# 92. Photochemistry of 2-Cyclohexene-imines and 2,3,4,4a,5,6-Hexahydroquinolines

Preliminary communication

by **Paul Margaretha**

Section de Chimie, Université de Genève, 30, quai Ernest-Ansermet CH-1211 Geneva, Switzerland

(7.I.78)

---

## *Summary*

The 2-cyclohexene-imines **2b**–**2d** and the hexahydroquinolines **5a**,**b** are synthesized. $n,\pi^*$-Excitation of these $\alpha,\beta$-unsaturated imines leads to (*E*/*Z*) isomerization for compounds **2** while compounds **5** are unreactive. No cyclobutanes are formed from **2** or **5** under these conditions in the presence of olefins, and only **2d** adds to 2,3-dimethyl-2-butene *via* the C=N bond to give an azetidine. On $\pi,\pi^*$ excitation **2** and **5** rearrange to the corresponding $\beta,\gamma$-unsaturated imines **8** and **9** with low efficiency. It is concluded that the failure of such imines to undergo [2+2]-photocycloadditions with olefins is not mainly due to radiationless decay *via* (*E*/*Z*) isomerization.

---

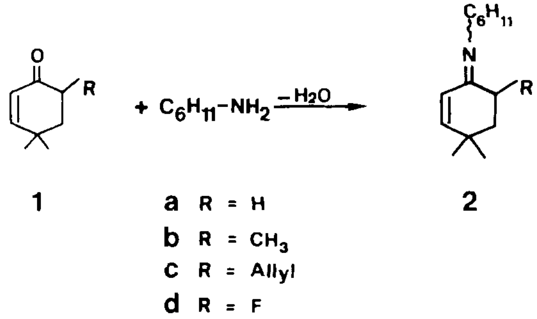
The mechanistic aspects of light induced [2+2]-cycloadditions of $\alpha,\beta$-unsaturated ketones to olefins have been investigated extensively in the last years [1-4]. The factors influencing oxetane *vs.* cyclobutane formation, *i.e.* ring formation at the C=O or C=C bond of the enone, have also been discussed [5-7]. In contrast no information exists in the literature on the behaviour of $\alpha,\beta$-unsaturated imines under similar conditions. The photochemistry of compounds containing a C=N bond has been the subject of recent reviews [8] [9], and it is assumed that azetidines are formed *via* photocycloaddition only if the C=N bond is attached to a conjugated electron withdrawing group, *e.g.* a carbonyl group [10] [11].

We now report preliminary results on the synthesis and the photochemical behaviour of the 2-cyclohexene-imines **2** and the 2,3,4,4a,5,6-hexahydroquinolines **5**. The latter ones were chosen as model compounds in which (*E*/*Z*) isomerization about the C=N bond should be excluded. As such reduced quinolines had not been described [12] we developed a synthetic approach similar to the one used by *Zimmerman* [13] in the preparation of tetrahydroindenes. A first approach *via* alkylation of 6-cyano-4,4-dimethyl-2-cyclohexenone (**1e**, R=CN) had led to different products [14]. The now reported synthesis of **2**[1]) and **5** is illustrated in *Schemes 1* and *2* and the related spectroscopic data are summarized in *Table 1*. The

---

[1]) Mixture of diastereoisomers.

*Scheme 1*



NMR. data of the synthetic intermediates **3** and **4** are given in *Table 2*. The UV. spectrum of **5b** being typical for these $\alpha,\beta$-unsaturated imines is shown in *Figure 1*.

In earlier investigations we had found a wavelength dependency in the photoreactivity of the 2-cyclohexenone oximes **6** [15]. Irradiation in the $n,\pi^*$ absorption band or sensitized irradiations (benzene, acetone) had led to (*E*/*Z*) isomerization about the C=N bond while $\pi,\pi^*$ excitation afforded the 2-cyclohexenone **1a** *(Scheme 3)*. The results of the irradiations of **2a**-**2c** are very similar regarding $n,\pi^*$ excitation as only (*E*/*Z*) isomerization and no addition to C=C bonds is observed. No cycloadducts neither are formed from **5a** and **5b** with C=C bonds. **2d** behaves differently in adding efficiently to 2,3-dimethyl-2-butene to give the spiro-azetidine **7** *(Scheme 4)*.

