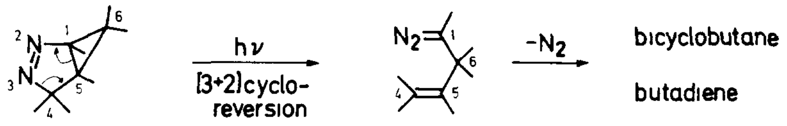
Tetrahedron Letters No. 18, pp 1571 - 1574.
0040-4039/79/0429-1571$02.00/0

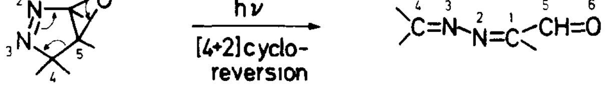
PHOTOCHEMICALLY INDUCED [4+2]- VERSUS [3+2]-CYCLOREVERSION REACTION OF HEXASUBSTITUTED 2,3-DIAZA-BICYCLO[3.1.0]HEX-2-ENES [1,2]

Gunter Ege, Karlheinz Gilbert and Birgit Hahn
Organisch-Chemisches Institut der Universitat
Im Neuenheimer Feld 270, D-6900 Heidelberg 1

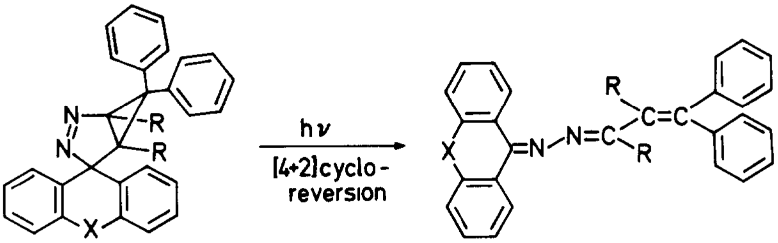
Hexasubstituted 2,3-diaza-bicyclo[3.1.0]hex-2-enes containing large substituents at C-4 and C-6 upon irradiation undergo a novel [4+2]cycloreversion reaction leading to 2,3-diaza-hexatrienes besides the normal [3+2]cycloreversion.

Upon irradiation 2,3-diaza-bicyclo[3.1.0]hex-2-enes react in a [3+2]cycloreversion reaction under cleavage of a C-N-bond to give diazo compounds or secondary products, respectively[3]. On the contrary 2,3-diaza-6-oxa-bicyclo-[3.1.0]hex-2-enes show a [4+2]cycloreversion photoreaction without cleavage of a C-N-bond[4].





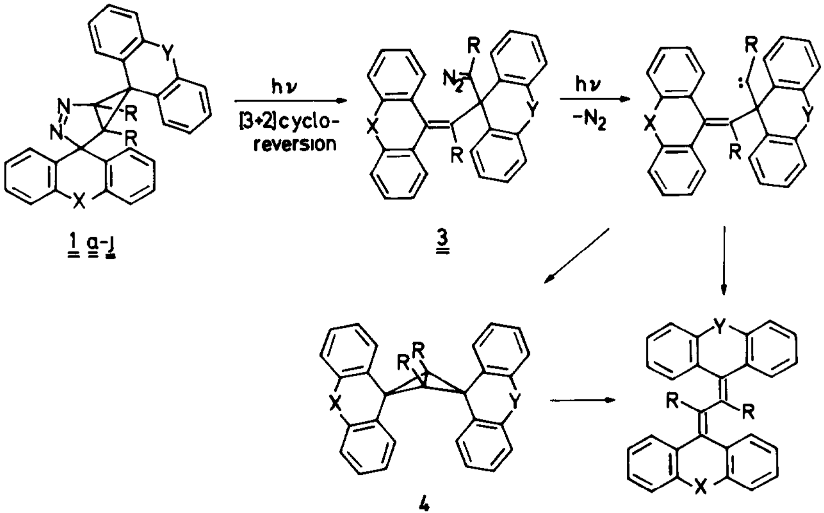
We now report the first photochemically induced [4+2]cycloreversion reaction of a 2,3-diaza-bicyclo[3.1.0]hex-2-ene. On irradiation (Hanovia 450 Watt, quartz, THF as solvent, 15°C) the 7-ring compounds **1a** and **1b** isomerize to the yellow 2,3-diaza-hexatrienes **2a** and **2b**, respectively (see table 1).



1 a,b 2 a,b

1,2	X	R
a	CH=CH	$COOCH_3$
b	CH_2-CH_2	$COOCH_3$

In addition to the [4+2]cycloreversion-products 2a and 2b the bicyclic systems 1a and 1b also yield the photolysis-products 5a and 5b, respectively, secondary products of a [3+2]cycloreversion reaction. Compounds 1c - 1j, however, when irradiated do not lead to [4+2]cycloreversion-products of type 2. Instead, in a normal [3+2]cycloreversion reaction the diazo compounds 3 and/or their degradation products 4 and 5 are formed exclusively (see table 2). The diazo compounds 3 are obtained as primary products only on irradiation at -60°C. Obviously the type of the ring cleavage, [4+2] versus [3+2], depends on the substituents of the diazabicyclohexene 1.



