84. Photochemistry of *N*-(2-Cyclohexen-1-ylidene)alkylamines

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Summary

Irradiation (λ = 254 nm) of *N*-(4,4,6,6-tetramethyl-2-cyclohexen-1-ylidene)-1,1,3,3-tetramethylbutylamine (**1d**) in cyclohexane affords *N*-(3-cyclohexyl-4,4,6,6-tetramethyl-2-cyclohexen-1-ylidene)-1,1,3,3-tetramethylbutylamine (**7d**), which in turn is photodecomposed by light of the same wavelength, but at a four times slower rate than it is formed. The rate of formation of photoproduct **7d** is a function of the concentration of starting material **1d**, suggesting the involvement of a bimolecular (**1d*** + **1d**) step. The structure of **7d** was established by spectroscopy and by its hydrolysis to 3-cyclohexyl-4,4,6,6-tetramethyl-2-cyclohexenone (**8**). The previously made assumption that *N*-(2-cyclohexen-1-ylidene)cyclohexylamine (**1a**) and 2,3,4,4a,5,6-hexahydroquinolines **2** photorearrange to *N*-cyclohexylidenecyclohexanamine **3a** and 3,4,4a,5,6,8a-hexahydroquinolines **4**, respectively, *via* a light-induced 1,3-hydrogen shift proves incorrect.

In a preliminary communication [1] we had reported that enimines **1a**, **2a** and **2b** were photodecomposed in cyclohexane with light of λ = 254 nm, no such reaction being observed on n-π^* (λ = 300 nm) excitation. When monitoring the reaction by UV spectroscopy the building up of a new absorption band with $\lambda_{max} \approx$ 265–270 nm was observed. Although we were unable to isolate any photoproduct, we had proposed that this reaction from the S_2-state consisted in a 1,3-hydrogen shift with formation of the β,γ-unsaturated enimines **3a** and **4**, respectively *(Scheme 1)*. Such a reaction had a precedent in the photochemistry of saturated imines [2], and very often molecules react from a higher excited state by cleavage of the weakest bond next to the chromophore [3]. At that time almost no data on UV spectra of aliphatic β,γ-enimines were available[2]).

To clarify this aspect we have synthesized the *N*-(2-cyclohexen-1-ylidene)amines **1b–e** and investigated their photochemical behaviour on $\pi - \pi^*$ excitation. Monitoring the photolysis (λ = 254 nm) of enimines **1b–e** in cyclohexane by UV spectroscopy gave similar results as for the previously studied compound **1a**, *i.e.* the starting material is decomposed and a new absorption band with $\lambda_{max} \approx$ 265–280 nm is built up. Imines **1c**

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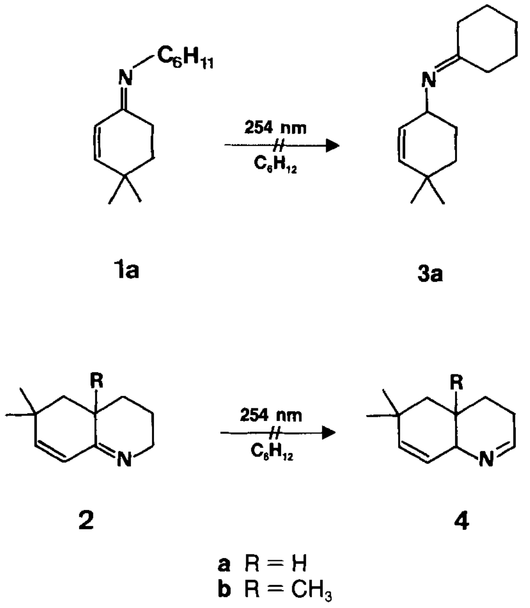
[1]) Taken in part from the Ph. D. thesis, University of Hamburg 1984.

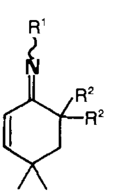
[2]) One of the few spectra given in the literature was that of *N*-isopropylidenephenylmethylamine with λ_{max} = 252 nm in $CHCl_3$ as solvent [4].