A different type of photoreaction is observed on $\pi,\pi^*$ excitation of compounds **2** and **5**. Although experiments on a large scale with the aim to isolate the product were unsuccessful, due to the apparent lability of the product and the very low reaction quantum yields, analytical irradiations in diluted solutions monitored

*Scheme 2*

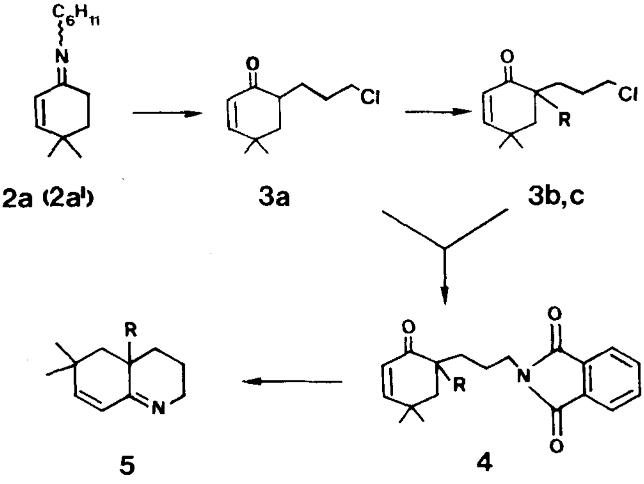


Table 1. *Spectral Data of α,β-Unsaturated Imines* **2** *and* **5**

| Compound | MS. | IR. ($CCl_4$) | UV.($C_6H_{12}$) | NMR. ($CCl_4$) |
|---|---|---|---|---|
| **2a**+**2a'** | | 3030, 1643<br>1620 | 282 (200)<br>223 (20500) | 6.20, 5.85 (*AB*, *J* = 10.2, 2 H)[a]); 5.82 (*s*, 2 H)[b]); 3.38 (*m*, 1 H); 2.30 (*m*, 2 H); 1.90-1.30 (*m*, 12 H); 1.08 (*s*, 6 H) |
| **2b**+**2b'** | | 3030, 1642<br>1621 | 282 (300)<br>224 (23000) | 6.30, 5.95 (*AB*, *J* = 10.0, 2 H)[a]); 5.95 (*s*, 2 H)[b]); 3.50 (*m*, 1 H); 2.40 (*m*, 1 H); 2.05-1.25 (*m*, 12 H); 1.20 (*s*, 6 H); 1.10 (*s*, 3 H) |
| **2c**+**2c'** | | 3080, 3020,<br>1650, 1642,<br>1621 | 297 (320)<br>225 (20800) | 6.20, 5.85 (*AB*, *J* = 10.0, 2 H)[a]); 5.83 (*s*, 2 H)[b]); 6.05-5.50 (*m*, 3 H); 3.45 (*m*, 1 H); 2.50 (*m*, 1 H); 2.40 (*m*, 2 H); 1.90-1.20 (*m*, 12 H); 1.10 (*s*, 6 H) |
| **2d**+**2d'** | | 3040, 1652 | 295 (280)<br>227 (25300) | 6.20, 5.95 (*AB*, *J* = 10.0, 2 H)[a]); 5.98 (*s*, 2 H)[b]); 5.40 (*d*×*t*, *J* = 4.5, 48.0, 1 H)[c]); 4.90 (*d*×*t*, *J* = 4.3, 49.0, 1 H)[d]); 3.48 (*m*, 1 H); 2.20-1.30 (*m*, 12 H); 1.20 (*s*, 3 H); 1.05 (*s*, 3 H) |
| **5a** | 163($M^+$) | 3030, 1640,<br>1620 | 282 (170)<br>223 (17100) | 5.82 (*s*, 2 H)[e]); 3.60 (*m*, 2 H); 2.10 (*m*, 1 H); 1.80-1.30 (*m*, 6 H); 1.15 (*s*, 3 H); 1.08 (*s*, 3 H) |
| **5b** | 177($M^+$) | 3025, 1641,<br>1620 | 277 (160)<br>221 (20800) | 5.80 (*s*, 2 H)[e]); 3.60 (*m*, 2 H); 1.60 (*m*, 6 H); 1.20 (*s*, 3 H); 1.12 (*s*, 3 H); 1.01 (*s*, 3 H) |

