196. A Torquospecific 1,5-Electrocyclization

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(14.IX.87)

Saponification of homodiazepine **1a** and **1b**, in the absence of any proton donors, led to the formation of the 6π electron anionic species **A** which, by virtue of a 1,5-electrocyclization, is in equilibrium with the allylic anion **B**. This latter tricyclic species is thermodynamically less favoured than its bicyclic isomer **A**. Nevertheless, **B** could be trapped by acylation and led to type-**2** compounds which are the major reaction products. This is due to the fact that **B** is more nucleophilic and, therefore, much more reactive than **A**. The *transoid* topology of the tricyclic products **2** was demonstrated by ^{1}H-NMR and by an X-ray diagram of **2d**. The *transoid* geometry of **2** is a consequence of a torquospecific 1,5-electrocyclization (of **A**), which is due to a steric, and possibly even to an electronic factor.

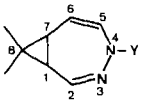
Introduction. – The 1,5-electrocyclizations have been reviewed and discussed extensively by *Huisgen,* who showed in particular that their reaction mechanism represents a unifying concept in organic chemistry [1]. In the epilogue of his review article, this author made the statement that 'should the concept of electrocyclization of the pentadienyl anion type prove to be fruitful in heterocyclic chemistry, it would add to the great scientific harvest associated with the names of *R. B. Woodward* and *R. Hoffmann*' [1].

We describe herein the 1,5-electrocyclization of the diaza analogue **A** of a pentadienyl anion which, according to the FMO theory [2], proceeds according to a disrotatory mode. We shall demonstrate that this particular electrocyclization proceeds in a *torquospecific* manner[1]). This is to say that out of two possible disrotations, only the one which avoids steric crowding takes place (see below)[2]).

Chemical Properties of Homodiazepines 1a, 1b, and 5 in the Presence of Bases. – Reaction of the *N*-benzoyl-homodiazepine **1a** [4] in benzene with NaOH in MeOH led to the disappearance of the starting material and to the formation – after treatment with Ac_2O in pyridine – of the two products **1c** (16%) and **2c** (68%). When successively reacted with Na_2CO_3 in MeOH and then with PhCOCl in pyridine, **1a** led to the isomer **2a** (31%) and to some additional reaction products which were neither isolated nor identified. A similar treatment of **1a**, but replacing PhCOCl with TsCl, gave both isomers **1d** (20%)

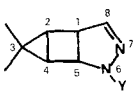
[1]) The concept of *torquospecificity* has been coined by *K. N. Houk* who tentatively proposed it at the EUCHEM Conference on Stereochemistry which was held on May 3–9, 1987, Bürgenstock, Switzerland. Torquospecificity applies to disrotatory (or to conrotatory) electrocyclic reactions, which proceed according to *only one* out of the two possible disrotatory (or conrotatory) modes.

[2]) For a preliminary communication, see [3].



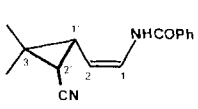
1 Y

a	COPh
b	CO_2Et
c	$COCH_3$
d	Ts
e	$COCF_3$
f	H



2 Y

a	COPh
c	$COCH_3$
d	Ts
e	$COCF_3$



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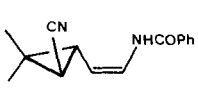

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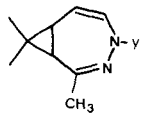

5 y = COPh
6 y = $COCH_3$

and **2d** (42%) as colourless crystalline compounds. Eventually **1b** [4], when successively reacted with a K(*t*-BuO) suspension in benzene and then with $(CF_3CO)_2O$ in pyridine, led in poor yield to **1e** (5%) and **2e** (12%).

Considering the above isolated products only, it appears that the simple transacylation or transsulfonylation of **1a** and **1b** to the corresponding homodiazepines **1c–e** represent but a minor reaction pathway. The major reaction products, *i.e.* the tricyclic isomers **2a** and **2c–e**, are the result of a more complex reaction mechanism *(vide infra)*.

In the presence of strong bases, the reactivity of homodiazepines **1a** and **1b** turns out to be even more complex, as demonstrated in the following experiment. When a benzene solution of **1a** was slowly added to a stirred K(*t*-BuO) suspension in benzene under Ar, an orange colour appeared. After addition of MeOH, the mixture turned colourless and gave the two oily cyclopropane derivatives **3** (36%) and **4** (24%). Additional reaction products were not isolated. This latter experiment shows that a third reaction pathway competes with the two ones cited above. It explains why **1e** and **2e** were obtained in poor yields under similar conditions, the main reaction pathway being obviously the base-catalyzed ring opening of **1b**.

The base-induced ring opening of **1a** to its monocyclic isomers **3** and **4** was expected, since simple *N*-acyl-1*H*-1,2-diazepines are known to undergo a base-induced ring opening to the corresponding aminodienenitriles [5]. This third base-induced reaction of homodiazepines **1** is due to the slight acidity of the CH=N–N–COR group, for which there is ample precedence in the literature[3]). It prevails when bulky bases are used, *e.g.* K(*t*-BuO), which can more easily approach H–C(2) of diazepines **1** than their amide carbonyl group.

In order to suppress this competing base-catalyzed ring opening, the C(2)-methylated and, therefore, non-acidic homodiazepine **5** [4] was successively treated with NaOH in MeOH and then with Ac_2O in pyridine, whereby only the transacylated product **6** could be isolated (47%). It is noteworthy that the type-**2** tricyclic isomer of **6** did not form at all.

Structure Determination of the Reaction Products. – *Homodiazepines* **1**. The homodiazepines **1a**, **1b**, and **5** have been described and their structures demonstrated by ^{1}H-NMR [4] [6]. The newly formed homodiazepines **1c**, **1d**, **1e**, and **6** showed very similar spectral data and could easily be identified (*cf.* below *Table 6* and *Exper. Part*) by spectral correlation with the already known ones.

Tricyclic Compounds **2**. The tricyclic architecture of these molecules could be demonstrated by NMR spectroscopy and by an X-ray diffraction analysis of **2d**. Comparative ^{1}H-NMR *(Table 1)* clearly demonstrated the structural similarity of **2a**, **2c**, **2d**, and **2e**,

[3]) See [5] and references cited therein.