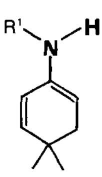
Scheme 1

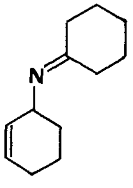


and **1e** cannot undergo the rearrangement originally proposed for **1a** as the C-atom next to the N-atom is tertiary, but on the other side an 1,3-H shift with formation of a 2-amino-1,3-cyclohexadiene **5** is still feasible [5]. Imine **1b** cannot undergo this latter reaction, and finally imine **1d** should be photostable if the proposed mechanism was correct. In order to further exclude the possibility of a β,γ-enimine formation we repeated the recently published synthesis of *N*-(2-cyclohexen-1-ylidene)-2-cyclohexylamine (**6**) [6]. The UV spectrum of this compound in cyclohexane exhibits a shoulder at 235 nm but almost zero absorption at λ > 265 nm.

1b $R^1 = C_6H_{11}$, $R^2 = CH_3$
c $R^1 = (CH_3)_3CCH_2(CH_3)_2C$, $R^2 = H$
d $R^1 = (CH_3)_3CCH_2(CH_3)_2C$, $R^2 = CH_3$
e $R^1 = (CH_3)_3C$, $R^2 = H$







5 **6**

Monitoring the photolysis (λ = 254 nm) of the enimines **1a–e** in cyclohexane or *i*-PrOH by GC/MS indicates the formation of more or less complex mixtures, compounds of the mass $M + RH - 2H$ ($R = C_6H_{11}$ or $(CH_3)_2COH$) being formed in amounts up to 30% *(Table 1)*. For **1d** the conversion to this new product **7d** being a rather clean process, this reaction was investigated in detail.

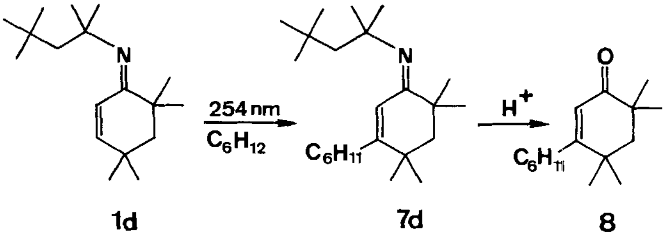
Table 1. *GC/MS-Analytical Data for Irradiation* (λ = 254 nm) *of Enimines* **1a–e** ($2 \cdot 10^{-3}$M)[a])

Compound	Solvent	Product distribution[b])		
		Starting material	Product (M + RH – 2H)	Others
1a	C_6H_{12}	29	8	63
1b	C_6H_{12}	32	13	55
1c	C_6H_{12}	21	2	77
1d	C_6H_{12}	59	31	10
	i-PrOH	8	11	81
1e	C_6H_{12}	47	7	46

[a]) *Rayonet RPR-100,* merry-go-round, 5-ml samples, 1.5 h.
[b]) Peak-area percentage.

Preparative irradiation (λ = 254 nm) of **1d** in cyclohexane afforded a new compound **7d** in 15–20% isolated yield. From the spectroscopic data summarized in *Table 2,* it becomes obvious that **7d** itself is also an α,β-unsaturated imine. The position of the cyclohexyl group on C(3) is clearly given by the chemical shifts and coupling constants in the ^{1}H- and ^{13}C-NMR spectra [7]. The structure of **7d** was further established by hydrolysis to 3-cyclohexyl-4,4,6,6-tetramethyl-2-cyclohexenone (**8**), which again can be unambiguously differentiated from its 2-cyclohexyl isomer by NMR spectroscopy [8]. When the photolysis (λ = 254 nm) of **7d** in cyclohexane is monitored by UV spectroscopy again the build-up of a band with λ_{max} = 279 nm is observed. This clearly demonstrates that the observation of this band is *not* linked to the photochemistry of enimines **1a–e** but to that of their primary photoproducts *(Scheme 2).*