[a]) Olefinic protons of diastereoisomer **2**. [b]) Olefinic protons of diastereoisomer **2'**. [c]) C*H*F proton of diastereoisomer **2d'**. [d]) C*H*F proton of diastereoisomer **2d**. [e]) *AB*-system in $C_6D_6$ ($J$ = 10.0).

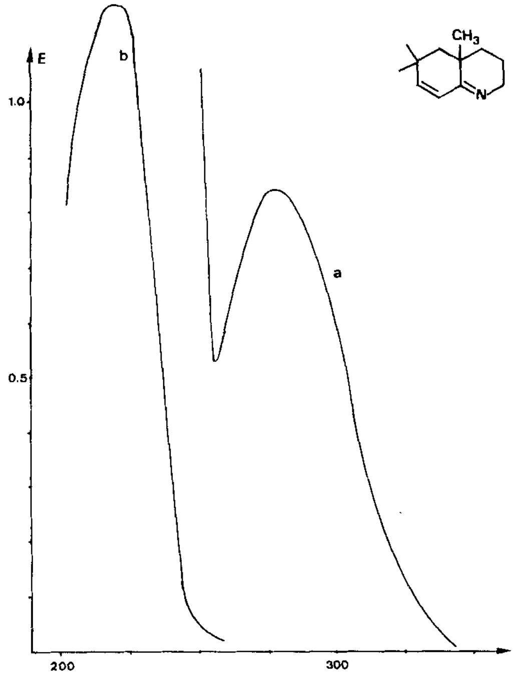


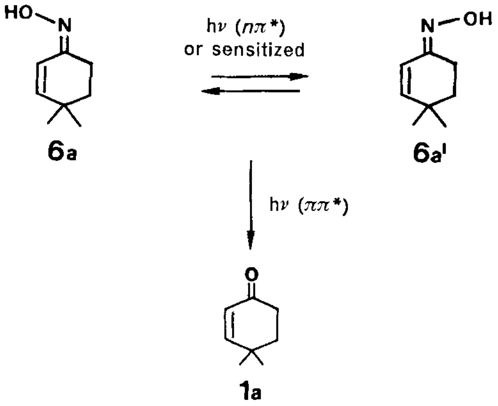
Fig. 1. *UV. spectrum of* **5b** *in* $C_6H_{12}$.
a) 1 mg/ml b) 1.10$^{-2}$ mg/ml

