the 2-Dewar pyridines **9**, **15**, and **20** by irradiation and these isomerizations can be reversed by heating. The 1-azabicyclic compounds **6a** and **6b** can be converted photochemically to the azaprismanes **10** and **16**; compound **6c** only undergoes ring opening to furnish the pyridine **22** under these conditions. The prismanes **10** and **16** can be isomerized by thermal or photochemical treatment to give the pyridines **13** and **18** which have substitution patterns comparable to that of **22**.

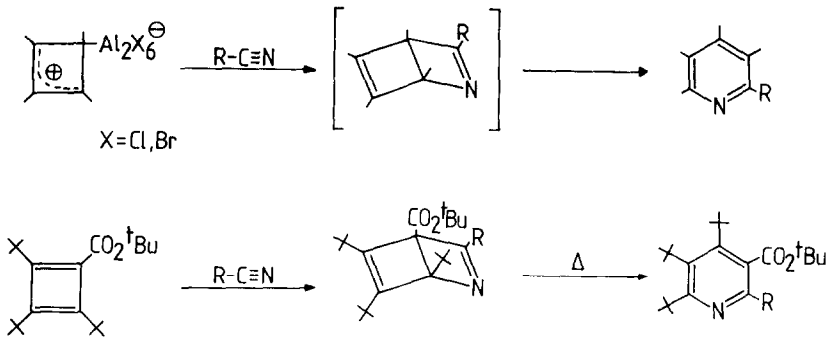
INTRODUCTION

In contrast to the valence isomerizations in the benzene system, which have been known for a long time [2], evidence for the occurrence of valence isomers of pyridine has only been available since 1970 [3]. Thus it was found that, on irradiation, 2-methylpyridine forms an equilibrium mixture with the 4-isomer; this could be explained by the intermediate formation of valence isomers (Dewar pyridine and azaprismane) which, however, were not detected directly [4]. With the exception of the not very stable, unsubstituted 2-Dewar pyridine [5,6], preparative interest has been concentrated especially on the fluorinated and perfluoroalkyl-substituted valence isomers of pyridine. Individual representatives with 1- or 2-Dewar pyridine and azaprismane structures have been isolated and found to possess unusual thermal stabilities [7].

A possible access to the 2-Dewar pyridine system consists of the reaction of the aluminium halide complexes of cyclobutadienes with nitriles. It was found experimentally, however, that the bicyclic primary products underwent spontaneous isomerization to form the pyridines (Scheme 1) [8].

The reactions of tert-butyl tri-tert-butylcyclobutadienecarboxylate itself with nitriles were more successful with regard to the bicyclic valence isomers of pyridine. It was possible to isolate the 2-Dewar pyridines from these reactions and subsequently to isomerize them thermally to the heteroarenes (Scheme 1) [9].

* Dedicated to Professor Dr. Dr. h.c. Adolf Steinhofer on the occasion of his 80th birthday.



Scheme 1

A further, new possibility to investigate the chemistry of the valence isomers of pyridine is based on the recently reported synthesis of the tri-tert-butylazete (**4**). This compound can be synthesized easily in any desired preparative amounts by thermolysis of azido-tri-tert-butylcyclopropene (**1**) [10]. We expected to be able to prepare the 1-Dewar pyridines **6** by the cycloaddition reactions of the electron-poor acetylenes **5** to the electron-rich hetero-1,3-diene **4**. As shown in the present report, the 1-azabicyclo[2.2.0]hexa-2,5-dienes **6** are ideal starting materials for an investigation of photochemical and thermal valence isomerizations. Of course, the kinetic stabilization of individual compounds by sterically demanding groups also plays an important role in this process.

RESULTS

Cycloaddition Reaction of 1 to 5a

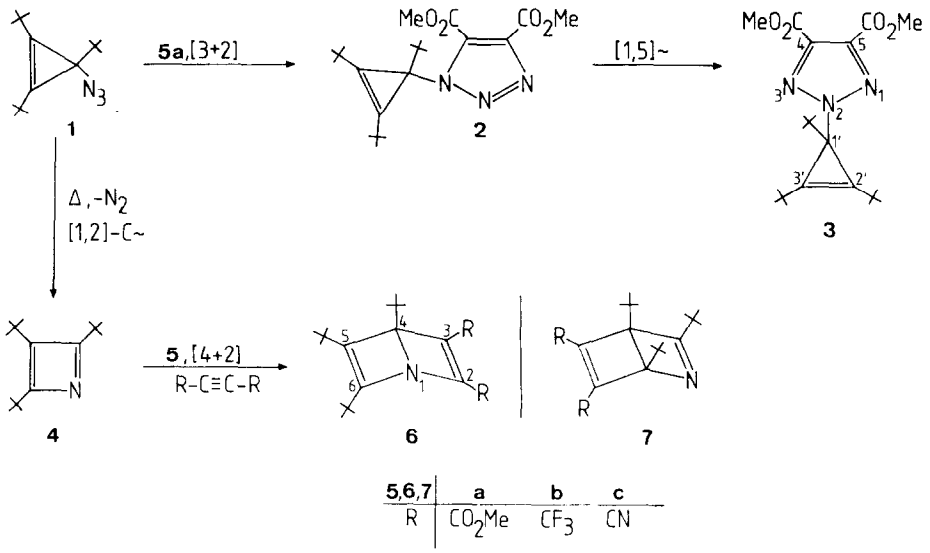
The cyclopropenyl azide **1**, the starting material for the preparation of **4**, also offers, at least superficially, the possibility of an access to the valency isomerization chemistry of pyridine. This statement presupposes, however, that **1** undergoes [3 + 2]-cycloaddition reactions with, for example, dimethyl acetylenedicarboxylate (**5a**) to form **2** and that this resultant 3H-1,2,3-triazole eliminates nitrogen under thermal conditions.

The results from an experiment carried out in dichloromethane at 60 °C showed that the proposed route is not possible since, in place of **2** (or a subsequent product formed by loss of nitrogen), the constitutional isomer **3** (10% yield) was isolated from the complex product mixture by flash chromatography. The sterically highly demanding tri-tert-butylcyclopropenyl moiety has, therefore, undergone a [1,5]-shift to N-2 and has thus achieved the largest possible separation from the ester groups [11].

The substituent shift on going from **2** to **3** has given rise to the C_s symmetry of the isolated product; this is demonstrated by the appearance of only three resonances for the ring carbon atoms of **3** [δ = 138.1 (C-4/C-5), 64.7 (C-1'), and 125.6 (C-2'/C-3')] in the ^{13}C-NMR spectrum.

Syntheses of the 1-Dewar Pyridines 6a-c

For the objectives of the present investigation, the reactions of **4** with the electron-poor alkynes **5a-c** were, in contrast, more successful. In spite of the, in part, very high steric hindrance at the reaction centre of the [4]anulene **4**, the reactions took place very rapidly in the temperature range from -10 to +25 °C and produced the 1-Dewar pyridines **6a-c** in high yields (73-97%). These colourless, crystalline products can be stored at room temperature [12]. There is no evidence for the formation of even small amounts of the 2-Dewar pyridine isomers **7a-c**.