The initial step in the [3+2]cycloreversion of 1 is probably the cleavage of the N^3-C^4-bond, whereas in the [4+2]cycloreversion of 1 the cleavage of the C^4-C^5-bond takes place. Framework models of the diazabicyclic systems 1a - 1e,

Table 1 : Data of diaza-hexatrienes 2 [a].

2	yield [%]	m.p. [°C]	UV (CH_2Cl_2) λ_{max} [nm] (ε)	^{1}H-NMR (δ, $CDCl_3$/TMS, 60 MHz)
a	53	247	375(9500), 297(24700) 275(28900), 233(41700)	3.42(s; 3H, OCH_3), 3.51(s; 3H, OCH_3) 6.90(s; 2H, CH=CH), 7.0-8.2(m; 18H)
b	15	213	375(5400), 308(18600) 257(20700), 232(27100)	3.17(s; 4H, CH_2-CH_2), 3.40(s; 3H, OCH_3), 3.43(s; 3H, OCH_3), 6.7-7.6(m; 17H), 7.8-8.0(m; 1H)

Table 2: Yields, melting points of compounds 3, 4, 5 and diazo band of 3 [a

1 $^{6)}$, 3 , 4 , 5	X	Y	R
a	CH=CH	H , H	$COOCH_3$
b	CH_2-CH_2	H , H	$COOCH_3$
c	H , H	H , H	$COOCH_3$
d	zero-bridge	H , H	$COOCH_3$
e	- O -	H , H	$COOCH_3$
f	H , H	zero-bridge	$COOCH_3$
g	H , H	zero-bridge	$COCH_3$
h	zero-bridge	zero-bridge	$COOCH_3$
i	H , H	$C(CH_3)_2$	$COOCH_3$
j	H , H	CH_2-CH_2	$COOCH_3$

3 , 4 , 5	yield [%]			m.p. [°C]			$\nu_{N\equiv N}$ [cm^{-1}] of 3
	3	4	5	3	4	5	
a	[b]	0	8	-	-	89-92	-
b	[b]	0	28	-	-	125-128	-
c	90	11	4	155-160	168-170	228-230	2090
d	6	0	31	170-172	-	141[c]	2080
e	[b]	0	16	-	-	182-184	-
f	30	0	13	146-147	-	141[c]	2105
g	[b]	0	14	-	-	181-182	-
h	3	0	9	oil[d]	-	220-222	2100
i	5	0	37	132-134	-	198-199	2080
j	6	0	30	134-136	-	oil[d]	2080

[a] The analytical data (microanalyses and/or mass spectra, ^{1}H-NMR, IR, UV) of all products are in accordance with the assigned structures.

[b] No reaction performance.

[c] The compounds 5d and 5f are identical. [d] Not pure.

which differ in their substituents at C-4, show an increase of repulsion between the endo phenylgroup at C-6 and the aromatic substituents at C-4 in the order non-bridged(1c) < spiro-5-ring(1d) < spiro-6-ring(1e) < saturated spiro-7-ring(1b) < unsaturated spiro-7-ring(1a). The repulsion between large ligands at C-4 and C-6 of the diazabicyclohexene system 1 probably causes a distorsion along the C^4-C^5-bond and on excitation its cleavage. This may be the reason for the occurence of the [4+2]cycloreversion reaction.

This [4+2]cycloreversion represents the reverse reaction of the $[\pi_{4s}+\pi_{2a}]$-photocycloaddition of hexatrienes, the latter of which has been observed for carbon chains only[5].

References and notes :

1) Dedicated to Professor O.E. Polansky on the occasion of his 60th birthday.
2) Ring cleavage of cyclic azo compounds, 8th communication. This work was supported by the Deutsche Forschungsgemeinschaft, the BASF Aktiengesellschaft and the Haarmann+Reimer GmbH. - 7th communication: G. Ege, Ph. Arnold, E. Beisiegel, I. Lehrer, H. Suschitzky and D. Price, Liebigs Ann. Chem. 1976, 946.
3) M. Franck-Neumann and C. Buchecker, Tetrahedron Lett. 1969, 2659; B. Hahn, dissertation, Heidelberg, 1971; D.F. Eaton, R.G. Bergman and G.S. Hammond, J. Am. Chem. Soc. 94, 1351 (1972); P.G. Gassman and W.J. Greenlie, ibid. 95, 980 (1973); M. Franck-Neumann, D. Martina and C. Dietrich-Buchecker, Tetrahedron Lett. 1975, 1763; W. Welter and M. Regitz, ibid. 1976, 1473; M. Schneider and B. Csacsko, Angew. Chem. 89, 905 (1977); Angew. Chem. Int. Ed. Engl. 16, 867 (1977).
4) L.E. Friedrich, N.L. de Vera, W.P. Hoss and J.T. Warren, Tetrahedron Lett. 1974, 3139; L.E. Friedrich, N.L. de Vera and Y.-S.P. Lam, J. Org. Chem. 43, 34 (1978).
5) A. Padwa and S. Clough, J. Am. Chem. Soc. 92, 5803 (1970).
6) Synthesized by 1,3-dipolar cycloaddition of the corresponding cyclopropenes and the appropriate diazoalkanes: B. Hahn, cf. ref. 3) and K. Gilbert, projected dissertation, Heidelberg, 1979.

(Received in Germany 19 February 1979)