Table 2. *NMR. Data of Enones* **3** *and* **4**

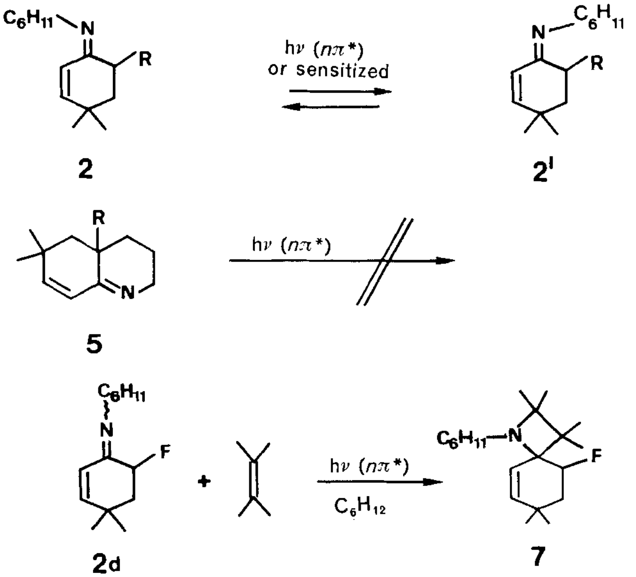
| Compound | NMR. ($CCl_4$) |
|---|---|
| **3a** | 6.50 (*d*×*d*, *J* = 1.5, 10.0, 1 H); 5.70 (*d*, *J* = 10.0, 1 H); 3.50 (*m*, 2 H); 2.25 (*m*, 1 H); 2.10-1.40 (*m*, 6 H); 1.20 (*s*, 3 H); 1.15 (*s*, 3 H) |
| **3b** | 6.50, 5.70 (*AB*, *J* = 10.0, 2 H); 3.50 (*m*, 2 H); 1.90-1.60 (*m*, 6 H); 1.20 (*s*, 6 H); 1.10 (*s*, 3 H) |
| **3c** | 6.50, 5.70 (*AB*, *J* = 10.0, 2 H); 6.00-4.90 (*m*, 3 H); 3.50 (*m*, 2 H); 2.35 (*d*, 2 H); 1.80-1.50 (*m*, 4 H); 1.20 (*s*, 6 H) |
| **4a,b,c** | 7.70 (*m*, 4 H, arom.); 3.65 (*m*, $CH_2N$);[a]) |

[a]) All other protons have the same chemical shift as in **3**.

*Scheme 3*

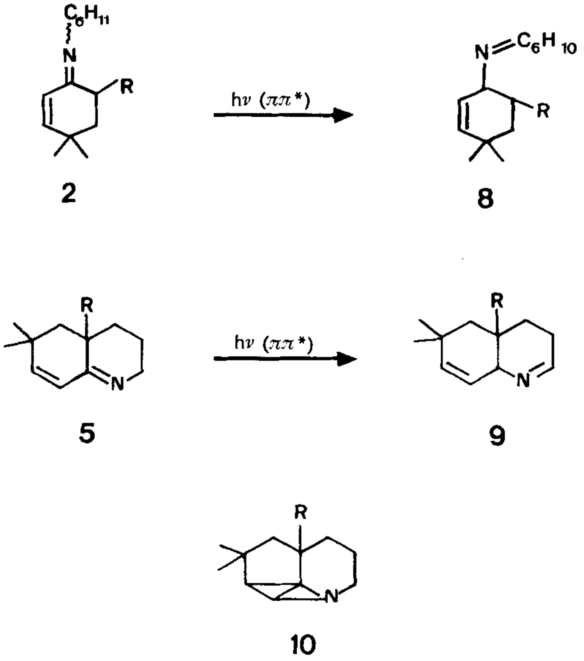


*Scheme 4*



by UV. spectroscopy show, that on disappearance of the starting material a new compound with $\lambda_{max} = 265-271$ nm ($\varepsilon = 750$) is formed. Such an absorption spectrum can be attributed to a $\beta,\gamma$-unsaturated imine [16], and therefore we propose structures **8** and **9** for the photoproducts. The formation of a 2-azabicyclo[1.1.0]butane derivative, *e.g.* **10** can thus be excluded *(Scheme 5)*. The quantum yields of disappearance of **2** and **5** with light of $\lambda = 254$ nm are given in *Table 3*.

*Scheme 5*



The low reactivity of excited imines has been explained to be due to rapid radiationless decay by twisting about the C=N bond [17]. Other - not specified - decay processes have been proposed by *Hornback* [18], who had found that imines with a cyclic C=N bond were as unreactive towards photochemical hydrogen abstraction as are acyclic imines.