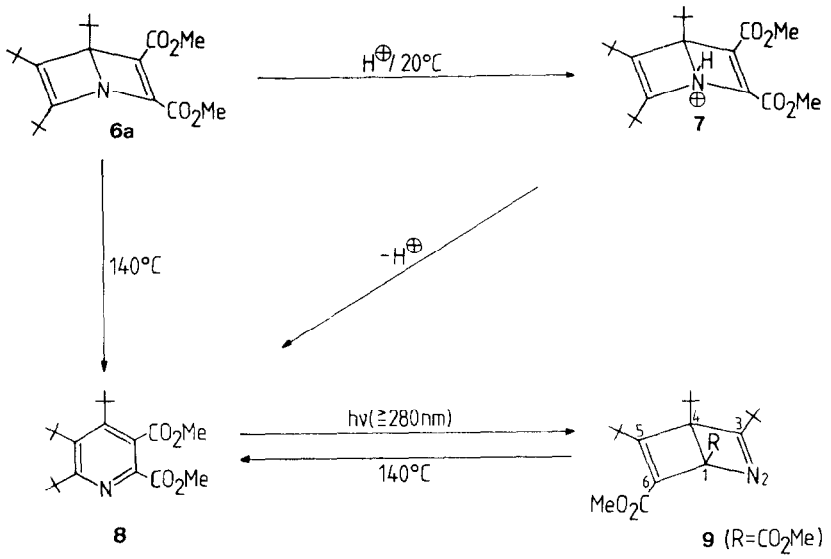
The fact that the alkynes specifically attack at N-1 and C-4 (or C-2, respectively) of the azete is most certainly the result of the general steric situation. Only cycloaddition partners with a small "linear extension" such as, for example, oxygen or diazomethane, are able to overcome the steric hindrance resulting from the tert-butyl substituents on two neighbouring carbon atoms (for example, C-2 and C-3) [12]. The establishment of the constitutions of the bicyclic products **6a-c** was deduced unequivocally from their ^{13}C-NMR spectra which each contained signals for four olefinic carbon atoms and only one sp^3-hydridized carbon atom (δ = 85.5-89.7). These data are not compatible with the alternative stuctures **7a-c**. The signals for C-3 (δ = 119.0-132.5) and C-5 (δ = 137.6-139.1) are clearly distinguishable from those of C-2 (δ = 141.9-156.3) and C-6 (δ = 163.1-163.7). The low-field positions of the latter are due to the adjacent bridgehead nitrogen atom. Decisive for the identification of C-2 and C-3 in **6b** are the $^2J_{C,F}$ coupling constants of 40.5 and 39.7 Hz. Incidentally, the skeletal carbon atoms bearing tert-butyl substituents are easily recognizable in the proton coupled ^{13}C-NMR spectra: as a result of small $^3J_{C,H}$ couplings, these resonances are noticeably broadened [13].

Proton-Catalyzed and Thermal Isomerizations of 6a

The 1-Dewar pyridine **6a** is thermally very stable and undergoes transformation to the pyridine **8** only after several hours heating at 140 °C in 1,2-dideutero-

tetrachloroethane. In contrast, the transformation of **6a** to **8** occurs at room temperature under trifluoroacetic acid catalysis. No side reactions were observed in either case. It may be speculated that the proton-catalyzed ring-opening reaction starts from the protonated form **7** of the bicyclic compound. A concerted, electrocyclic ring opening mechanism for the thermal isomerization is very improbable. This would lead first to an azacyclohexatriene with a trans-double bond; hence, a radical reaction process seems more plausible.

On heating, the pyridine **8** remains unchanged; in contrast, it is photochemically transformed to the 2-Dewar pyridine **9**. This step can be reversed (**9** to **8**) by thermal treatment (140 °C). To the best of our knowledge, the reaction sequence **6a** to **8** to **9** represents the first example of a 1-Dewar pyridine/2-Dewar pyridine rearrangement. From a thermodynamic point of view, **8** is certainly the most stable isomer in this sequence. Furthermore, it may be assumed that **9** is energetically more favoured than **6a** especially on account of the fact that the spatial situation of the three tert-butyl groups is considerably improved by the transformation of **6a** to **9**. Comparable Dewar benzene/Dewar benzene isomerizations have been reported previously [14,15].



The structure of the 3-tert-butyl 2-ethyl 4,5,6-tri-tert-butylpyridine-2,3-dicarboxylate [9] (Scheme 1, lower part, R = CO_2Et), obtained from tert-butyl tri-tert-butylcyclobutadienecarboxylate and ethoxycarbonylnitrile by cycloaddition and subsequent thermal isomerization, has been confirmed unequivocally by X-ray crystallographic analysis. This additionally demonstrated the boat conformation of the heteroarene [16]. These results were especially helpful for the structural elucidation of the pyridine **8**. A comparison of the ^{13}C-NMR data, in particular, of the above compound with those of **8** (which differs only in the nature of the ester groups) banished all remaining doubts with regard to the constitution. Even when the ester groups in **8** are smaller, a boat conformation [16] resulting above all from the neighbouring tert-butyl groups must also be assumed for this molecule.

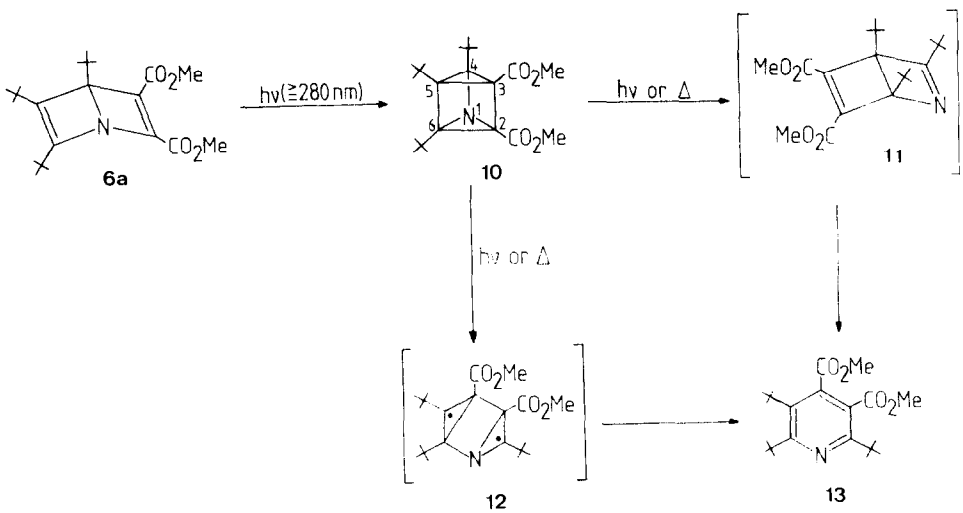
The isomerization of **6a** to **9** is accompanied by pronounced changes in the ^{13}C-NMR spectrum of the 2-Dewar pyridine. Obviously, two bridgehead carbon atoms are now visible (δ = 70.5 and 82.6 for C-1 and C-4, respectively); of these, the

latter can be recognized unambiguously on account of the signal broadening (refer to the above-mentioned effect of tert-butyl groups on skeletal carbon atoms). Furthermore, C-5 and C-6 now exhibit decisive differences in their chemical shifts ($\delta \approx 44.1$) as a result of the differing substituents. Finally, the appearance of an azomethine carbon atom at $\delta = 202.7$ confirms the rearrangement process. In this case as well, the absorptions of the skeletal carbon atoms harmonize very well with those of 6-tert-butyl 1-ethyl 3,4,5-tri-tert-butyl-2-azabicyclo[2.2.0]hexa-2,5-diene-1,6-dicarboxylate (cf. Scheme 1, lower part, R = CO_2Et), the structure of which has been confirmed by crystallographic analysis [9].

Photochemical Isomerization of 6a to the Azaprismane 10

When the 1-Dewar pyridine **6a** is subjected to irradiation ($\lambda \geq 280$ nm) in deuterochloroform, the azaprismane **10** (92% yield) is formed by a highly selective, intramolecular [2 + 2]-cycloaddition reaction. Perfluoroalkylazaprismanes are accessible by comparable routes [7]; this is also the case for the tert-butyl substituted prismanes [15,17,18,19] and phosphaprismanes [20] which were unknown until recently.