Table 1. *^{1}H-NMR Spectra* (60 MHz, $CDCl_3$) *of Tricyclic Compounds* **2a** *and* **2c–e**. Data of *N*-substituents are not reproduced. δ in ppm, *J* in Hz; int. standard TMS.

	H–C(1)	H–C(2)	H–C(4)	H–C(5)	H–C(8)	Me_{exo}	Me_{endo}
2a	3.29	1.90	1.66	4.60	6.95	0.96	1.32
	(*dt*, *J* = 4.2, 1.7)	(*dd*, *J* = 4.5, 1.6)	(*dd*, *J* = 4.5, 2)	(*dd*, *J* = 4.2, 2)	(*d*, *J* = 1.8)	(*s*)	(*s*)
2c	3.3	1.7	1.7	4.4	7.0	0.92	1.27
	(*dt*, *J* = 4.5, 1.5)	(*m*)	(*m*)	(*dd*, *J* = 4.5, 2)	(*d*, *J* = 2.0)	(*s*)	(*s*)
2d	3.2	1.85	1.7	4.15	7.05	0.95	1.25
	(*dt*, *J* = 4, 1.5)	(*dd*, *J* = 4.5, 1.5)	(*dd*, *J* = 4.5, 2)	(*dd*, *J* = 4, 2)	(*d*, *J* = 2)	(*s*)	(*s*)
2e	3.35	1.8	1.8	4.45	7.2	1.0	1.33
	(*dt*, *J* = 4.5, 1.5)	(*m*)	(*m*)	(*dd*, *J* = 4.5, 2)	(*d*, *J* = 2)	(*s*)	(*s*)

Table 2. *^{13}C-NMR Spectra* (20.1 MHz, $CDCl_3$) *of* **2a** *and* **2c**. Data of *N*-substituents are not reproduced. δ in ppm; *J* in Hz; int. standard TMS.

	C(1)	C(2)	C(3)	C(4)
2a	48.21 (*ddt*, *J* = 149, 12, 3)	31.13 (*dm*, *J* = 186)	21.57 (*m*)	29.77 (*dm*, *J* = 186)
2c	49.34 (*ddt*, *J* = 147, 12, 3)	31.48 (*dm*, *J* = 182)	21.69 (*m*)	30.03 (*dm*, *J* = 182)

	C(5)	C(8)	Me_{endo}	Me_{exo}
2a	56.69 (*ddd*, *J* = 163, 4, 2)	149.47 (*ddt*, *J* = 195, 3, 1)	13.78 (*qq*, *J* = 129, 4)	22.98 (*qq*, *J* = 130, 4)
2c	55.85 (*ddd*, *J* = 160, 4, 2)	148.86 (*ddd*, *J* = 192, 4.5, 2)	13.99 (*qq*, *J* = 127, 4)	23.29 (*qq*, *J* = 128, 4)

Table 3. *^{1}H-NMR* (360 MHz, $CDCl_3$) *Coupling Constants* [Hz] *of the Ring H-Atoms of* **2a**

	H–C(1), H–C(2)	H–C(1), H–C(5)	H–C(1), H–C(8)	H–C(2), H–C(4)	H–C(4), H–C(5)
^3J	1.7	4.5	1.8	4.5	2.5

which is also corroborated by the ^{13}C-NMR spectra of **2a** and of **2c** *(Table 2)*. It appears clearly that only 1 sp^2 C-atom (C(8)) is present in these compounds, whereas there are 3 such atoms in the educts **1** (see *Exper. Part*). The magnitude of the coupling constants between the cyclobutane H-atoms cannot by interpreted using the *Karplus* rule (*Karplus* graph), this being due to the ring strain. In the high-field ^{1}H-NMR (360 MHz) of **2a**, these 4 protons were nicely resolved and led to a precise determination of their coupling constants *(Table 3)*: the eclipsed vicinal *cis* H-atoms appear with a larger ^3J value than the two vicinal *transoid* H-pairs.

That the steric relation between the two *cis*-bridgehead H-pairs is *transoid* could be demonstrated by nuclear *Overhauser* effects (NOE) which were measured with **2a** at 360 MHz: irradiation of the Me_{exo} group led to a pronounced and specific enhancement of the peaks of H–C(2) and H–C(4), whereas irradiation of the Me_{endo} group led to a pronounced and specific enhancement of the peaks of H–C(1) and H–C(5) *(Fig. 1)*. If **2a** had a *cisoid* relationship for the *cis*-bridgehead H-pairs, no NOE would have been detected for H–C(1) and H–C(5), whichever of the two Me groups is irradiated.

Cyclopropane Derivatives **3** *and* **4**. The presence of a nitrile group (IR: 2230 cm^{-1}) in both isomers **3** and **4** clearly indicated that the seven-membered diazepine ring of **1a** had been opened. The overall structure of these isomers could be ascertained unambiguously

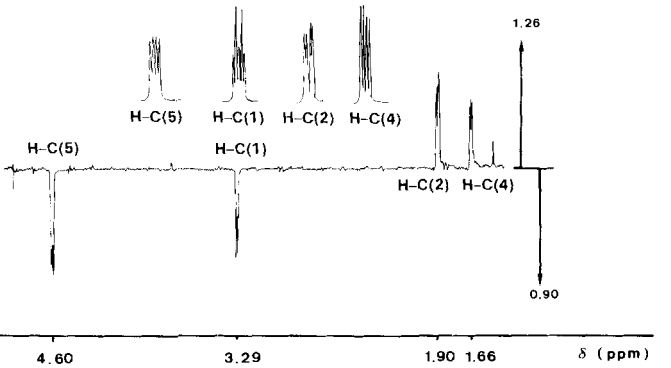

Fig. 1. *Nuclear* Overhauser *effects* (360 MHz, $CDCl_3$) *measured during irradiation of the* Me_{exo} *group* (0.90 ppm) *and of the* Me_{endo} *group* (1.26 ppm), *followed by substraction of the two enhanced spectra from the reference spectrum of* **2a**. The enlarged *m* of the 4 cyclobutane protons are superimposed upon the substraction spectra. δ in ppm; int. standard HMDS.

by ^{1}H-NMR, using selective decoupling experiments as well as NH/ND exchange with D_2O, in order to determine in particular the linear sequence of the H-atoms (from H–C(2′) to NH) *(Table 4)*.