Our results support this interpretation, *i.e.* that (*E*/*Z*) isomerization about the C=N bond cannot represent an important path for radiationless decay, since the

Table 3. *Quantum Yields of Disappearance of* **2** *and* **5** *at* $\lambda = 254$ *nm in degassed* $C_6H_{12}$ ($c_{imine} = 5 \cdot 10^{-5}$ mol/l)

| Compound | **2a** | **2b** | **2c** | **2d** | **5a** | **5b** |
|---|---|---|---|---|---|---|
| $\Phi$-imine | $9.10^{-5}$ | $3.10^{-5}$ | $1.7 \cdot 10^{-4}$ | $1.5 \cdot 10^{-4}$ | $4.8 \cdot 10^{-4}$ | $1.4 \cdot 10^{-4}$ |

bicyclic compounds **5** are as unreactive towards either cyclobutane or azetidine formation as are **2a**-**2c**. Inasmuch the inefficiency in cycloadduct formation of the 1-aza-1,3-butadiene moiety (especially when compared to its 1-oxa analogue) is due to rapid decay of the excited imine by an alternative mechanism or is due to important differences in the rates of formation and decay of the intermediates leading to products, respectively, *i.e.* exciplex or biradical formation [6], is unknown at the present time. A favorable geometrical arrangement should increase the probability of such cycloadditions as even N=N bonds have been found to add to C=C bonds under proper conditions [19]. On the other hand the azetidine formation from **2d** and 2,3-dimethyl-2-butene is not surprising and can be explained with the same arguments brought up to interprete oxetane formation from **1d** or similar enones and the same olefin [5] [6], *i.e.* polarization of the C=N bond by the inductive effect of F on C($\alpha'$) and unfavorable dipole-dipole interaction between a C–F bond and an adjacent $sp^2$-hybridized carbon atom. It is thus shown that in order to increase the reactivity of a C=N bond towards [2+2]-photocycloaddition the group attached to the C=N bond must not be conjugated [10] [11] but can as well act *via* an inductive effect.

Compounds **2** and **5** thus exhibit a similar dichotomy in behaviour from upper and lower excited states as has been reported for 2-cyclohexenone-oximes [15] and observed for $\alpha,\beta$-unsaturated hydrazones [20]. Therefore, these *N*-derivatives of $\alpha,\beta$-unsaturated ketones represent another class of compounds undergoing molecular rearrangements from a higher excited state [21]. It is known that the probability for a reaction to occur from a higher excited state increases with the energy gap *e.g.* between $S_2$ and $S_1$. As seen from *Figure 2* this gap is about 30-35 kcal/mol for the compounds mentioned above, and therefore of the same order of magnitude as for $\alpha,\beta$-unsaturated ketones undergoing molecular rearrangements from $S_2$ [22] but smaller than that of thiones (45-50 kcal/mol). These latter compounds are known to undergo even intermolecular reactions from $S_2$ [23].

In a similar way as for the enones mentioned [22] the rearrangements **2**→**8** and **5**→**9** are most probably initiated by cleavage of the weakest bond, in our case the C–H bond vicinal to the nitrogen atom (formation of a 2-azapentadienyl radical). The lower quantum yields for these rearrangements ($\Phi \approx 10^{-5} - 10^{-4}$) compared to those of the oxime-enone conversion ($\Phi \approx 10^{-2}$) might be due to the

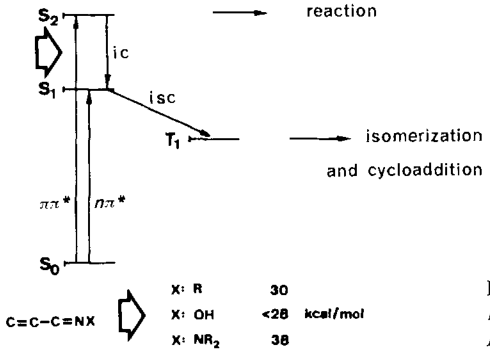


Fig. 2. *Qualitative State Diagram for N-derivatives of $\alpha,\beta$-Unsaturated Ketones*

fact that the 2-azapentadienyl radical can react back to the starting material while for the oximes **6** the cleavage of the weakest bond, *i.e.* the N–O bond, should be less reversible. Further studies with labeled compounds are in progress and the results will be reported in the full paper.

## Experimental Part

*General.* Chemical shifts in the NMR. spectra are given in ppm relative to TMS (=0 ppm) as internal standard (coupling constants $J$ in Hz), absorptions in the IR. spectra in $cm^{-1}$, and in the UV. spectra in nm ($\varepsilon$).