With the exception of the carbonyl carbon atoms, the region of the ^{13}C-NMR spectrum of **10** that is typical for sp^2-hybridized carbon atoms is free of signals. For the assignment of the skeletal carbon atoms, we assumed that the carbon atoms directly bonded to nitrogen and additionally bearing tert-butyl substituents [13] would resonate at lowest field [$\delta = 75.0$, 85.0 (C-4/C-6)]. Ester-substituted skeletal carbon atoms are usually shifted to higher field [$\delta = 40.6$ (C-3), 59.2 (C-2)] [15,17,18,19]. The remaining resonance at $\delta = 72.4$ is in accord with C-5. The structure of the azaprismane **10** has been independently confirmed by an X-ray crystallographic analysis (see below).



The azaprismane **10** undergoes highly selective ($\geq 85\%$) isomerizations to the pyridine **13** in 1,2-dideuterotetrachloroethane under both thermal (140 °C) and photochemical conditions. An intermediate such as, for example, the 2-Dewar pyridine **11** could not be detected by ^1H-NMR spectroscopy. Altogether, the solvent exerts a major influence on the product distribution resulting from the irradia-

tion of **6a** (or **10**, respectively). If the irradiation time of **6a** in chloroform is increased, only **13** is formed - the same product as is formed from **10** in 1,2-dideuterotetrachloroethane. The photolysis of **6a** in pentane or acetonitrile, in contrast, stops at the stage of the tetracyclic product **10**. It is possible that, in all reactions in halogenated hydrocarbon solvents, the bond between C-5 and C-6 is cleaved radically. This bond is, in any case, very long and is sterically highly stressed by the presence of the two tert-butyl groups (see Table 2). The diradical **12** would then be responsible for the formation of **13**.

^{13}C-NMR spectroscopic argumentation was employed above all for the constitutional assignment of **13**. Firstly, the signals of the ring carbon atoms bearing ester substituents were identified on the basis of incremental methods (which were performed for all possible positions) [δ = 120.8 (C-3), 141.9 (C-4)] [21]. Then, the ring carbon atoms bearing tert-butyl groups (broadened signals [13]) were recognized by spectral comparisons with pyridines having similar substitution patterns [9] [δ = 138.0 (C-5), 155.5 (C-2), 166.7 (C-6)]. As to be expected, compound **13** is photochemically stable. In contrast to **8** with its three neighbouring tert-butyl substituents, the necessity to give way in favour of a Dewar isomer is lacking.

Crystal Structure of the Azaprismane 10

Since the structural parameters for the previously described azaprismanes [7] were unknown, we have performed a crystal structure analysis of **10**. The additional question arises concerning interactions between the ester groups and the three-membered rings in the prismane skeleton which could give rise to significant structural changes (shortening of the distal bonds, lengthening of the proximal bonds). These, however, can only occur when the torsional angle between O3-C9-C3 or O1-C7-C2, respectively, and the centre of the respective three-membered ring bond [C4-C5 (τ_1) or N-C6 (τ_2) is 0 or 180° [22].

Figure 1 shows the molecular plot of the azaprismane **10**; positional parameters together with the isotropic temperature factors are given in Table 1. Table 2 lists selected bond lengths and angles.

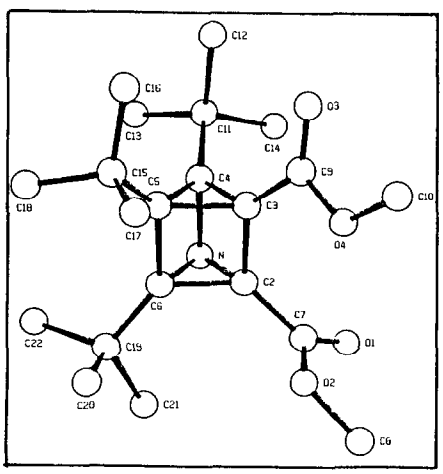


Figure 1. Molecular plot of the azaprismane **10** [23].

The calculated torsional angles τ_1 and τ_2 amount to -25.7 and 71.5°, respectively so that, at the most, a small influence of the two acceptor substituents on the lengths of the bonds of the three-membered rings is to be expected. Although C3-C5 with 1.588(3) Å is the longest bond in the tetracyclic skeleton of **10**, however, the separation between C3 and C4 is, with 1.518(3) Å, still shorter than the distal bond C4-C5 [1.529(3) Å]. The separation C3-C9 with 1.465(3) Å is somewhat smaller than that in prismanes with a similar, non-bisecting position of an ester group [18,24].

Table 1. Positional parameters of the atoms in **10** with isotropic temperature factors. Standard deviations are given in parentheses.

Atom	x/a	y/b	z/c	B_{eq} [Å^2]
O1	0.3490(2)	0.2789(3)	0.7123(1)	6.9(1)
O2	0.3824(1)	0.4817(2)	0.6761(1)	5.2(1)
O3	0.6755(1)	0.2192(3)	0.6804(1)	6.2(1)
O4	0.5837(1)	0.4038(2)	0.6956(1)	5.2(1)
N	0.4154(1)	0.1094(2)	0.6319(1)	3.2(1)
C2	0.4384(2)	0.2624(3)	0.6497(1)	3.0(1)
C3	0.5343(2)	0.2209(3)	0.6499(1)	3.1(1)
C4	0.5118(2)	0.0700(3)	0.6301(1)	3.3(1)
C5	0.5302(2)	0.1985(3)	0.5986(1)	3.1(1)
C6	0.4312(2)	0.2402(3)	0.6017(1)	3.0(1)
C7	0.3853(2)	0.3392(3)	0.6830(1)	3.8(1)
C8	0.3310(3)	0.5721(4)	0.7065(1)	7.7(1)
C9	0.6061(2)	0.2766(3)	0.6763(1)	4.0(1)
C10	0.6509(2)	0.4761(4)	0.7214(1)	6.7(1)
C11	0.5356(2)	-0.0906(3)	0.6394(1)	4.4(1)
C12	0.6313(2)	-0.1229(4)	0.6425(1)	7.8(1)
C13	0.4940(3)	-0.1877(4)	0.6053(2)	9.8(1)
C14	0.4964(3)	-0.1271(5)	0.6838(1)	8.6(1)
C15	0.6008(2)	0.2448(4)	0.5670(1)	3.7(1)
C16	0.6857(2)	0.1626(4)	0.5752(1)	5.7(1)
C17	0.6149(2)	0.4131(4)	0.5718(1)	5.3(1)
C18	0.5728(2)	0.2105(4)	0.5200(1)	5.0(1)
C19	0.3597(2)	0.2847(3)	0.5709(1)	3.6(1)
C20	0.3761(2)	0.4395(4)	0.5515(1)	5.2(1)
C21	0.2745(2)	0.2888(4)	0.5962(1)	4.9(1)
C22	0.3503(2)	0.1658(4)	0.5353(1)	5.0(1)

Table 2. Selected bond lengths and bond angles in **10**.

