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69. Synthesis and Photochemical Behaviour of 2-Amino-1,3-cyclohexadienes

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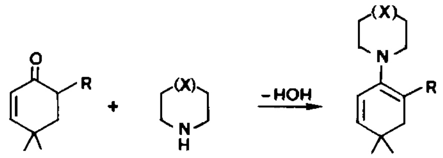
Summary

The reaction of the 4,4-dialkylated 2-cyclohexenones **1** or **2** with a twofold excess of a secondary amine **3** affords the 2-amino-1,3-cyclohexadienes **4** and **5**, respectively. Irradiation ($\lambda \geqq 300$ nm) of the morpholino derivative **4a** yields a mixture of the isomeric 3-morpholino-6-methyl-1,3,5-heptatrienes **6** and **7**, while **5** gives only one corresponding product **8**. The reaction of enone **1** with an equimolar amount of pyrrolidine (**3c**) affords the *bis*-enamine **9** which is converted to the unsaturated diketone **10** by oxidative hydrolysis.

Light induced electrocyclic conversion of 1,3-cyclohexadienes to 1,3,5-hexatrienes and further transformation of the primary photoproduct has become a preparative useful photochemical reaction [1] [2]. Some time ago we had reported [3] that a 2-amino-1,3-cyclohexadienecarbonitrile rearranges selectively to the *tEt*-hexatriene[2]). We now present results on the synthesis and the photochemical behaviour of simple 2-amino-1,3-cyclohexadienes.

Usually the reaction of 2-cyclohexenones with an excess of a secondary amine affords 1-amino-1,3-cyclohexadienes [4] [5]. A shift of the double bonds can be avoided by using 4,4-dialkylated 2-cyclohexenones. Thus the reaction of 4,4-di-

Scheme 1



1 R=H
2 R=CH_3

3a: X=O
3b: X=CH_2
3c: X= –

4 R=H
5 R=CH_3

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[1]) Part of the planned doctoral thesis, University of Hamburg.

[2]) This nomenclature for 1,3,5-hexatrienes describes the configuration of the single bonds C(2)–C(3) and C(4)–C(5) (small letters) and the double bond C(3)–C(4) (capital letter) [1].

Table 1. *Spectroscopic data of compounds* **4** *and* **5**[a])

	UV.[b])	IR. (liquid film)	^{1}H-NMR.[c]) ($CDCl_3$)	^{13}C-NMR.[d]) ($CDCl_3$)	MS. (70 eV)
4a	218 (3.94) 283 (3.28)	3030 1646 1590	5.70 (*d*×*d*, J = 10.1 and 2.0, H–C(3)) 5.57 (*d*, J = 10.1, H–C(4)) 4.62 (*d*×*t*, J = 4.7, 4.7 and 2.0, H–C(1)) 2.08 (*m*, 2 H, 2 H–C(6)) 0.95 (*s*, 6 H)	144.2 (*s*, C(2)), 139.8 (*d*, C(3)), 121.4 (*d*, C(4)), 98.7 (*d*, C(1)), 37.3 (*t*, C(6)), 31.0 (*s*, C(5)), 27.5 (*qa*, CH_3)	193 (M^+) *178*
4b	223 (3.93) 286 (3.24)	3035 1645 1585	5.73 5.55 4.62 [e]) 2.09 0.97	145.1 (*s*, C(2)), 139.1 (*d*, C(3)), 122.7 (*d*, C(4)), 98.4 (*d*, C(1)), 37.5 (*t*, C(6)), 30.9 (*s*, C(5)), 27.5 (*qa*, 2 CH_3)	191 (M^+) *176*
4c[f])		3040 1645 1580	5.90 5.55 4.25 [e]) 2.13 1.00		177 (M^+) *162*
5	238 (3.66) 270 (sh)	3030 1650 1590	5.87 (*d*, J = 10.1, H–C(3)) 5.46 (*d*, J = 10.1, H–C(4)) 2.02 (*m*, 2 H, 2 H–C(6)) 1.74 (*s*, 3 H) 0.94 (*s*, 6 H)	138.3 (*s*, C(2)), 136.9 (*d*, C(3)), 123.2 (*s*, C(1)), 118.6 (*d*, C(4)), 44.6 (*t*, C(6)), 31.1 (*s*, C(5)), 27.8 and 17.8 (2 *qa*, 3 CH_3)	207 (M^+) *192*

[a]) Satisfactory elemental analyses were obtained for **4a**, **4b** and **5**.