Scheme 2



Monitoring the disappearance of **1d** and the formation of **7d** by GC with an internal standard (eicosane) shows that only 20–25% **7d** are formed at complete conversion of **1d**. Parallel irradiation (λ = 254 nm) of **1d** and **7d** (10^{-4}M in C_6H_{12}) indicates that **1d** is decomposed 4.3 times faster than **7d**. Irradiation of **1d** at different concentrations ($1.1 \cdot 10^{-3} - 1.1 \cdot 10^{-2}$M in C_6H_{12}) leads to the result shown in the *Figure, i.e.,* the formation of **7d** is enhanced at higher concentration of **1d**. This result suggests the involvement of a step wherein an excited molecule **1d** reacts with the same ground state species. A reasonable reaction step between **1d*** and **1d** seems to be formation of a radical ion pair *via* electron transfer. Subsequently the cation radical **9** will give product **7d** and starting material **1d** by interaction with the solvent (deprotonation of **9** and reaction of the vinyl radical with either $C_6H_{11}\cdot$ or $H\cdot$, or in an alternate sequence,

Table 2. *Spectroscopic Data of Compounds* **1d**, **6**, **7d**, **8** *and* **13**

Compound	UV (C_6H_{12})	IR (CCl_4)	^1H-NMR ($CDCl_3$)	^{13}C-NMR	MS (70 eV)
1d[a])	223 (4.24) 309 (2.22)	1640 1605	6.20 and 5.86 (*AB*, *J* = 10.5); 1.65 (*s*, 2H); 1.61 (*s*, 2H); 1.28 (*s*, 6H); 1.09 (*s*, 12H); 0.98 (*s*, 9H).	164.7, 145.4, 119.5, 58.4, 57.4, 50.3, 39.0, 32.3, 32.2, 31.6, 30.9, 29.1	263 (M^+) *192*
6	235 (sh, 2.76)	3030 1655 1640	5.87 and 5.49 (*m*, *AB*, *J* = 10.1); 4.09 (*m*, 1H); 2.4–2.3 (*m*, 4H); 1.9–1.5 (*m*, 12H).	171.8, 129.8, 128.7, 54.1, 40.3, 30.6, 29.2, 27.9, 27.5, 26.2, 24.9, 20.3	177 (M^+) *81*
7d[a])	234 (4.25) 307 (2.33)	1640 1610	6.08 (*s*, 1H); 1.97 (*m*, 1H); 1.62 (*s*, 2H); 1.8–1.6 (*m*, 4H); 1.52 (*s*, 2H); 1.23 (*s*, 6H); 1.2–1.1 (*m*, 6H); 1.02 (*s*, 6H); 0.98 (*s*, 6H); 0.89 (*s*, 9H).	166.0, 160.0, 116.7, 58.2, 57.0, 52.3, 40.0, 39.7, 35.3, 35.0, 32.2, 31.7, 29.0, 28.8, 27.1, 26.3	345 (M^+) *177*
8	230 (4.20) 320 (2.05)	1665 1615	5.79 (*s*, 1H); 2.10 (*m*, 1H); 1.75 (*s*, 2H); 1.8–1.6 (*m*, 4H); 1.4–1.2 (*m*, 6H); 1.21 (*s*, 6H); 1.14 (*s*, 6H).	204.6, 174.9, 122.1, 51.2, 40.8, 40.1, 36.2, 34.2, 28.6, 27.0, 26.5, 25.8	234 (M^+) *178*
13[b])	242 (sh, 2.35)	1655	3.28 (*m*, 1H); 2.6–1.1 (*m*, 19H); 0.9 (*d*, *J* = 6.3, 3H).		193 (M^+) *178*

[a]) (*Z*)-Isomer [7].
[b]) 3:2 mixture of diastereoisomers.

reaction of **9** with $C_6H_{11}^{\cdot}$ or $H^{\cdot}$ and deprotonation of the so-formed carbenium ion). The anion radical **10** is expected to give the reduced products **11** and **12**. As no saturated imines had been detected in the product mixture, we investigated the photostability of imine **13** to find that it is decomposed very fast by light of $\lambda = 254$ nm forming exclusively polymeric material but no trace of unsaturated imines *(Scheme 3)*.