1. *Starting materials.* The 2-cyclohexenones **1a** [24], **1b** [25], **1c** [7] and **1d** [5] and the imine **2a** [26] were synthesized according to literature procedures. Cyclohexane and benzene used in photolyses were of spectroscopic grade.

2. *New Compounds.* 2.1. *Cyclohexene-imines* **2b**, **2c** *and* **2d**. 0.1 mol of **1b**, **c** or **d** and 0.2 mol of cyclohexylamine were heated in boiling toluene (200 ml) under a water separator and $N_2$ for 30 h (**1b**, **1c**) or 200 h (**1d**). After evaporation of the solvent and excess amine the residue was distilled. Boiling points at 0.1 Torr and yields: **2b** (104–106°, 73%), **2c** (86–89°, 75%), **2d** (90–92°, 85%).

2.2. *6-(3'-Chloropropyl)-4,4-dimethyl-2-cyclohexenone* (**3a**). In analogy to [13]: 20.5 g (0.1 mol) of **2a** in 100 ml of THF were added to a solution of 0.12 mol of isopropyl magnesium bromide in 100 ml of THF at 80° during 30 min under $N_2$. The solution was cooled to 0° and 21 ml (0.2 mol) of 1-bromo-3-chloropropane added. After 1 h the solution was warmed to RT. and left for 1 h. 104 ml of 10% HCl-solution were added and the mixture was heated under reflux for 12 h. After cooling the organic layer was separated and the aqueous phase extracted twice with $CH_2Cl_2$. The combined organic phases were washed with $H_2O$ and aqueous NaCl-solution and dried. After evaporation of the solvent distillation afforded 6.4 g (32%) of **3a**, b.p. 92–94°/0.1 Torr.

2.3. *6-(3'-Chloropropyl)-6-alkyl-4,4-dimethyl-2-cyclohexenones* **3b** *and* **3c**. In analogy to [27]: 2.0 g ($1.10^{-2}$ mol) of **3a** were dissolved in 25 ml of toluene. At −70° 6 ml of 2M sodium-bis(trimethylsilyl)amide in toluene were added under $N_2$. After 1 h $5 \cdot 10^{-2}$ mol of methyl iodide or allyl bromide were added and the solution warmed to RT. After evaporation of the solvent the residue was chromatographed on a column ($SiO_2$, $C_6H_6$) to yield 29% **3b** and 36% **3c**, respectively.

2.4. *Preparation of phthalimides* **4**. In analogy to [28]: From 0.01 mol of **3**, 0.011 mol of potassium phthalimide in 10 ml of DMF. Melting points and yields: **4a** (71°, 80%), **4b** (oil, 72%), **4c** (45°, 64%).

2.5. *Preparation of 2,3,4,4a,5,6-hexahydroquinolines* **5**. 0.01 Mol of **4** were heated in 20 ml of conc. HCl solution at 130° for 50 h. The solvent was evaporated and 20 ml of 2N HCl were added to the residue. The precipitate was filtered and the solution again evaporated. 10 ml of $C_6H_6$ were added to the residue and then 2N NaOH to reach pH = 12. The organic layer was separated and the aqueous layer extracted twice with $C_6H_6$. The combined extracts were dried and then heated under reflux and $N_2$ under a water separator for 12 h. Evaporation of the solvent and distillation at 0.1 Torr afforded **5a**, b.p. 53°, in 56% and **5b**, b.p. 75°, in 18% yield, resp. No cyclization product at all was obtained from **4c** under these conditions.

3. *Photolyses.* Irradiations on a large scale at 313 nm were carried out by filtering the light of a *Philips* HPK-125W lamp through pyrex glass and at 254 nm with a *Minerallight* PCQX1 low pressure mercury lamp.