[b]) In cyclohexane.

[c]) Proton signals of amino component not given.

[d]) C-signals of amino component not given.

[e]) Assignement and coupling constants as above.

[f]) Data for crude product; attempts to purify **4c** were unsuccessful.

methyl- or 4,4,6-trimethyl-2-cyclohexenone with a twofold excess of morpholine, piperidine or pyrrolidine gives the 2-amino-1,3-cyclohexadienes **4** and **5** in acceptable to good yields *(Scheme 1)*. Dienamines **4a**, **4b** and **5** can be stored at – 15° under N_2 for long periods while **4c** decomposes relatively fast. The spectroscopic data of compounds **4** and **5** are summarized in *Table 1*.

Irradiation ($\lambda \geqq 300$ nm) of the morpholino compounds **4a** and **5**, as monitored by ^{1}H-NMR. spectroscopy, leads to complete conversion of starting material. While **4a** affords a 2:1 mixture of **6** and **7**, **5** is converted selectively to one new product **8**. Photoproducts **6–8** have a 1,3,5-hexatriene structure as deduced from their UV.- and ^{1}H-NMR. spectra. The configuration of trienes **6–8** was assigned by ^{1}H-NMR. analysis *(Scheme 2, Table 2)*.

Scheme 2

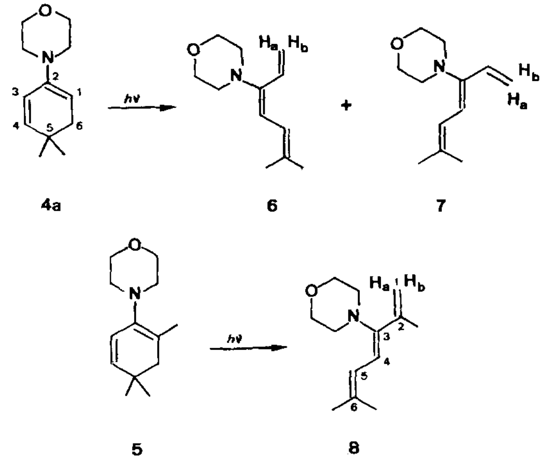


Table 2. *Spectroscopic data of compounds* **6**, **7** *and* **8**

	UV.[a]	^{1}H-NMR.[b]	
6	259 (3.74)[c]	6.43 (*d*×*d*, *J* = 17.2 and 10.8, H–C(2))	3.47 (*m*, 4 H–C(2′))
	303 (3.69)	6.23 (*d*×*m*, *J* = 11.1, H–C(5))	2.59 (*m*, 4 H–C(3′))
		5.57 (*d*×*d*, *J* = 11.1 and 1.2, H–C(4))	
		5.47 (*d*×*d*, *J* = 17.2 and 2.5, H_a–C(1))	
		5.12 (*d*×*d*×*d*, *J* = 10.8, 2.5 and 1.2, H_b–C(1))	
		1.67 and 1.62 (*m*, 2 CH_3)	
7		6.37 (*d*×*m*, *J* = 11.4, H–C(5))	3.47 (*m*, 4 H–C(2′))
		6.17 (*d*×*d*, *J* = 16.9 and 10.8, H–C(2))	2.80 (*m*, 4 H–C(3′))
		5.93 (*d*, *J* = 11.4, H–C(4))	
		5.45 (*d*×*d*, *J* = 16.9 and 1.9, H_a–C(1))	
		4.93 (*d*×*d*, *J* = 10.8 and 1.9, H_b–C(1))	
		1.66 and 1.58 (*m*, 2 CH_3)	
8	265 (3.77)	6.30 (*d*×*m*, *J* = 10.8, H–C(5))	3.47 (*m*, 4 H–C(2′))
		5.38 (*d*, *J* = 10.8, H–C(4))	2.59 (*m*, 4 H–C(3′))
		5.15 (*d*×*qa*, *J* = 2.5 and 1.5, H_a–C(1))	
		5.07 (*d*×*qa*, *J* = 2.5 and 1.0, H_b–C(1))	
		1.79 and 1.77 (*m*, 2 H_3C–C(6) and H_3C–C(2))	