Bond lengths [Å]

N -C2	1.514(3)	C3-C9	1.465(3)
N -C4	1.536(3)	C4-C5	1.529(3)
N -C6	1.511(3)	C5-C6	1.582(3)
C2-C3	1.532(3)		
C2-C6	1.491(3)		
C2-C7	1.481(3)		
C3-C4	1.518(3)		
C3-C5	1.588(3)		

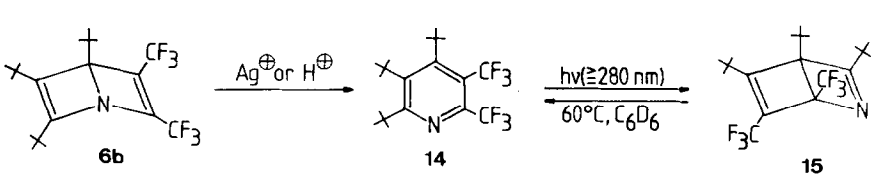
Bond angles [°]

C2-N-C4	89.4(1)	N -C2-C3	90.6(2)	C3-C4-C5	62.8(1)
C2-N-C6	59.0(1)	N -C2-C6	60.1(1)	C3-C5-C4	58.3(1)
C4-N-C6	90.9(1)	N -C2-C7	122.5(2)	C3-C5-C6	87.1(2)
		C3-C2-C6	92.5(2)	C4-C5-C6	87.5(2)
		C2-C3-C4	89.5(2)	N -C6-C2	60.6(1)
		C2-C3-C5	89.4(2)	N -C6-C5	90.7(2)
		C4-C3-C5	58.9(1)	C2-C6-C5	91.1(2)
		N -C4-C3	90.4(2)		
		N -C4-C5	91.8(2)		

When the structural analytical data of the heterocyclic three-membered ring in **10** are compared with those of other aziridines [25,26,27], the C2-C6 separation is seen to have the typical, shortened value of 1.498(4) Å [26]. In contrast, the bond lengths N-C2 and N-C6 with 1.514(3) and 1.511(3) Å, respectively, are significantly lengthened. The N-C values in a 1,4-diazaquadricyclane (also tetracyclic) with a comparable substitution pattern are 1.473-1.494 Å [27]. When the separation C2-C7 [1.481(3) Å] is also taken into consideration, it can additionally be concluded that no significant interactions occur between the aziridine ring and the acceptor groups. With 1.582(3) Å, the bond C5-C6 is one of the longest in the whole molecular skeleton (see Table 2) and is probably the first to be cleaved under thermal or photochemical conditions (sequence **10** to **12** to **13**).

Isomerization Reactions of 6b

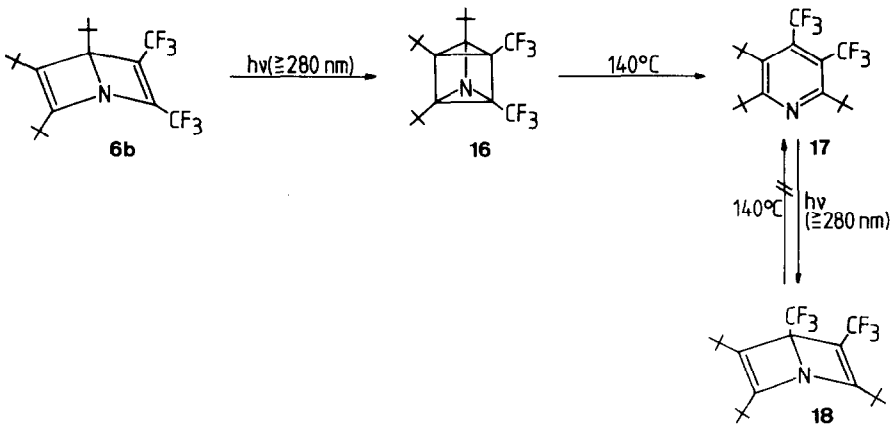
The Dewar pyridine **6b** is, in contrast to **6a**, thermally stable and is not changed even after several weeks heating at 140 °C in 1,2-dideuterotetrachloroethane (^{1}H-NMR monitoring). On the other hand, when the azabicyclic compound is treated in chloroform with a catalytic amount of silver tetrafluoroborate [28] or in benzene with trifluoroacetic acid at room temperature, a smooth ring-opening reaction to furnish the pyridine **14** (79 and 95% yield, respectively) takes place.



6b **14** **15**

Under photochemical conditions, **14** is smoothly converted to the heterobicyclic product **15**; this represents a further example of the 1-Dewar pyridine/2-Dewar pyridine rearrangement. The bicyclic compound **15** is thermally less stable than **9** and is quantitatively converted to the aromatic form at 60 °C.

On irradiation in chloroform, the bicyclic compound **6b** is transformed to the tetracyclic product **16** in high yield; even after a photolysis duration of several weeks, no subsequent reactions - as were observed in the case of **10** - have occurred. The heteroarene **17** (64% yield) is obtained from the pyrolysis of **16** (140 °C in the absence of a solvent). For the formation of **17**, the same considerations as applied in the case of the conversion of **10** to **13** are valid.



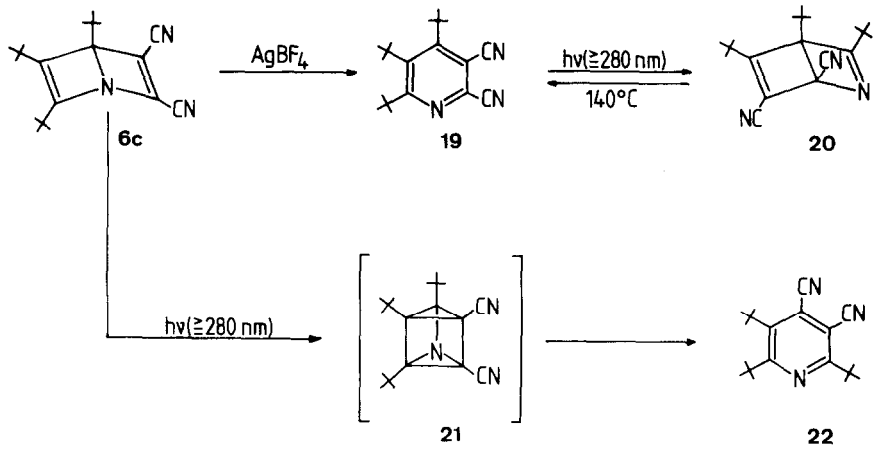
It is interesting to note that **17** is transformed under photolysis conditions. Flash chromatographic work-up of the reaction mixture gives a 53% yield of the 1-Dewar pyridine **18**. This compound - like its isomer **6b** - is also not changed by heating at 140 °C. Thus, it may be concluded that both compounds **6b** and **18** are thermodynamically more stable than the heteroarene **17** (or at least require an exceptionally large activation energy for the aromatization process). An entirely comparable phenomenon was observed for some Dewar benzenes, namely esters of tri-tert-butyl-bis(trifluoromethyl)-bicyclo[2.2.0]hexa-2,5-dienecarboxylic acid, which did not isomerize to the corresponding benzoic acid esters at even higher temperatures [18]. The reason for this is that the trifluoromethyl groups have much larger spatial requirements than methyl substituents [29] and that neighbouring CF_3 groups additionally repell each other by dipole/dipole interactions[30]. Both effects oppose the formation of the inherently planar, lower-energy heteroarene and are better endured by the bicyclic structure.

Detailed structural explanations on the basis of their ^{13}C-NMR data (see experimental part) are not necessary for the bis(trifluoromethyl)-substituted compounds **14**, **15**, **16**, and **17** since these are principally the same as those applied for the isomers originating from **6a** (see above). It need only be mentioned that the skeletal carbon atoms bearing CF_3 substituents are unequivocally identified by $^2J_{C,F}$ coupling constants of 33.4-38.7 Hz. The ^{13}C-NMR data of **18** alone require a short comment. The fact that the nitrogen atom is in the zero bridge can be deduced indirectly from the absence of a signal at $\delta \gtrsim 200$ resulting from an azomethine carbon atom. The bridgehead carbon atom C-4 (δ = 72.8) must carry a trifluoromethyl substituent to account for the quartet structure of its signal

($^2J_{C,F}$ = 35.3 Hz). Two olefinic carbon atom signals are shifted strongly to low field (adjacent to nitrogen) and can be recognized as bearing tert-butyl substituents on account of the signal broadening [δ = 168.9 (C-6), 181.5 (C-2)]. The chemical shifts of C-3 (δ = 115.5) and C-5 (δ = 137.1) require no further comment.