Examples of photoalkylations (substitution of H by R) have been reported in the literature, *e.g.* for pyridine and other aromatic N-heterocycles [9]. The mechanism proposed for these reactions consists in H-atom abstraction from the solvent RH by the excited molecule followed by coupling of the two radicals to afford the *RH*-reduction product. This latter species is spontaneously reoxidized (elimination of H_2) thus regenerating an aromatic molecule. Such a 'reductive' mechanism can clearly be excluded in

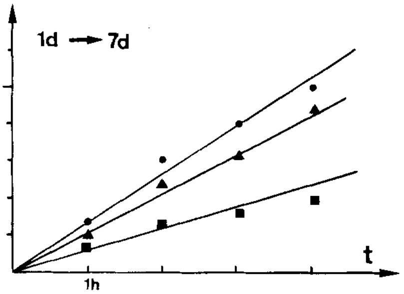
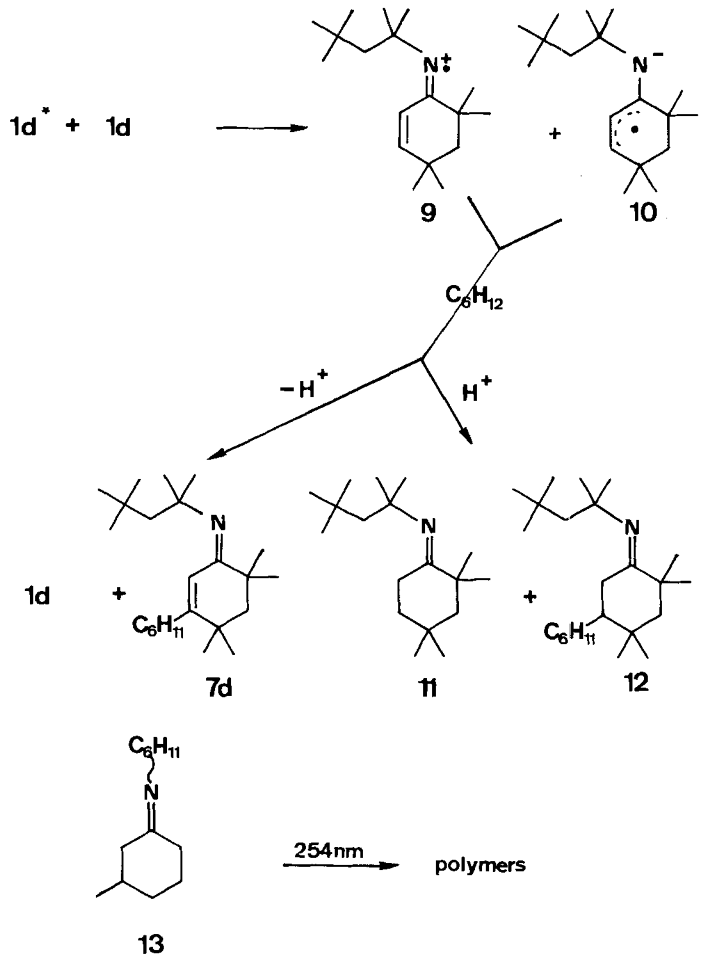


Figure. *Relative rate of conversion of* **1d** *to* **7d** *as a function of concentration of* **1d**. ■ 1.1 · 10^{-3}M, ▲ 5.5 · 10^{-3}M, ● *1.1 · 10^{-2}M in C_6H_{12}* (corrected for the amount of absorbed light/concentration of **1d**).

Scheme 3



the conversion **1d**→**7d** as the alkylated enimine is obviously *not* formed from a saturated imine precursor. The low overall yield of **7d** is consistent with the proposed disproportionation mechanism assuming that the cation radical **9** will give more starting material **1d** (reaction with RH) than product **7d** (reaction with $C_6C_{11}\cdot$), and that the anion radical **10** will give reduced products which undergo fast light-induced reactions to polymers. As seen from *Table 1* the other enimines **1a–c** and **1e** undergo the same type of reaction on $\pi - \pi^*$ excitation, but most probably for the corresponding 3-alkylenimines the ratio of rate of decomposition *vs.* rate of formation is higher than for **7d**, and therefore these products are never present in concentrations high enough to allow their isolation.