The enamide double bond appears to be (*Z*)-configurated in both isomers, as indicated by the magnitude of $^3J(1,2)$ (10 Hz in **3**; 9 Hz in **4**) in the ^{1}H-NMR. As to the relative configuration of these diastereoisomers, it follows clearly from the $^3J(1',2')$ values (J_{cis} = 8 Hz, J_{trans} = 4.5 Hz; see *Table 4*) in the ^{1}H-NMR and from ^{13}C-NMR data *(Table 5)*: in the stereoisomer **3**, Me_{cis} is strongly shielded (16.92 ppm) by virtue of a double *'γ-gauche'* effect, whereas Me_{trans} (25.99 ppm) is not affected at all by any such effect. In the stereoisomer **4**, both Me_{cis} (19.93 ppm) and Me_{trans} (23.16 ppm) are shielded by virtue of one *'γ-gauche'* effect each. As a consequence, the $\Delta\delta$ between the chemical shifts of the 2 geminal Me groups is much larger in isomer **3** ($\Delta\delta$ = 9.07 ppm), than in **4** ($\Delta\delta$ = 3.23 ppm).

Table 4. *^{1}H-NMR Spectra* (60 MHz, $CDCl_3$) *of Cyclopropane Derivatives* **3** *and* **4**. Data of benzoyl moieties are omitted, δ in ppm; *J* in Hz; int. standard TMS.

	NH	H–C(1)	H–C(2)	H–C(1′)	H–C(2′)	Me_{cis}/Me_{trans}[a])	
3	8.7	7.2	4.7	2.2	1.6	1.23	1.30
	(*d*, *J* = 12)	(*dd*, *J* = 12, 10)	(*t*, *J* = 10, 9)	(*ddd*, *J* = 9, 8, 1.5)	(*d*, *J* = 8)	(*s*)	(*s*)
4	8.55	7.1	4.6	2.17	1.15[b])	1.20	1.36
	(*d*, *J* = 10)	(*dd*, *J* = 10, 9)	(*t*, *J* = 9, 8, 4)	(*ddd*, *J* = 8, 4.5, 1.5)		(*s*)	(*s*)

[a]) *cis*/*trans* refer to the relation between the Me group and C(2)=C(1).
[b]) No coupling constant could be measured for this absorption band.

Table 5. *^{13}C-NMR Spectra* (20.1 MHz, $CDCl_3$) *of* **3** *and* **4**. Data of the benzoyl moieties are omitted. δ in ppm; *J* in Hz; int. standard TMS.

	C(3′)	C(2′)	C(1′)	C(2)
3	24.98 (*m*)	17.10 (*dm*, *J* = 178)	26.76 (*dm*, *J* = 166)	104.42 (*dm*, *J* = 167)
4	25.76 (*m*)	18.01 (*d*, *J* = 177)	29.86 (*dm*, *J* = 164)	105.60 (*dtm*, *J* = 167, 5, 1)

	C(1)	Me_{cis}[a])	Me_{trans}[a])	CN
3	126.06 (*dm*, *J* = 181)	16.92 (*qtq*, *J* = 131, 5, 2.5)	25.99 (*q sext.*, *J* = 131.5)	118.27 (*m*)
4	126.19 (*dm*, *J* = 185)	19.93 (*q*, *J* = 131)	23.16 (*q*, *J* = 132)	119.77 (*d*, *J* = 6)

[a]) *cis*/*trans* refer to the relation between the Me group and C(2)=C(1).

Mechanism of the 1,5-Electrocyclization. – That the multistep transformation of the homodiazepine **1** into the tricyclic compounds **2** is due to a disrotatory 1,5-electrocyclization of the 6π-electron anion **A** to the 4π-electron anion **B** was demonstrated as follows. A C_6D_6 solution of **1a** was reacted with NaOMe in an NMR tube, whereby the solution turned gradually orange. A new spectrum appeared which was very similar to the one of **1a**: the three olefinic protons were still present and retained their coupling constants, but H–C(5) underwent a shielding effect of *ca.* 1.8 ppm *(Table 6)*. We believe that the new spectrum is best accounted for by the delocalized anion **A**. According to the NMR data, this base-induced reaction seemed to be quantitative. The postulated anion **B** could not be detected by NMR. Nevertheless, as soon as Ac_2O and some pyridine were added, the solution turned colourless and the tricyclic compound **2c** appeared. The same spectrum (of **A**) was obtained when a C_6D_6 solution of **1f** was treated with NaH.

Table 6. *^{1}H-NMR Spectra* (60 MHz) *of* **1a**, **1f**, *and of the Anion* **A**. Data of the benzoyl groups are omitted. δ in ppm; J in Hz; int. standard TMS.

	Solvent	H–C(1)	H–C(2)	H–C(5)
1a [4]	$CDCl_3$	1.76 (*m*)	6.93 (*t*, J = 2.0)	7.23 (*d*, J = 10)
1f	$CDCl_3$	1.6 (*t*, J = 2.5)	6.67 (*t*, J = 1.5)	6.03 (*dd*, J = 9.5, 5)
	C_6D_6	1.3 (*m*)	6.63 (*m*)	5.67 (*dd*, J = 9.5, 5)
Anion **A**	C_6D_6	1.5 (*m*)	6.55 (*t*, J = 1.5)	5.45 (*d*, J = 10)

	H–C(6)	H–C(7)	Me_{endo}	Me_{exo}	NH
1a [4]	5.23 (*ddd*, J = 10, 3, 2.5)	1.76 (*m*)	1.33 (*s*)	0.90 (*s*)	–
1f	4.6 (*dm*, J = 9.5)	1.6 (*t*, J = 2.5)	1.15 (*s*)	0.8 (*s*)	7.7
	4.45 (*ddt*, J = 9.5, 4, 2)	1.3 (*m*)	1.0 (*s*)	0.7 (s)	7.3
Anion **A**	4.18 (*ddd*, J = 10, 4, 2)	1.5 (*m*)	1.15 (*s*)	0.85 (*s*)	–