Isomerization Reactions of 6c

As in the case of the 1-Dewar pyridine **6b**, the structural analogue **6c** also cannot be converted thermally to the pyridine **19**. Here again, however, the use of silver tetrafluoroborate catalysis [28] in chloroform may be applied and gives rise to **19** in 67% yield. The steric characteristics responsible for the courses of the reactions **8** to **9** and **14** to **15** also favour the photochemical transformation of **19** to **20**. However, in this case, the photo-reaction gives rise only to an equilibrium mixture in which the starting material predominates (**19**⇌**20**, 50:45 according to ^{1}H-NMR spectroscopy). Product **20** can be separated from the reaction mixture in 40% yield by flash chromatography. Again, the retro reaction can be achieved thermally (140 °C; 100% yield).



On irradiation of **6c** in deuterochloroform at room temperature, the prismane **21**, in contrast to the experiences with **6a** and **6b**, cannot be isolated. Instead, the pyridine isomer **22** (92% yield) is formed by a highly selective reaction sequence. For the formation of this product, the same speculations as given for the isomerization of **10** to **13** are assumed to be valid whereby the formation of an azaprismane intermediate is implicitely assumed. The result of the photolysis is unchanged even when it is performed at -40 °C.

The structural elucidations of the products **19**, **20**, and **22** are based mainly on their ^{13}C-NMR spectra. The argumentation corresponds to that used for the archetypes **8**, **9**, and **13** of the biester series with the exception that anistropic effects of the cyano groups have to be taken into consideration additionally.

EXPERIMENTAL PART

Melting points: Mettler FP 61 melting point apparatus (not corrected).- Elemental anaylsis: Perkin-Elmer Elemental Analyzer 240.- IR spectra: Beckmann IR-20 A, Perkin-Elmer 394.- ^{1}H-NMR spectra: Varian EM 390, TMS as internal standard.- ^{13}C-NMR spectra: Bruker WP 200, TMS as internal standard.- Photolyses: Philips HPK 125 W high-pressure mercury lamp (Pyrex glass, $\lambda \geq 280$ nm); for photolyses in NMR tubes, the tubes were fixed to the cold finger of the irradiation apparatus.- Column chromatography: silica gel ICN Biomedicals, 32-63 µm; column dimensions 30 x 4.2 cm; flash chromatography [31] was performed at 1-1.5 bar.- The reactions with **4** were carried out under an argon atmosphere (Schlenk tube technique). Before use, all reaction vessels were evacuated, heated, and filled with argon.- All solvents were anhydrous and had been distilled under argon before use. The petroleum ether used had a boiling range of 35-70 °C.

Dimethyl 2-(1',2',3'-Tri-tert-butyl-2-cyclopropen-1-yl)-1,2,3-triazole-4,5-dicarboxylate (3). A solution of the azide **1** [32] (2.85 g, 11.0 mmol) in dichloromethane (10 ml) is treated with the acetylene **5a** [33] (1.62 g, 11.0 mmol) and the mixture is heated at 60 °C for 104 h. Evaporation at 20 °C/20 mbar and flash chromatography of the residue on 140 g of silica gel with 400 ml of diethyl ether/petroleum ether (1:1) yields 0.42 g (10%) of colourless crystals, m.p. 92 °C (from petroleum ether at -30 °C).- IR (KBr): 2950 (CH), 1750 cm^{-1} (CO).- ^{1}H-NMR ($CDCl_3$): δ = 1.24 (s, 27H, t-Bu), 3.94 (s, 6H, OMe).- ^{13}C-NMR ($CDCl_3$): δ = 28.3, 29.2 (2x) [C($\underline{C}H_3$)$_3$], 34.1 (2x), 35.8 [$\underline{C}$(CH_3)$_3$], 51.9 (OCH_3), 64.7 (C-1'), 125.6 (C-2'/C-3'), 138.1 (C-4/C-5), 161.5 (CO).- $C_{21}H_{33}N_3O_4$ (391.00) calc. C, 64.45; H, 8.44; N, 10.74. Found C, 64.4; H, 8.38; N, 10.8.

Dimethyl 4,5,6-Tri-tert-butyl-1-azabicyclo[2.2.0]hexa-2,5-diene-2,3-dicarboxylate (6a). To a solution of the azete **4** [10] (0.55 g, 2.5 mmol) in pentane (10 ml) is added the acetylene **5a** [33] (0.35 g, 2.5 mmol). The solution immediately loses its colour. Evaporation at 20 °C/20 mbar yields 0.69 g (76%) of colourless crystals, m.p. 82 °C (from petroleum ether at -30 °C).- IR (KBr): 2960 (CH), 1710 (CO), 1619 cm^{-1} (C=N).- ^{1}H-NMR ($CDCl_3$): δ = 1.08 (s, 9H, t-Bu), 1.22 (s, 18H, t-Bu), 3.80, 3.87 (each s, each 3H, OMe).- ^{13}C-NMR ($CDCl_3$): δ = 26.9, 29.2, 31.0 [C($\underline{C}H_3$)$_3$], 31.9, 33.8, 34.8 [$\underline{C}$(CH_3)$_3$], 51.5, 52.0 (OCH_3), 85.5 (C-4), 132.5 (C-3), 138.9 (C-5), 156.3 (C-2), 160.7, 161.1 (CO), 163.1 (C-6).- $C_{21}H_{33}NO_4$ (363.51) calc. C, 69.39; H, 9.15; N, 3.85. Found C, 69.0; H, 9.16; N, 3.8.

4,5,6-Tri-tert-butyl-2,3-bis(trifluoromethyl)-1-azabicyclo[2.2.0]hexa-2,5-diene (6b). To a solution of the azete **4** [10] (1.35 g, 6.2 mmol) in dichloromethane (5 ml) is condensed at -78 °C the acetylene **5b** [34] (1.00 g, 6.2 mmol) and the mixture is allowed to thaw, whereupon loss of colour takes place (at about -10 °C). Evaporation at 20 °C/20 mbar yields 2.3 g (97%) of colourless crystals, m.p. 54 °C (from petroleum ether at -30 °C).- IR (KBr): 2950 (CH), 1705 cm^{-1} (F_3C-C=C-CF_3).- ^{1}H-NMR ($CDCl_3$): δ = 1.08, 1.16, 1.22 (each s, each 9H, t-Bu).- ^{13}C-NMR ($CDCl_3$): δ = 26.4, 28.9, 30.4 [C($\underline{C}H_3$)$_3$], 31.3, 33.5, 34.9 [$\underline{C}$(CH_3)$_3$], 86.1 (C-4), 118.3 (q, $^{1}J_{C,F}$ = 271.8 Hz, CF_3), 119.7 (q, $^{1}J_{C,F}$ = 268.5 Hz, CF_3), 128.5 (q, $^{2}J_{C,F}$ = 39.7 Hz, C-3), 139.1 (C-5), 152.0 (q, $^{2}J_{C,F}$ = 40.5 Hz, C-2), 163.7 (C-6).- $C_{19}H_{27}F_6N$ (383.42) calc. C, 59.52; H, 7.10; N, 3.65. Found C, 59.7; H, 7.09; N, 3.6.