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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 400-MHz ^{1}H- and 100.63-MHz ^{13}C-NMR spectra are given in ppm relative to TMS (= 0 ppm) as internal standard. The mass spectra were measured at 70 eV. GC/MS analyses were performed using a 2-m 3% SE 30 column on *Suppelcoport 80/100.*

Starting Materials. 4,4-Dimethyl-2-cyclohexenone [10], 4,4,6,6-tetramethyl-2-cyclohexenone [11] and enimine **1a** [1] were synthesized according to published procedures.

N-*(4,4,6,6-Tetramethyl-2-cyclohexen-1-ylidene)cyclohexylamine* (**1b**) *and* N-*(4,4-Dimethyl-2-cyclohexen-1-ylidene)-1,1,3,3-tetramethylbutylamine* (**1c**). A solution of 4 · 10^{-2} mol enone, 6 · 10^{-2} mol amine and 50 mg TsOH in 30 ml toluene was refluxed under N_2 for 50 h with azeotropic removal of H_2O. After washing with 10 ml H_2O, drying over Na_2SO_4 and evaporation of the solvent, distillation afforded 2.8 g (30%) **1b**, b.p. 76–78°/0.01 mm and 4.0 g (43%) **1c**, b.p. 76–81°/0.01 mm, respectively.

N-*(4,4,6,6-Tetramethyl-2-cyclohexen-1-ylidene)-1,1,3,3-tetramethylbutylamine* (**1d**) *and* N-*(4,4-Dimethyl-2-cyclohexen-1-ylidene)-1,1-dimethylethylamine* (**1e**). To a solution of 4 · 10^{-2} mol enone and 1.3 · 10^{-1} mol amine in 60 ml toluene at −5 – 0° were added 3 · 10^{-2} mol $TiCl_4$ in 30 ml toluene. After refluxing for 16 h (**1d**) 2 h (**1e**), respectively, cooling to r.t. and addition of 200 ml pentane, the precipitate was filtered and washed twice with 100 ml pentane. After evaporation of the solvent, distillation afforded 3.7 g (35%) **1d**, b.p. 51–54°/0.01 mm, and 1.6 g (22%) **1e**, b.p. 36–41°/0.01 mm, respectively.

N-*(2-Cyclohexen-1-ylidene)cyclohexylamine* (**6**). 2-Cyclohexenamine (2.91 g, 3 · 10^{-2} mol) [12] was added at 5–10° to 10 g cyclohexanone and 4 g molecular sieves (4 Å). After stirring for 20 min at 10° and 15 h at r.t. and subsequent filtration, distillation afforded 3.2 g (60%) **6**, b.p. 64–66°/0.01 mm.

Photolyses. These were run in a *Rayonet RPR-100* photoreactor with light of λ = 254 nm. For analytical purposes a merry-go-round set-up was used.

N-*(3-Cyclohexyl-4,4,6,6-tetramethyl-2-cyclohexen-1-ylidene)-1,1,3,3-tetramethylbutylamine* (**7d**). A solution of 200 mg (7.6 · 10^{-4} mol) **1d** in 350 ml cyclohexane was irradiated under N_2 for 24 h. After evaporation of the solvent, chromatography (Al_2O_3, $MeCl_2$/MeOH 70:1) afforded 40 mg (15%) **7d**, m.p. 45–50°.

Hydrolysis of **7d**. A solution of 103 mg (3 · 10^{-4} mol) **7d** and 0.1 ml AcOH in 10 ml $CHCl_3$ was refluxed for 20 h. The amine component was extracted with 2N HCl and the org. phase was washed with H_2O and sat. NaCl solution. After drying over $MgSO_4$ and evaporation of the solvent, distillation afforded 31 mg (43%) *3-cyclohexyl-4,4,6,6-tetramethyl-2-cyclohexenone* (**8**), b.p. 95–99°/0.01 mm.

N-*(3-Methylcyclohexylidene)cyclohexylamine* (**13**). Imine **13** was prepared in 88% yield from 3-methylcyclohexanone and cyclohexylamine according to [13] and had b.p. 62–64°/0.01 mm.

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