Albeit saponification of **2a**, **2c**, and **2d** did not lead, in our hands, to any defined products, treatment of **2e** at reflux in MeOH in the presence of Na_2CO_3 gave the expected homodiazepine **1f** *(Table 6)* after 2 days. The same reaction, when conducted in MeOD, led to *N*-deuterated **1f** in which H–C(5) appeared as a *d*. From these experiments, it follows that the postulated equilibrium between the anionic species **A** and **B** *(Scheme)* lies strongly on the side of **A**. That products **2** are formed nevertheless predominantly is due to the fact that N(6) of **B** (an *allylic anion*) is by its very nature more nucleophilic and, therefore, much more reactive than N(4) of **A** (a *pentadienyl anion*). It was indeed expected that the equilibrium would be strongly in favour of **A**, since the gain of energy

Scheme

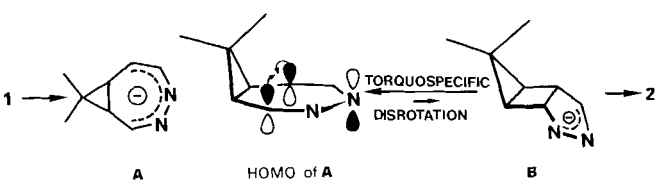

Table 7. *Positional and Thermal Parameters and their Standard Deviations for* **2d** (2 molecules, the second one being B).
The temperature factors are of the form: $T = \exp[-2\pi^2(U_{11}h^2a^{*2} \ldots U_{12}hka^*b^*)]$.

Atom	*x/a*	*y/b*	*z/c*	U_{11} or U	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(1)	0.7765(19)	0.6757(22)	0.5693(8)	0.0488(117)	0.0588(139)	0.1034(153)	−0.0059(121)	0.0005(109)	−0.0172(95)
H(1)	0.8464(165)	0.5989(168)	0.5639(60)	0.0600					
C(2)	0.7428(19)	0.8032(22)	0.5242(9)	0.0556(106)	0.0390(111)	0.1041(155)	−0.0047(109)	−0.0023(94)	−0.0239(89)
H(2)	0.7511(216)	0.8992(228)	0.5216(76)	0.0600					
N(3)	0.7552(14)	0.7369(14)	0.4636(5)	0.0657(87)	0.0563(81)	0.0433(81)	−0.0023(62)	0.0030(62)	−0.0172(68)
N(4)	0.5976(18)	0.7101(18)	0.4390(6)	0.0605(93)	0.0991(117)	0.0765(108)	−0.0010(85)	−0.0217(85)	−0.0487(88)
C(5)	0.4875(21)	0.7430(19)	0.4805(10)	0.0499(118)	0.0665(123)	0.1184(174)	0.0048(111)	−0.0212(118)	−0.0244(98)
H(5)	0.3565(21)	0.7261(19)	0.4717(10)	0.0600					
C(6)	0.5530(19)	0.8022(21)	0.5387(8)	0.0412(104)	0.0462(108)	0.0922(141)	0.0100(99)	0.0089(96)	−0.0018(92)
H(6)	0.4690(118)	0.9074(129)	0.5481(40)	0.0600					
C(7)	0.5871(21)	0.6724(22)	0.5800(8)	0.0718(125)	0.0391(124)	0.0960(153)	−0.0043(113)	0.0177(107)	−0.0185(105)
H(7)	0.5497(257)	0.5412(261)	0.5964(89)	0.0600					
C(8)	0.7009(18)	0.7301(20)	0.6289(7)	0.0632(105)	0.0937(131)	0.0459(106)	0.0019(91)	0.0194(87)	−0.0160(97)
C(9)	0.7410(22)	0.5979(22)	0.6767(7)	0.1105(148)	0.1016(154)	0.0579(123)	0.0005(100)	0.0410(106)	−0.0267(125)
H(91)	0.6668(22)	0.6246(22)	0.7145(7)	0.0600					
H(92)	0.8698(22)	0.6212(22)	0.6881(7)	0.0600					
H(93)	0.7199(22)	0.4700(22)	0.6634(7)	0.0600					
C(10)	0.6988(24)	0.9051(21)	0.6507(9)	0.0818(141)	0.0877(138)	0.0951(159)	−0.0031(119)	0.0335(122)	−0.0188(109)
H(101)	0.8199(24)	0.8868(21)	0.6692(9)	0.0600					
H(102)	0.6198(24)	0.9495(21)	0.6849(9)	0.0600					
H(103)	0.7084(24)	0.9947(21)	0.6161(9)	0.0600					
S(11)	0.9018(5)	0.7753(5)	0.4164(2)	0.0585(27)	0.0499(26)	0.0473(25)	−0.0076(20)	0.0085(21)	−0.0151(21)
O(12)	0.9207(13)	0.6437(12)	0.3767(5)	0.0985(88)	0.0571(70)	0.0800(84)	−0.0077(63)	0.0300(66)	−0.0127(64)
O(13)	1.0373(10)	0.8071(12)	0.4542(4)	0.0343(53)	0.0716(74)	0.0675(72)	−0.0008(55)	−0.0128(51)	−0.0086(54)
C(15)	0.7881(12)	0.9392(11)	0.3168(5)	0.0492(99)	0.0613(123)	0.0567(118)	−0.0062(96)	0.0136(81)	−0.0141(93)
C(16)	0.7504(12)	1.0784(11)	0.2849(5)	0.0527(95)	0.0511(110)	0.0493(104)	−0.0010(92)	−0.0020(79)	−0.0255(85)
C(17)	0.7680(12)	1.2347(11)	0.3116(5)	0.0448(96)	0.0936(144)	0.0505(119)	0.0213(106)	0.0072(82)	−0.0191(93)
C(18)	0.8235(12)	1.2519(11)	0.3701(5)	0.0434(91)	0.0255(90)	0.0794(121)	0.0042(86)	0.0081(83)	−0.0124(73)
C(19)	0.8612(12)	1.1127(11)	0.4020(5)	0.0281(82)	0.0467(105)	0.0719(113)	0.0119(91)	−0.0011(73)	−0.0112(77)
C(14)	0.8436(12)	0.9564(11)	0.3753(5)	0.0333(85)	0.0468(101)	0.0463(100)	−0.0055(76)	0.0270(71)	−0.0033(73)
H(15)	0.8044(105)	0.8147(110)	0.3036(38)	0.0600					
H(16)	0.7009(138)	1.0606(141)	0.2374(52)	0.0600					
H(18)	0.8503(116)	1.3776(128)	0.3950(42)	0.0600					
H(19)	0.9292(144)	1.0555(150)	0.4367(53)	0.0600					
C(20)	0.7301(21)	1.3941(19)	0.2772(7)	0.0822(130)	0.0603(118)	0.0892(144)	0.0183(98)	−0.0049(106)	−0.0262(104)
H(201)	0.7047(21)	1.3250(19)	0.2366(7)	0.0600					
H(202)	0.8346(21)	1.4792(19)	0.2714(7)	0.0600					
H(203)	0.6236(21)	1.4620(19)	0.2889(7)	0.0600					