4,5,6-Tri-tert-butyl-1-azabicyclo[2.2.0]hexa-2,5-diene-2,3-dicarbonitrile (6c). To a solution of the azete **4** [10] (1.25 g, 5.6 mmol) in dichloromethane (5 ml) is added dropwise with stirring at room temperature a solution of the acetylene **5c** [35] (0.43 g, 5.6 mmol) in dichloromethane (5 ml). The colour of the solution becomes lighter and then rapidly darkens again. Evaporation at 20 °C/20 mbar and flash chromatography of the residue on 140 g of silica gel with 300 ml of petroleum ether/diethyl ether (10:1) yields 1.2 g (73%) of colourless crystals, m.p. 92 °C (from petroleum ether at -30 °C). IR (KBr): 2900 (CH), 2210 cm^{-1} (C≡N).- ^{1}H-NMR ($CDCl_3$): δ = 1.10, 1.26, 1.28 (each s, each 9H, t-Bu).- ^{13}C-NMR ($CDCl_3$): δ = 25.8, 29.0, 30.4 [C($\underline{C}H_3)_3$], 31.7, 33.7, 34.8 [$\underline{C}(CH_3)_3$], 89.7 (C-4), 110.2, 110.4 (C≡N), 119.0 (C-3), 137.6 (C-5), 141.9 (C-2), 163.2 (C-6).- $C_{19}H_{27}N_3$ (297.45) calc. C, 76.72; H, 9.15; N, 14.13. Found C, 76.5; H, 9.07; N, 14.2.

Dimethyl 4,5,6-Tri-tert-butylpyridine-2,3-dicarboxylate (8). a) From 6a by Thermolysis: A solution of the 1-Dewar pyridine **6a** (2.56 g, 7.0 mmol) in 1,2-dideuterotetrachloroethane (3 ml) is heated in a Schlenk tube at 140 °C for 3 h. Evaporation at 30 °C/20 mbar yields an oil which crystallizes rapidly to give 2.42 g (95%) of colourless crystals, m.p. 104 °C (from petroleum ether at -30 °C).- IR (KBr): 2900 (CH), 1730 cm^{-1} (CO).- ^{1}H-NMR ($CDCl_3$): δ = 1.38 (s, 18H, t-Bu), 1.43 (s, 9H, t-Bu), 3.90 (s, 6H, OMe).- ^{13}C-NMR ($CDCl_3$): δ = 31.9, 34.2, 35.4 [C($\underline{C}H_3)_3$], 41.3, 42.3, 43.0 [$\underline{C}(CH_3)_3$], 52.5 (OCH_3, 2x), 126.6 (C-3), 137.5 (C-2), 147.7 (C-5), 159.3 (C-4), 166.0 (CO), 166.7 (C-6), 169.7 (CO).- $C_{21}H_{33}NO_4$ (363.57) calc. C, 69.39; H, 9.15; N, 3.85. Found C, 69.5; H, 9.17; N, 3.8.

b) From 6a under Acid Catalysis: To a solution of the 1-Dewar pyridine **6a** (0.20 g, 0.55 mmol) in benzene (20 ml) in a Schlenk tube is added a solution of trifluoroacetic acid (10 mg, 0.09 mmol) in benzene (5 ml). The mixture is allowed to stand at room temperature for 3 days whereupon **8** is formed in quantitative yield. The product was identified by increases in the peak heights of the ^{1}H-NMR spectrum of the compound obtained under a) above.

Dimethyl 3,4,5-Tri-tert-butyl-2-azabicyclo[2.2.0]hexa-2,5-diene-1,6-dicarboxylate (9). A solution of the pyridine **8** (0.52 g, 1.4 mmol) in deuterochloroform (3 ml) in an NMR tube (Ø 10 mm) is irradiated for 88 h using a high-pressure mercury lamp. Evaporation at 20 °C/20 mbar yields 0.52 g (100 %) of an analytically pure oil which crystallizes completely at room temperature, m.p. 104 °C.- IR (KBr): 2875 (CH), 1725 (CO), 1620 cm^{-1} (C=N).- ^{1}H-NMR ($CDCl_3$): δ = 1.21, 1.35, 1.43 (each s, each 9H, t-Bu), 3.78, 3.87 (each s, each 3H, OMe).- ^{13}C-NMR ($CDCl_3$): δ = 28.8 (2x), 29.7 [C($\underline{C}H_3)_3$], 33.7, 35.2, 37.6 [$\underline{C}(CH_3)_3$], 51.6, 52.2 (OCH_3), 70.5 (C-1), 82.6 (C-4), 135.5 (C-6), 161.2, 170.2 (CO), 179.6 (C-5), 202.7 (C-3).- $C_{21}H_{33}NO_4$ (363.51) calc. C, 69.39; H, 9.15; N, 3.85. Found C, 69.4; H, 9.03; N, 3.9.

Thermal Isomerization of 9 to 8. A solution of the 2-Dewar pyridine **9** (50 mg, 0.14 mmol) in 1,2-dideuterotetrachloroethane (1 ml) in a Schlenk tube is heated at 140 °C for 15 min. Product **8** is formed in quantitative yield and identified by increases in peak heights in the ^{1}H-NMR spectrum of the compound obtained by thermal treatment of **6a**.

Dimethyl 4,5,6-Tri-tert-butyl-1-azatetracyclo[2.2.0^{2,6}.0^{3,5}]hexane-2,3-dicarboxylate (10). A solution of the 1-Dewar pyridine **6a** (0.91 g, 2.5 mmol) in deuterochloroform (3 ml) is irradiated with a high-pressure mercury lamp for 16 h. Evaporation at 20 °C/20 mbar yields a pale yellow oil which crystallizes after dissolution in petroleum ether and cooling to -30 °C to give 0.84 g (92%) of colourless crystals, m.p. 84 °C.- IR (KBr): 3000 (CH), 1745 cm^{-1} (CO).- ^{1}H-NMR ($CDCl_3$): δ = 1.01 (s, 9H, t-Bu), 1.24 (s, 18H, t-Bu), 3.72, 3.75 (each s, each 3H, OMe).- ^{13}C-NMR ($CDCl_3$): δ = 26.2, 26.5, 29.8 [C($\underline{C}H_3$)$_3$], 31.3, 32.8, 33.3 [$\underline{C}$(CH_3)$_3$], 40.6 (C-3), 51.5, 51.9 (OCH_3), 59.3 (C-2), 72.4 (C-5), 75.0, 85.0 (C-4/C-6), 165.8, 168.4 (CO).- $C_{21}H_{33}NO_4$ (363.51) calc. C, 69.39; H, 9.15; N, 3.85. Found C, 69.3; H, 9.07; N, 3.8.

Dimethyl 2,5,6-Tri-tert-butylpyridine-3,4-dicarboxylate (13). a) From 10 by Thermolysis: A solution of the azaprismane **10** (0.72 g, 2.0 mmol) in 1,2-dideuterotetrachloroethane (2 ml) in a Schlenk tube is heated at 140 °C for 35 min. Evaporation at 20 °C/20 mbar yields an oil which rapidly crystallizes to give 0.62 g (85%) of colourless crystals, m.p. 109 °C (from petroleum ether at -30 °C).- IR (KBr): 2950 (CH), 1730 cm^{-1} (CO).- ^{1}H-NMR ($CDCl_3$): δ = 1.36, 1.45, 1.47 (each s, each 9H, t-Bu), 3.83 (s, 6H, OMe).- ^{13}C-NMR ($CDCl_3$): δ = 29.7, 32.5, 33.5 [C($\underline{C}H_3$)$_3$], 36.5, 39.1, 43.3 [$\underline{C}$(CH_3)$_3$], 52.2 (OCH_3), 120.8 (C-3), 138.0 (C-5), 141.9 (C-4), 155.5 (C-2), 166.7 (C-6), 169.0, 169.4 (CO).- $C_{21}H_{33}NO_4$ (363.51) calc. C, 69.39; H, 9.15; N, 3.85. Found C, 69.6; H, 8.94; N, 3.7.

b) From 10 by Photolysis: A solution of the azaprismane **10** (90 mg, 0.20 mmol) in deuterochloroform (2 ml) in an NMR tube (Ø 10 mm) is irradiated with a high-pressure mercury lamp for 48 h whereupon 90% isomerization occurs. The product was identified by peak height increases in the ^{1}H-NMR spectrum of the product obtained under a) above.