[a] In cyclohexane. [b] In hexadeuteriobenzene. [c] Corresponds to a 2:1 mixture of **6** and **7**.

Table 3. *Spectroscopic data of compounds* **9** *and* **10**[a])

	UV. (C_6H_{12})	IR. (KBr)	^{1}H-NMR.[b]) ($CDCl_3$)	^{13}C-NMR.[c]) ($CDCl_3$)	MS. (70 eV)
9	244 (3.10)	3040	4.41 (*d*×*d*, *J* = 7.1 and 2.2, H–C(3))	146.9 (*s*, C(2))	354 (M^+)
		1675	3.11 (*d*, *J* = 7.1, H–C(4))	130.4 (*s*, C(5))	*242*
		1610	2.70 (*m*, *J* = 2.8, 2.8 and 2.2, H–C(1))	129.5 (*s*, C(4a))	
			2.09 (*m*, *J* = 16.8, 1.8 and 1.8, H_a–C(6))	94.1 (*d*, C(3))	
			1.98 (*m*, *J* = 16.8, 8.7 and 7.2, H_b–C(6))	49.3 (*d*), 44.9 (*d*), 44.8 (*t*)	
			1.89 (*m*, H–C(8a))	39.2 (*t*), 35.7 (*d*)	
			1.40 (*m*, *J* = 12.8, 8.7 and 1.8, H_a–C(7))	33.3 (*s*), 31.8 (*s*)	
			1.31 (*m*, *J* = 12.8, 7.2 and 1.8, H_b–C(7))	31.3 (*qa*), 31.2 (*qa*)	
			1.28 (*d*×*d*, *J* = 12.1 and 2.8, 2 H–C(10))	29.5 (*qa*), 20.1 (*t*, C(10))	
			1.19 (*d*×*d*, *J* = 12.1 and 2.8, 2 H–C(10))	18.2 (*qa*)	
			0.96, 0.94, 0.86, 0.49 (4 *s*, 4 CH_3)		
10	298 (2.97)	1720	3.28 (*t*, *J* = 2.3, H–C(1))	210.7 (*s*, C(2))	*246* (M^+)
	254 (3.98)	1660	3.14 (*d*×*d*, *J* = 3.2 and 2.4, H–C(4))	194.3 (*s*, C(5))	
	246 (3.97)	1610	2.48 (*m*, 2 H–C(6))	161.3 (*s*, C(8a))	
			2.42 (*d*×*d*, *J* = 19.2 and 2.4, H_a–C(3))	139.1 (*s*, C(4a))	
			1.89 (*m*, 2 H–C(7))	51.9 (*d*, C(1))	
			1.83 (*d*×*d*, *J* = 19.2 and 3.2, H_b–C(3))	39.9 (*d*, C(4))	
			1.74 (*d*×*d*, *J* = 13.5 and 2.3, 2 H–C(10))	39.3 (*t*), 37.5 (*t*), 36.2 (*t*)	
			1.40 (*d*×*d*, *J* = 13.5 and 2.3, 2 H–C(10))	34.4 (*s*), 33.9 (*t*), 33.7 (*s*)	
			1.15, 1.12, 0.84 (3 *s*, 4 CH_3)	31.1 (*qa*), 28.2 (*qa*)	
				26.1 (*qa*), 25.3 (*qa*)	

[a]) Both compounds gave satisfactory elemental analyses.