C(1B)	1.8317(20)	0.7257(26)	−0.0702(7)	0.0349(97)	0.1022(164)	0.0543(116)	0.0051(101)	0.0136(87)	−0.0152(105)
H(1B)	1.9037(244)	0.6410(250)	−0.0577(85)	0.0600					
C(2B)	1.6991(17)	0.7610(22)	−0.0241(9)	0.0364(99)	0.0519(103)	0.1007(142)	0.0245(90)	−0.0015(110)	−0.0270(83)
H(2B)	1.6121(163)	0.7372(188)	−0.0229(68)	0.0600					
N(3B)	1.7613(14)	0.7475(15)	0.0368(5)	0.0634(80)	0.0686(92)	0.0441(82)	0.0048(64)	−0.0179(62)	−0.0389(69)
N(4B)	1.7883(16)	0.9043(18)	0.0601(6)	0.0858(101)	0.0574(95)	0.0727(102)	−0.0291(82)	0.0160(78)	−0.0484(82)
C(5B)	1.7563(18)	1.0151(20)	0.0217(9)	0.0647(114)	0.0419(117)	0.0977(157)	−0.0165(104)	0.0099(103)	−0.0308(91)
H(5B)	1.7718(18)	1.1459(20)	0.0312(9)	0.0600					
C(6B)	1.6964(19)	0.9470(20)	−0.0363(8)	0.0417(104)	0.0399(107)	0.1103(151)	0.0130(103)	0.0025(99)	−0.0041(89)
H(6B)	1.6320(141)	1.0312(147)	−0.0499(48)	0.0600					
C(7B)	1.8274(20)	0.9154(21)	−0.0840(8)	0.0533(114)	0.0668(119)	0.0825(138)	0.0219(100)	0.0079(102)	−0.0371(96)
H(7B)	1.9177(261)	0.9515(278)	−0.1013(91)	0.0600					
C(8B)	1.7687(21)	0.7997(20)	−0.1282(8)	0.0988(133)	0.0499(105)	0.0809(131)	0.0230(97)	0.0088(103)	−0.0094(102)
C(9B)	1.5942(22)	0.7973(23)	−0.1507(9)	0.0811(124)	0.0795(135)	0.1177(162)	0.0161(110)	−0.0298(125)	−0.0207(113)
H(91B)	1.6039(22)	0.6870(23)	−0.1777(9)	0.0600					
H(92B)	1.5689(22)	0.8998(23)	−0.1786(9)	0.0600					
H(93B)	1.4952(22)	0.7790(23)	−0.1198(9)	0.1946(936)					
C(10B)	1.9016(22)	0.7583(27)	−0.1753(7)	0.1140(165)	0.1225(186)	0.0463(120)	0.0174(111)	−0.0092(99)	−0.0268(135)
H(101B)	1.8819(22)	0.8281(27)	−0.2147(7)	0.0600					
H(102B)	1.8881(22)	0.6280(27)	−0.1859(7)	0.0758(570)					
H(103B)	2.0244(22)	0.7872(27)	−0.1578(7)	0.0600					
S(11B)	1.7242(5)	0.5971(5)	0.0835(2)	0.0426(23)	0.0658(28)	0.0447(25)	0.0034(20)	−0.0049(19)	−0.0143(20)
O(12B)	1.8544(12)	0.5814(14)	0.1244(4)	0.0533(66)	0.1164(99)	0.0682(80)	0.0172(65)	−0.0038(60)	−0.0115(64)
O(13B)	1.6940(11)	0.4596(10)	0.0460(4)	0.0796(72)	0.0398(58)	0.0533(66)	−0.0138(50)	0.0084(53)	−0.0126(56)
C(15B)	1.3864(12)	0.6414(10)	0.0976(3)	0.0511(94)	0.0537(96)	0.0490(103)	−0.0152(75)	−0.0006(82)	−0.0406(79)
C(16B)	1.2475(12)	0.6784(10)	0.1299(3)	0.0362(94)	0.0547(99)	0.0796(120)	−0.0049(83)	0.0140(85)	−0.0278(76)
C(17B)	1.2651(12)	0.7329(10)	0.1886(3)	0.0662(110)	0.0382(88)	0.0526(109)	0.0066(73)	0.0111(85)	−0.0246(78)
C(18B)	1.4217(12)	0.7503(10)	0.2150(3)	0.0506(100)	0.0553(101)	0.0786(133)	−0.0081(88)	0.0223(96)	−0.0213(84)
C(19B)	1.5606(12)	0.7133(10)	0.1827(3)	0.0741(123)	0.0464(102)	0.0633(119)	−0.0108(80)	−0.0032(99)	−0.0162(87)
C(14B)	1.5430(12)	0.6588(10)	0.1240(3)	0.0652(106)	0.0263(83)	0.0602(109)	0.0172(73)	−0.0056(84)	−0.0126(77)
H(15B)	1.3728(12)	0.5993(10)	0.0522(3)	0.0600					
H(16B)	1.1263(12)	0.6650(10)	0.1095(3)	0.0600					
H(18B)	1.4353(12)	0.7924(10)	0.2605(3)	0.0600					
H(19B)	1.6818(12)	0.7268(10)	0.2032(3)	0.0600					
C(20B)	1.1064(19)	0.7695(21)	0.2250(8)	0.0799(124)	0.0862(131)	0.0902(135)	−0.0389(105)	0.0672(108)	−0.0400(106)
H(201B)	1.1221(19)	0.8048(21)	0.2710(8)	0.0600					
H(202B)	1.0314(19)	0.6561(21)	0.2211(8)	0.0600					
H(203B)	1.0464(19)	0.8657(21)	0.2017(8)	0.0600					

[a]) For numbering scheme, see *Fig. 2.*

for the conversion of a π-bond into a σ-bond (*ca.* −20 kcal mol^{-1}) does not compensate the added ring strain which is due to the formation of the cyclobutane ring (*ca.* +27 kcal mol^{-1}). For a similar example, albeit of a reversed reaction pathway (disrotatory ring opening of 2,3-diazabicyclo[3.2.0]hept-2-ene, leading to the corresponding monocyclic diazacycloheptadiene), see [7].