4,5,6-Tri-tert-butyl-2,3-bis(trifluoromethyl)pyridine (14). a) From 6b under Silver Tetrafluoroborate Catalysis: To a solution of the 1-Dewar pyridine **6b** (0.66 g, 1.7 mmol) in chloroform (10 ml) is added silver tetrafluoroborate (50 mg, 0.3 mmol) and the mixture is stirred for 24 h at room temperature. Work-up by shaking with saturated aqueous sodium chloride solution (30 ml), washing of the aqueous phase three times with chloroform (15 ml each), drying of the combined chloroform phases with sodium sulfate, and evaporation at 20 °C/20 mbar furnishes a colourless oil. Flash chromatography on 140 g of silica gel with 500 ml of petroleum ether yields 0.52 g (79%) of colourless crystals, m.p. 62 °C (from petroleum ether at -30 °C).- IR (KBr): 2985 cm^{-1} (CH).- ^{1}H-NMR ($CDCl_3$): δ = 1.42 (s, 9H, t-Bu), 1.48 (s, 18H, t-Bu).- ^{13}C-NMR ($CDCl_3$): δ = 30.7, 33.8, 34.3 [C($\underline{C}H_3$)$_3$], 42.2, 42.5, 43.8 [$\underline{C}$(CH_3)$_3$], 119.4 (q, $^{2}J_{C,F}$ = 36.0 Hz, C-3), 122.8 (q, $^{1}J_{C,F}$ = 273.4 Hz, CF_3), 123.7 (q, $^{1}J_{C,F}$ = 276.0 Hz, CF_3), 135.9 (q, $^{2}J_{C,F}$ = 34.2 Hz, C-2), 151.3 (C-5), 163.3 (C-4), 163.8 (C-6).- $C_{19}H_{27}F_6N$ (383.42) calc. C, 59.52; H, 7.10; N, 3.65. Found C, 59.7; H, 7.08; N, 3.6.

b) From 6b under Trifluoroacetic Acid Catalysis: A solution of the 1-Dewar pyridine **6b** (0.20 g, 0.5 mmol) in diethyl ether (15 ml) is treated with trifluoroacetic acid (30 mg, 0.02 mmol), the mixture is allowed to stand at room temperature for 48 h and is then evaporated at 20 °C/20 mbar. ^{1}H-NMR spectroscopic analysis of the residue shows that isomerization has occurred to 95% [increases in peak heights in the spectrum of the product obtained under a) above].

3,4,5-Tri-tert-butyl-1,6-bis(trifluoromethyl)-2-azabicyclo[2.2.0]hexa-2,5-diene (15). A solution of the pyridine **14** (0.55 g, 1.4 mmol) in deuterochloroform (5 ml) in an NMR tube (Ø 10 mm) is irradiated with a high-pressure mercury lamp for 3 days. Evaporation at 20 °C/20 mbar yields 0.55 g (100%) of analytically pure, colourless crystals, m.p. 50 °C.- IR (KBr): 2970 (CH), 1610 cm^{-1} (C=N).- ^{1}H-NMR ($CDCl_3$): δ = 1.34 (s, 27H, t-Bu).- ^{13}C-NMR ($CDCl_3$): δ = 31.6 (2x), 31.8 [C($\underline{C}H_3$)$_3$], 32.5, 34.5, 35.0 [$\underline{C}$(CH_3)$_3$], 50.8 (q, $^2J_{C,F}$ = 32.5 Hz, C-1), 85.9 (C-4), 119.2 (q, $^1J_{C,F}$ = 272.9 Hz, CF_3), 121.8 (q, $^1J_{C,F}$ = 273.1 Hz, CF_3), 128.3 (q, $^2J_{C,F}$ = 35.2 Hz, C-6), 173.5 (C-5), 204.9 (C-3).- $C_{19}H_{27}F_6N$ (383.42) calc. C, 59.52; H, 7.10; N, 3.65. Found C, 59.5; H, 7.05; N, 3.6.

Thermal Isomerization of 15 to 14. A solution of the 2-Dewar pyridine **15** (60 mg, 0.15 mmol) in hexadeuterobenzene (3 ml) in a Schlenk tube is heated at 60 °C for 10 h whereupon quantitative isomerization occurs. The product was identified by peak height increases in the ^{1}H-NMR spectrum of the compound obtained from **6b** under silver tetrafluoroborate catalysis.

4,5,6-Tri-tert-butyl-2,3-bis(trifluoromethyl)-1-azatetracyclo[2.2.0^{2,6}.0^{3,5}]-hexane (16). A solution of the 1-Dewar pyridine **6b** (0.80 g, 2.1 mmol) in hexadeuterobenzene (5 ml) in an NMR tube (Ø 10 mm) is irradiated with a high-pressure mercury lamp for 10 days. Evaporation at 20 °C/20 mbar and flash chromatography of the residue on 140 g of silica gel with 350 ml of petroleum ether/diethyl ether (10:1) gives a colourless, viscous oil which crystallizes after standing for a short time to yield 0.69 g (86%) of colourless crystals, m.p. 71 °C.- IR (KBr): 2950 cm^{-1} (CH).- ^{1}H-NMR ($CDCl_3$): δ = 1.10, 1.22, 1.27 (each s, each 9H, t-Bu).- ^{13}C-NMR ($CDCl_3$): δ = 25.7, 27.3, 29.9 [C($\underline{C}H_3$)$_3$], 30.5, 32.5, 32.7 [$\underline{C}$(CH_3)$_3$], 38.6 (q, $^2J_{C,F}$ = 38.1 Hz, C-3), 56.9 (q, $^2J_{C,F}$ = 39.2 Hz, C-2), 65.9 (C-5), 77.4, 80.3 (C-4/C-6), 122.1 (q, $^1J_{C,F}$ = 274.3 Hz, CF_3), 124.4 (q, $^1J_{C,F}$ = 269.9 Hz, CF_3).- $C_{19}H_{27}F_6N$ (383.42) calc. C, 59.52; H, 7.10; N, 3.65. Found C, 59.6; H, 7.10; N, 3.7.

2,5,6-Tri-tert-butyl-3,4-bis(trifluoromethyl)pyridine (17). In the absence of a solvent, the azaprismane **16** (1.16 g, 3.0 mmol) is heated in a Schlenk tube at 140 °C for 24 h whereupon a light brown oil forms. Flash chromatography on 140 g of silica gel with 350 ml of petroleum ether yields 0.71 g (64%) of a colourless oil that is not completely analytically pure.- IR (film): 2970 cm^{-1} (CH).- ^{1}H-NMR ($CDCl_3$): δ = 1.29, 1.32, 1.34 (each s, each 9H, t-Bu).- ^{13}C-NMR ($CDCl_3$): δ = 30.0, 30.4, 33.8 [C($\underline{C}H_3$)$_3$], 38.5, 40.0, 42.2 [$\underline{C}$(CH_3)$_3$], 113.4 (q, $^2J_{C,F}$ = 38.7 Hz, C-3), 123.0 [q, $^1J_{C,F}$ = 272.1 Hz, CF_3 (2x)], 134.3 (q, $^2J_{C,F}$ = 33.4 Hz, C-4), 135.4 (C-5), 158.8 (C-2), 165.9 (C-6).- $C_{19}H_{27}F_6N$ (383.42). Found 383.5 (MS, 70 eV).