[b]) Proton signals of amino component not indicated.

[c]) Carbon signals of amino component not indicated.

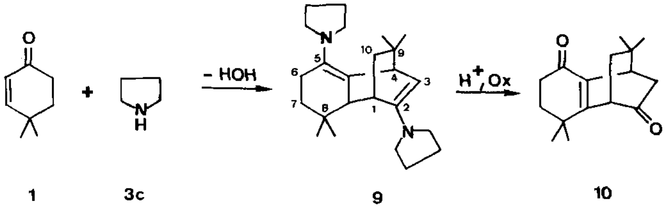
The *tZt*-configuration of **6** was assigned on the basis of the magnitude of the vicinal and long-range coupling constants of H–C(4) with H–C(5) and H_b–C(1) respectively [6]. The *cEt*-configuration of the minor product **7** was determined basing on: *a*) an upfield shift of 0.25 ppm for H–C(2), and downfield shifts of 0.35 ppm for H–C(4), of 0.15 ppm for H–C(5) and of 0.20 ppm for the H–C(3′) of the amino component as compared to **6**; such differences in chemical shifts being typical for a (*Z*)- and (*E*)-enamine couple [4]; *b*) the magnitude of the vicinal coupling constant between H–C(4) and H–C(5).

The assignement of the *tEt*-configuration for **8** is more tentative, being based in part on the fact that 2,3-disubstituted 1,3,5-hexatrienes will adopt this thermodynamically most stable configuration [7], although a *cZt*-configuration cannot be completely excluded. The same *all-trans*-configuration had been assigned to 3-*N*- and 3-*O*-substituted 2-cyano-1,3,5-hexatrienes [3].

In order to compare the relative rate of formation of **6** and **7** on the one side and **8** on the other side, solutions of **4a** and **5** (10^{-3} M in cyclohexane) were irradiated ($\lambda \geq 305$ nm) in a *merry-go-round* apparatus. The increase in absorbance at $\lambda = 340$ or 350 nm indicates that **4a** is converted to trienes twice as fast as **5**.

The reaction of **1** with an equivalent amount of pyrrolidine (**3c**) affords the *bis*-enamine **9** as already described in the literature [8]. Compound **9** is possibly formed by [4+2]cycloaddition of **4c** to **1** followed by reaction of the intermediate carbonyl-enamine with a second molecule of pyrrolidine to give selectively the product with the tetrasubstituted double bond.

Scheme 3



Hydrolysis of **9** under acidic conditions afforded moderate yields of the corresponding tricyclic diketone [8]. Oxydative hydrolysis of **9** in our hands gave the unsaturated diketone **10** in good yields (*Scheme 3, Table 3*). The photochemical behaviour of **10**, a compound containing an α,β- and β,γ-enone moiety, will be described elsewhere.

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Experimental Part

General. Absorptions in the UV. spectra are given in nm(logε) and in the IR. spectra in cm^{-1}. Chemical shifts in the ^{1}H- (400 MHz) and ^{13}C- (20.17 MHz) NMR. spectra are given in ppm relative to TMS (= 0 ppm) as internal standard.

Starting materials. Enones **1** [9] and **2** [10] were synthesized according to the references indicated. Amines **3** were purified by distillation.

Preparation of 2-amino-1,3-cyclohexadienes **4** *and* **5**. A solution of the enone (4.10^{-2} mol) and amine (8.10^{-2} mol) in 30 ml toluene is refluxed under N_2 for 15-35 h until all the water has separated on a *Dean-Stark* trap. After evaporation of the solvent the residue is distilled at reduced pressure: **4a** (66%, b.p. 108°/6 Torr), **4b** (68%, b.p. 43°/0.01 Torr), **4c** (35%, b.p. 70-80°/0.01 Torr), **5** (34%, b.p. 110°/4 Torr).