The Torquospecific Disrotatory Ring Closure of A, Leading to B. – Considering the HOMO of **A** and applying the *Woodward-Hoffmann* rules to it [1] [2], it follows that the 1,5-electrocyclization had to proceed according to a disrotatory mode *(Scheme)*. This electrocyclization occurs in a *torquospecific* manner[4]), *i.e.* in such a way as to avoid any steric interference between the Me_{endo} group and the five-membered ring which is in the build-up stage. As a consequence, only the *transoid* tricyclic compounds **2** form, *via* anion **B** *(Scheme; cf. Fig. 1)*. According to *Houk*, an electronic factor may also be operating in addition to the steric one, the basic idea being that ring closure occurs in such a fashion as to minimize overlap of the developing σ-bond orbital with the cyclopropane *Walsh* orbital[4]).

Saponification followed by acetylation of the 2-methyl-4-benzoyl-homodiazepine **5** led to the corresponding 4-acetylhomodiazepine **6**, but not to the type-**2** tricyclic isomer of **6**. This is best explained by assuming that the 1,5-electrocyclization of the anion **5** is *inhibited for both disrotatory modes:* the *cisoid* topology cannot be attained for the steric (and electronic) reasons which have been discussed above; the formation of the *transoid* topology is inhibited by the steric repulsion between the *endo*-oriented C(8) and the Me group at C(2).

Crystallographic Data of 2d. – Crystallographic data of **2d** ($C_{15}H_{18}N_2O_2S$) are as follows: triclinic, space group $P\bar{1}$ (No. 2), $a = 8.116(5)$, $b = 8.115(2)$, $c = 22.637(7)$ Å, $\alpha = 91.09(2)$, $\beta = 90.95(3)$, $\gamma = 92.67(3)°$; $V = 1488.8$ Å^3, $\lambda(\text{Mo}K\alpha) = 0.71069$ Å; 4465 reflections were measured ($\omega/2\theta$-scan mode) of which 1314 with $F > 4\sigma(F)$ were used for the solution by direct methods (see below); final $R_w = 0.086$; weighting system: $1845/(\sigma^2(F) + 3.513 \cdot 10^{-2}F^2)$.

Unit-cell parameters were determined from accurate centering of 25 independent strong reflections by the least-squares method. Four standard reflections monitored every 3600 s during data collection showed no intensity loss. The raw data set was corrected for crystal decay and polarization effects. No correction for absorbance was

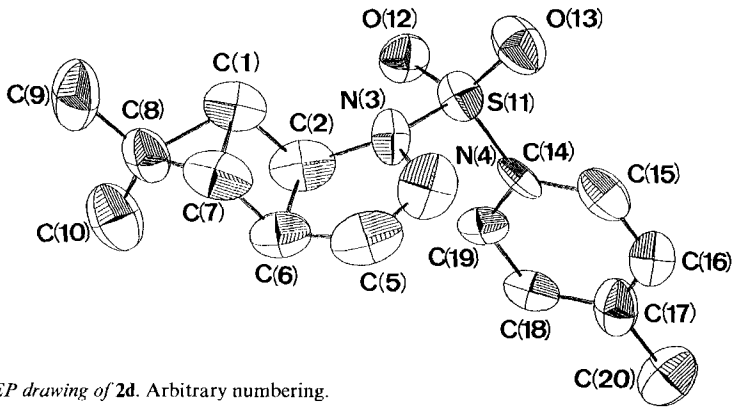

Fig. 2. *ORTEP drawing of* **2d**. Arbitrary numbering.

[4]) *K. N. Houk*, private communication.

Table 8. *Selected Bond Distances* [Å] *and Bond Angles* [°] *in* **2d**[a])

C(1)–C(2)	1.498(27)	C(1)–C(2)–N(3)	111.7(1.4)	C(7)–C(8)–C(1)	61.4(1.1)
C(2)–N(3)	1.471(23)	C(1)–C(2)–C(6)	92.9(1.3)	C(8)–C(1)–C(2)	108.5(1.4)
N(3)–N(4)	1.393(18)	C(8)–C(7)–C(1)	61.4(1.1)	C(8)–C(1)–C(7)	56.9(1.1)
N(4)–C(5)	1.339(25)	N(3)–N(4)–C(5)	108.3(1.4)	C(2)–N(3)–N(4)	109.5(1.2)
C(5)–C(6)	1.477(27)	C(2)–C(6)–C(5)	98.0(1.4)	C(6)–C(2)–N(3)	106.8(1.3)
C(6)–C(2)	1.580(22)	C(2)–C(6)–C(7)	86.1(1.3)	C(7)–C(1)–C(2)	85.3(1.3)
C(6)–C(7)	1.454(26)	N(4)–C(5)–C(6)	117.1(1.5)	N(3)–S(11)–O(12)	101.4(0.6)
C(7)–C(8)	1.485(23)	C(5)–C(6)–C(7)	114.7(1.5)	N(3)–S(11)–O(13)	112.4(0.6)
C(8)–C(1)	1.556(24)	C(6)–C(7)–C(8)	112.6(1.5)	N(3)–S(11)–C(14)	106.7(0.6)
C(7)–C(1)	1.559(23)			O(13)–S(11)–C(14)	109.1(0.6)
C(8)–C(9)	1.578(24)			C(6)–C(7)–C(1)	95.5(1.4)
C(8)–C(10)	1.496(24)				
N(3)–S(11)	1.636(12)				
O(12)–S(11)	1.392(09)				
O(13)–S(11)	1.399(11)				

[a]) The numbers refer to the first molecule of the asymmetric unit. The second molecule (B) has the same geometry, but bond distances may differ up to 0.04 Å and bond angles up to 3 degrees. For numbering scheme, see *Fig. 2*.

applied. The structure was solved by direct methods using the program SHELXS-86 [9]. Two independent molecules were localized per asymmetric unit. Anisotropic least-squares refinements using 1314 independent reflections were carried out in the SHELX-76 program [10], introducing H-atoms which were localized from final ΔF maps and refined positionally fixing U_{iso} to 0.06. The refinements were stopped when Δ/s was less than 0.1 for all H-atoms. Scattering factors for neutral atoms were taken from *Cromer et al.* [11], except those for H-atoms which are from *Stewart et al.* [12]. *Table 7* gives the positional and thermal parameters, and *Table 8* summarizes a sclection of relevant bond distances and bond angles. *Fig. 2* shows an ORTEP plot of **2d**.