2,5,6-Tri-tert-butyl-3,4-bis(trifluoromethyl)-1-azabicyclo[2.2.0]hexa-2,5-diene (18). A solution of the pyridine **17** (0.64 g, 1.7 mmol) in deuterochloroform (6 ml) in an NMR tube (Ø 10 mm) is irradiated with a high-pressure mercury lamp for 24 h. Evaporation at 20 °C/20 mbar and flash chromatography of the oily residue on 140 g of silica gel with 700 ml of petroleum ether yields 0.34 g (53%) of colourless crystals, m.p. 61 °C.- IR (KBr): 2950 cm^{-1} (CH).- ^{1}H-NMR ($CDCl_3$): δ = 1.25, 1.30, 1.34 (each s, each 9H, t-Bu).- ^{13}C-NMR ($CDCl_3$): δ = 30.4, 32.2, 32.3 [C($\underline{C}H_3$)$_3$], 33.9, 36.2, 37.3 [$\underline{C}$(CH_3)$_3$], 72.8 (q, $^2J_{C,F}$ = 35.3 Hz, C-4), 115.5 (q,

$^2J_{C,F}$ = 42.0 Hz, C-3), 119.9 (q, $^1J_{C,F}$ = 268.8 Hz, CF_3), 123.9 (q, $^1J_{C,F}$ = 283.2 Hz, CF_3), 137.1 (C-5), 168.9 (C-6), 181.5 (C-2).- $C_{19}H_{27}F_6N$ (383.42) calc. C, 59.52; H, 7.10; N, 3.65. Found C, 59.4; H, 7.0; N, 3.4.

4,5,6-Tri-tert-butylpyridine-2,3-dicarbonitrile (19). To a solution of the 1-Dewar pyridine **6c** (0.43 g, 1.5 mmol) in chloroform (20 ml) is added silver tetrafluoroborate (30 mg, 0.15 mmol) and the mixture is stirred at room temperature for 24 h. Work-up by shaking with saturated aqueous sodium chloride solution (30 ml), washing of the aqueous phase three times with chloroform (15 ml each), drying of the combined chloroform phases with sodium sulfate, and evaporation at 20 °C/20 mbar gives a pale yellow oil. Flash chromatography on 140 g of silica gel with 250 ml of petroleum ether/diethyl ether (10:1) again gives a pale yellow oil which is crystallized from petroleum ether at 20 °C to yield 0.29 g (67%) of colourless plates, m.p. 130 °C.- IR (KBr): 2950 (CH), 2220 cm^{-1} (C≡N).- ^{1}H-NMR ($CDCl_3$): δ = 1.34, 1.39, 1.62 (each s, each 9H, t-Bu).- ^{13}C-NMR ($CDCl_3$): δ = 31.2, 32.5, 35.1 [$C(\underline{C}H_3)_3$], 41.3, 41.8, 44.1 [$\underline{C}(CH_3)_3$], 107.0 (C-3), 115.0, 116.0 (CN), 129.2 (C-2), 148.5 (C-5), 164.0 (C-4), 172.8 (C-6).- $C_{19}H_{27}N_3$ (297.45) calc. C, 76.72; H, 9.15; N, 14.13. Found C, 76.6; H, 9.14; N, 14.1.

3,4,5-Tri-tert-butyl-2-azabicyclo[2.2.0]hexa-2,5-diene-1,6-dicarbonitrile (20). A solution of the pyridine **19** (0.45 g, 1.5 mmol) in deuterochloroform (5 ml) in an NMR tube (Ø 10 mm) is irradiated with a high-pressure mercury lamp for 48 h. A 55:45 mixture of **19** and **20** is formed (^{1}H-NMR spectroscopic analysis) and this composition does not change even after irradiation for a further 11 days. Evaporation at 20 °C/20 mbar and flash chromatography of the mixture on 140 g of silica gel with 1500 ml of petroleum ether/diethyl ether (5:1) yields 0.18 g (40%) of colourless crystals, m.p. 101 °C (from petroleum ether at -30 °C).- IR (KBr): 2980 (CH), 2230 cm^{-1} (C≡N).- ^{1}H-NMR ($CDCl_3$): δ = 1.28, 1.31, 1.38 (each s, each 9H, t-Bu).- ^{13}C-NMR ($CDCl_3$): δ = 27.4, 28.6, 29.6 [$C(\underline{C}H_3)_3$], 32.5, 36.1, 37.6 [$\underline{C}(CH_3)_3$], 58.5 (C-1), 84.3 (C-4), 112.0 (C-6), 115.4, 115.6 (CN), 184.1 (C-5), 205.8 (C-3).- $C_{19}H_{27}N_3$ (297.45) calc. C, 76.72; H, 9.15; N, 14.13. Found C, 76.9; H, 9.13; N, 14.0.

Thermal Isomerization of 20 to 19. In the absence of a solvent, the 2-Dewar pyridine **20** (0.1 g, 0.35 mmol) is heated for 1 h at 140 °C whereupon a light brown oil is formed. The product was formed in quantitative yield and identified by peak height increases in the ^{1}H-NMR spectrum of the compound obtained from the silver tetrafluoroborate-catalyzed isomerization of **6c**.

2,5,6-Tri-tert-butylpyridine-3,4-dicarbonitrile (22). A solution of the Dewar pyridine **6c** (1.13 g, 3.8 mmol) in deuterochloroform (10 ml) in an NMR tube (Ø 10 mm) is irradiated with a high-pressure mercury lamp for 60 h. Evaporation at 20 °C/20 mbar and sublimation of the residue at 140 °C/atmospheric pressure yields 1.04 g (92%) of colourless crystals, m.p. 75 °C.- IR (KBr): 2985 (CH), 2215 cm^{-1} (C≡N).- ^{1}H-NMR ($CDCl_3$): δ = 1.47, 1.53, 1.71 (each s, each 9H, t-Bu).- ^{13}C-NMR ($CDCl_3$): δ = 28.5, 30.9, 31.9 [$C(\underline{C}H_3)_3$], 36.5, 38.3, 43.0 [$\underline{C}(CH_3)_3$], 103.3 (C-3), 115.4, 115.5 (CN), 124.6 (C-4), 142.5 (C-5), 161.7 (C-2), 169.7 (C-6).- $C_{19}H_{27}N_3$ (297.45) calc. C, 76.72; H, 9.15; N, 14.13. Found C, 76.6; H, 9.14; N, 14.0.

X-Ray Crystal Structure Analysis of 10 [36]

Crystal Data: $C_{21}H_{33}NO_4$, M_r = 363.51; orthorhombic, space group P_{bca}; a = 15.501(1), b = 8.933(1), c = 30.676(3) Å, α = 90.01(3), β = 90.08(8), γ = 89.98(0); V = 4248.4 Å^3; Z = 8, $D_{calc.}$ = 1.137 g cm^{-3}, μ = 0.7 cm^{-1}.

Data Collection: The data collection was achieved using an automatic four circle diffractometer (Enraf-Nonius CAD 4). Crystal dimensions 0.6 x 0.55 x 0.25 mm. Measurement of a hemisphere in the range $2° \leq \theta \leq 22°$, Mo-K_α, scan width (0.85 + 0.35 tan θ)°, ω/2θ scan, scan speed 0.86-5.03° min^{-1}, 2595 independent reflections. An average intensity loss of 2.2% was observed for the three monitoring reflections ($0\bar{7}4$, $\bar{1}143$, $\bar{1}\bar{1}\bar{2}0$).

Structure Solution and Refinement: The structure was solved with MULTAN 82. Missing atoms were localized in the ΔF-syntheses, 2 hydrogen atoms were calculated geometrically. The heavy atoms were anisotropic and the found hydrogen atoms with fixed B_{iso} and unit weights of up to R = 0.0563, R_w = 0.0479 were refined. Largest shift/error ratio: 0.47 (C-14), residual electron density: 0.17 e Å^{-3}.

Acknowledgements — We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for generous support of this work. We are grateful to Ms. M. Alester for performance of the elemental analyses. The Landesregierung Rheinland-Pfalz supported this work with graduate grants to Udo Hees and Gisbert Michels.

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