Photolyses. a) Ar-degassed solutions of 2.10^{-4} mol **4a** or **5** in 0.4 ml C_6D_6 were irradiated (λ = 300 nm) in a quartz NMR. tube in a *Rayonet* photoreactor for 10 h. The degree of conversion as measured by ^{1}H-NMR. was > 90%.

b) Ar-degassed solutions of **4a** or **5** (10^{-5}M in cyclohexane) were irradiated (λ > 305 nm) in an UV. cell on an optical bench using a 250 W-Hg lamp and a $SnCl_2$ filter solution [11]. The formation of **6-8** was monitored by UV. spectroscopy.

c) Ar-degassed solutions of **4a** and **5** (1.7 · 10^{-3}M in cyclohexane) were irradiated as under *b)* using a *merry-go-round* set-up for the UV. cells. The relative rates of formation of **6** and **7** and of **8** were monitored by UV. spectroscopy at λ = 340 and 350 nm.

Preparation of 2,5-dipyrrolidino-8,8,9,9-tetramethyl-1,4-ethano-1,4,6,7,8,8a-hexahydronaphthalene (**9**). A solution of **1** (12.4 g, 0.1 mol) and **3c** (7.1 g, 0.1 mol) in toluene (50 ml) is refluxed under N_2 for 3 h until all the water has separated on a *Dean-Stark* trap. Evaporation of the solvent and recrystallization of the residue from AcOEt affords 15.7 g (88%) **9**, m.p. 125-126° ([8]: 119°).

Preparation of 8,8,9,9-tetramethyl-1,4-ethano-1,3,4,6,7,8-hexahydro-2,5-naphthalenedione (**10**). A solution of **9** (3.54 g, 0.01 mol) in benzene (30 ml) is added dropwise at 0° to 8.95 g sodium dichromate in a mixture of 70 ml acetic acid/benzene 4:3. Stirring is then continued for 3 h. After addition of 30 ml MeOH and further stirring for 30°, an excess of 2N NaOH is added, the benzene layer separated, and the alcaline aqueous phase extracted four times with 50 ml benzene. The combined organic phases are washed with H_2O and with a sat. aq. NaCl-solution and dried. Evaporation of the solvent and recrystallization of the residue from ether/pentane affords 1.3 g (53%) **10**, m.p. 97-99°.

REFERENCES

[1] *W.G. Dauben, E.L. McInnis & D.M. Michno,* in 'Rearrangements in Ground and Excited States', Vol. 3 (P. de Mayo, editor), Academic Press 1980, p. 91.
[2] *P. Margaretha,* Topics in Current Chem. *103,* 1 (1982).
[3] *P. Margaretha,* Helv. Chim. Acta *58,* 929 (1975).
[4] *P.W. Hickmott,* Tetrahedron *38,* 1975 & 3363 (1982).
[5] *G. Opitz & W. Merz,* Liebigs Ann. Chem. *652,* 139 (1962).
[6] *J.W. Laing, M.G. Sceats, S.A. Rice & R.M. Gavin,* Chem. Phys. Letters *41,* 419 (1976).
[7] *J.C. Tai & N.L. Allinger,* J. Amer. Chem. Soc. *98,* 7928 (1976).
[8] *J.W. Lewis & P.L. Myers,* J. Chem. Soc. C *1971,* 753.
[9] *M.E. Flaugh, T.A. Crowell & D.S. Farlow,* J. Org. Chem. *45,* 5399 (1980).
[10] *C. Paris, S. Geribaldi, G. Torri & M. Azzaro,* Bull. Soc. Chim. Fr. *1973,* 997.
[11] *H.E. Zimmerman,* Mol. Photochem. *3,* 281 (1971).