The support of the *Centre National de la Recherche Scientifique* (UA-135) is gratefully acknowledged, especially for a Ph.D. grant to *F. K.* We wish to thank Dr. *F. Gobert* and the *Rhone-Poulenc Company* for the NOE measurements and for a research grant to *P. G.*

Experimental Part

General. Flash chromatography (FC) [8]: silica gel (*Merck 60;* 230–400 mesh). TLC: alumina roll (*Merck 60 F_{254}*). M.p.: *Kofler* hot bench or *Büchi SMP 20* apparatus; corrected. UV spectra (λ_{max} in nm (ε)): *Varian Techtron 635*. IR spectra (cm^{-1}): *Perkin-Elmer 157-G*. ^1H- and ^{13}C-NMR spectra: *Varian T-60, Bruker WP-80-DS* and *WH-360,* using double-irradiation techniques; NOE measurements were performed under normal atmosphere, TMS (^1H-NMR) and $CDCl_3$ (77.00 ppm with respect to TMS; ^{13}C-NMR) as internal references; δ in ppm and J in Hz. High-resolution (HR) MS: *MAT-311* spectrometer; measured at the University of Rennes. Microanalyses were carried out by the Service Central de Microanalyses of the *CNRS*.

1-(8,8-Dimethyl-3,4-diazabicyclo[5.1.0]octa-2,5-dien-4-yl)ethanone (**1c**) *and 1-(3,3-Dimethyl-6,7-diazatricyclo[3.3.0.0^{2,4}]oct-7-en-6-yl)ethanone* (**2c**). To a stirred soln. of **1a** [3] [4] (0.45 g, 1.87 mmol) in benzene (20 ml) was added 1N NaOH/MeOH (20 ml) at r.t. unter N_2. After 45 min, the mixture was poured into H_2O (50 ml) and the resulting soln. extracted several times with $CHCl_3$. The combined org. solns. were washed with H_2O, dried ($MgSO_4$), and evaporated. The resulting oil was treated with pyridine (10 ml) and Ac_2O (2 ml). After 6 h at r.t., the solvent was evaporated and the oily residue separated by FC (EtOAc/cyclohexane 4:6): **1c** (30 mg, 16%) and **2c** (223 mg, 68%).

1c: Colourless oil. B.p. 60°/10^{-2} Torr. UV (EtOH): 249 (9200). IR ($CHCl_3$): 1670, 1630. ^{1}H-NMR ($CDCl_3$, 60 MHz): 7.23 (*d*, *J* = 9.5, H–C(5)); 6.96 (br. *s*, H–C(2)); 5.1 (*m*, H–C(6)); 2.4 (*s*, CH_3CO); 1.73 (*m*, H–C(1), H–C(7)); 1.33 (*s*, Me_{endo}–C(8)); 0.86 (*s*, Me_{exo}–C(8)). Anal. calc. for $C_{10}H_{14}N_2O$ (178.11): C 67.38, H 7.92, N 15.72; found: C 67.0, H 7.9, N 15.4.

2c: Colourless oil. B.p. 75°/10^{-2} Torr. UV (EtOH): 292 (135, sh), 244 (11000). IR ($CHCl_3$): 1645. ^{1}H-NMR: see *Table 1*. ^{13}C-NMR: see *Table 2*. HR-MS: 178.1111 ($C_{10}H_{14}N_2O$, calc. 178.110606).

3,3-Dimethyl-6,7-diazatricyclo[3.3.0.0^{2,4}]oct-7-en-6-yl Phenyl Ketone (**2a**). To a stirred soln. of **1a** (550 mg, 2.3 mmol) in MeOH (20 ml) was added Na_2CO_3 (550 mg, *ca.* 5 mmol). This mixture was heated at reflux for 1 h, cooled to r.t., filtered, and the soln. evaporated. The resulting oily residue was dissolved in pyridine (50 ml) to which benzoyl chloride (0.27 ml, 2.3 mmol) was added with a graduated syringe. The mixture was heated at reflux for 1 h, the solvent evaporated and the resulting mixture separated by FC (Et_2O/cyclohexane 4:6): **2a** (170 mg, 31%) as colourless crystals. M.p. 92° (hexane). IR (KBr): 1630, 1570, 1450, 1425. UV (MeOH): 257 (11200). ^{1}H-NMR: see *Table 1*. ^{13}C-NMR: see *Table 2*. Anal. calc. for $C_{15}H_{16}N_2O$ (240.29): C 74.97, H 6.71, N 11.65; found: C 74.8, H 6.8, N 11.7.

8,8-Dimethyl-4-tosyl-3,4-diazabicyclo[5.1.0]octa-2,5-diene (**1d**) *and 3,3-Dimethyl-6-tosyl-6,7-diazatricyclo-[3.3.0.0^{2,4}]oct-7-ene* (**2d**). Same procedure as above, using **1a** (550 mg, 2.3 mmol) and replacing benzoyl chloride with tosyl chloride (436 mg, 2.3 mmol). The resulting mixture was separated by CC using gradient elution (Et_2O/cyclohexane 2:8 to 5:5): methyl benzoate (100 mg), **1d** (130 mg, 20%), and **2d** (280 mg, 42%).

1d: Colourless crystals. M.p. 132° (benzene/hexane). ^{1}H-NMR ($CDCl_3$, 60 MHz): 7.0 (*d*, *J* = 10, H–C(5)); 6.95 (*m*, H–C(2)); 5.0 (*ddd*, *J* = 10, 4, 2, H–C(6)); 1.70 (*m*, H–C(1), H–C(7)); 1.30 (*s*, Me_{endo}); 0.67 (*s*, Me_{exo}). Anal. calc. for $C_{15}H_{18}N_2O_2S$ (290.38): C 62.04, H 6.24, N 9.64; found: C 61.9, H 6.0, N 9.5.

2d: Colourless crystals. M.p. 152.5° (benzene/hexane). UV (MeOH): 240 (9800), 225 (10800). IR (KBr): 3065, 3050, 1595, 1350. ^{1}H-NMR: see *Table 1*. Anal. calc. for $C_{15}H_{18}N_2O_2S$ (290.38): C 62.04, H 6.24, N 9.64; found: C 62.0, H 6.1, N 9.8.

2,2,2-Trifluoro-1-(8,8-dimethyl-3,4-diazabicyclo[5.1.0]octa-2,5-dien-4-yl)ethanone (**1e**) *and 2,2,2-Trifluoro-1-(3,3-dimethyl-6,7-diazatricyclo[3.3.0.0^{2,4}]oct-7-en-6-yl)ethanone* (**2e**). To a stirred suspension of K(*t*-BuO) (700 mg, 6.25 mmol) in anh. benzene (20 ml) was added dropwise under Ar a soln. of **1b** [3] [4] (1 g, 4.8 mmol) in benzene (10 ml). After 15 min, MeOH (4 ml) was added, the mixture evaporated, and the residue taken up with chilled H_2O. The aq. soln. was extracted several times with CH_2Cl_2, the resulting org. phase dried ($MgSO_4$) and evaporated. To the residue in pyridine (15 ml) was added dropwise a 20% $(CF_3CO)_2O$ soln. in pyridine. After 1 d at r.t., the mixture was evaporated, some toluene having been added twice to assist the evaporation. The residue was separated by FC (Et_2O/cyclohexane 4:6); **1e** (57 mg, 5%) and **2e** (130 mg, 12%).

1e: ^{1}H-NMR ($CDCl_3$): 7.17 (*m*, H–C(2)); 7.10 (*d*, *J* = 10, H–C(5)); 5.45 (*ddd*, *J* = 10, 3, 2, H–C(6)); 1.85 (*m*, H–C(1), H–C(7)); 1.43 (*s*, Me_{endo}); 0.97 (*s*, Me_{exo}).

2e: Colourless crystals. M.p. 64° (Et_2O). UV (MeOH): 242 (11500), 210 (4100). IR (KBr): 1690, 1590, 1465, 1430. ^{1}H-NMR: see *Table 1*. HR-MS: 232.0821 ($C_{10}H_{11}F_3N_2O$, calc. 232.08234).

*(±)-N-[2-(*cis-*and* trans-*2'-Cyano-3',3'-dimethylcyclopropyl)ethenyl]benzamide* (**3** and **4**, resp.). To a stirred suspension of K(*t*-BuO) (700 mg, 6.25 mmol) in anh. benzene (10 ml) under Ar was added dropwise a soln. of **1a** (500 mg, 2 mmol) in anh. benzene (10 ml). The mixture turned instantly orange and became slowly viscous. After 10 min, MeOH (1 ml) was added whereby the colour faded and the mixture became fluid. After evaporation, the residue was dissolved in CH_2Cl_2, the soln. washed several times with brine until neutrality, dried ($MgSO_4$), and evaporated, and the residue separated by FC (EtOAc/cyclohexane 2:8): **3** (180 mg, 36%) and **4** (120 mg, 24%; less polar). They could not be purified by vacuum distillation (isomerization).

3: Slightly yellow oil. UV (MeOH): 265 (9700), 218 (12000). IR ($CHCl_3$): 3450, 2240, 1675. ^{1}H-NMR: see *Table 4*. ^{13}C-NMR: see *Table 5*. MS: 240 (240.29, $M^{+\cdot}$, $C_{15}H_{16}N_2O$).

4: Slightly yellow oil. UV (MeOH): 265 (11200), 215 (13100). IR ($CHCl_3$): 3450, 2240, 1680. ^{1}H-NMR: see *Table 4*. ^{13}C-NMR: see *Table 5*. MS: 240 (240.29, $M^{+\cdot}$, $C_{15}H_{16}N_2O$).

1-(2,8,8-Trimethyl-3,4-diazabicyclo[5.1.0]octa-1,5-dien-4-yl)ethanone (**6**). To a stirred suspension of K(*t*-BuO) (950 mg, 8.48 mmol) in anh. benzene (20 ml) under Ar was added a soln. of **5** [4] (809 mg, 3.2 mmol). The mixture turned instantly orange. After 10 min, Ac_2O (2 ml) was added whereby the coulour disappeared. Et_2O (20 ml) was added, the mixture washed several times with H_2O, then with brine until neutrality, dried ($MgSO_4$), and evaporated. FC of the crude mixture (AcOEt/cyclohexane 4:6) led to **6** as a colourless crystalline compound (277 mg, 45%). M.p. 43–44° (hexane at low temp.). UV (EtOH): 255 (9700). IR ($CHCl_3$): 1675, 1640. ^{1}H-NMR ($CDCl_3$, 60 MHz): 7.10 (*d*, *J* = 9, H–C(5)); 5.06 (*ddd*, *J* = 9, 2, 2.5, H–C(6)); 2.35 (*s*, CH_3CO); 2.06 (*s*, Me–C(2)); 1.63 (*m*, H–C(1), H–C(7)); 1,31 (*s*, Me_{endo}); 0.91 (*s*, Me_{exo}). Anal. calc. for $C_{11}H_{16}N_2O$ (192.25): C 68.72, H 8.39, N 14.57; found: C 68.7, H 8.4, N 14.5.

Hydrolyses of **2e**. For the small-scale experiments performed in NMR tubes, a soln. of **2e** (20 mg) in MeOH (3 ml), in the presence of Na_2CO_3 (20 mg), was treated at reflux for 2 d, evaporated, dissolved in C_6D_6, and the ^{1}H-NMR of **1f** determined: see *Table 6* (5.67 (*dd*, J = 9.5, 5, H–C(5))).

A similar experiment in MeOD led to a ^{1}H-NMR in which the coupling constant ^3J = 5 no longer appeared (5.67 (*d*, J = 9.5, H–C(5))).

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