3.1. *Photoaddition of* **2d** *to 2,3-dimethyl-2-butene.* 670 mg ($3.10^{-3}$ mol) of **2d** and 5 ml of olefin were irradiated ($\lambda = 313$ nm) in 150 ml of $C_6H_{12}$ for 50 h under $N_2$. Evaporation of the solvent and distillation afforded 285 mg (31%) of **7**, b.p. 80–95°/0.5 Torr. - NMR. ($CCl_4$): 5.80 (*d*, $J = 10.5$, 1 H); 5.45 (*d*, $J = 10.5$, 1 H); 4.85 ($d \times d \times d$, $J = 4.0$, 7.5, 50.0, 1 H); 3.35 (*m*, 1 H); 2.15–1.40 (*m*, 12 H); 1.40–1.05 (6 $CH_3$).

4. *Quantum Yields.* These were determined by irradiating the imines ($c = 5 \cdot 10^{-5}$ mol/l) in degassed $C_6H_{12}$ in a UV. cell with a xenon-mercury high pressure lamp combined with a monochromator ($\lambda = 254$ nm) and by monitoring the decrease of the $\pi, \pi^*$ absorption band of the starting material ($\lambda$max = 222 nm). Chloroacetic acid was used as actinometer [29].

Acknowledgment is made to the *Fonds National Suisse pour la Recherche Scientifique* (Grant n° 2.301-0.75) for financial support.

## REFERENCES

[1] *P.E. Eaton,* Accounts chem. Res. *1,* 50 (1968).
[2] *P. de Mayo,* Accounts chem. Res. *4,* 41 (1971).
[3] *P. Margaretha,* Chimia *29,* 203 (1975).
[4] *R.O. Loutfy & P. de Mayo,* J. Amer. chem. Soc. *99,* 3559 (1977).
[5] *V. Desobry & P. Margaretha,* Helv. *58,* 2161 (1975).
[6] *G. VoThi & P. Margaretha,* Helv. *59,* 2236 (1976).
[7] *I. Altmeyer & P. Margaretha,* Helv. *60,* 874 (1977).
[8] *A. Padwa,* Chem. Rev. *77,* 37 (1977).
[9] *A.C. Pratt,* Chem. Soc. Reviews *1977,* 63.
[10] *J.S. Swenton & J.A. Hyatt,* J. Amer. chem. Soc. *96,* 4879 (1974).
[11] *D.R. Anderson, J.S. Keute, T.H. Koch & R.H. Moseley,* J. Amer. chem. Soc. *99,* 6332 (1977).
[12] *G. Jones,* 'Quinolines' in 'The Chemistry of Heterocyclic Compounds', J. Wiley, 1977.
[13] *H.E. Zimmerman, F.X. Albrecht & M.J. Haire,* J. Amer. chem. Soc. *97,* 3726 (1975).
[14] *P. Margaretha,* Helv. *58,* 929 (1975).
[15] *P. Margaretha,* Tetrahedron Letters *1974,* 4205.
[16] *F. Millich & R.G. Sinclair,* J. polym. Science C *22,* 33 (1968).
[17] *A. Padwa & J. Smolanoff,* J. Amer. chem. Soc. *93,* 548 (1971).
[18] *J.M. Hornback, G.S. Proehl & I. Starner,* J. org. Chemistry *40,* 1077 (1975).
[19] *W. Berning & S. Hünig,* Angew. Chem. Int. Ed. *16,* 777 (1977).
[20] *P. Margaretha,* unpublished work.
[21] *P. de Mayo,* Afinidad *34,* 32 (1977).
[22] *J. Gloor & K. Schaffner,* Helv. *57,* 1815 (1974).
[23] *P. de Mayo,* Accounts chem. Res. *9,* 52 (1976).
[24] *Y. Chan & W.W. Epstein,* Org. Synth. *53,* 48 (1973).
[25] *C. Paris, S. Geribaldi, G. Torri & M. Azzaro,* Bull. Soc. chim. France *1973,* 997.
[26] *M. Montury & J. Gore,* Bull. Soc. chim. France, *1975,* 2612.
[27] *W. Fröstl & P. Margaretha,* Helv. *59,* 2244 (1976).
[28] *J.C. Sheehan & W.A. Bolhofer,* J. Amer. chem. Soc. *72,* 2786 (1950).
[29] *L.B. Thomas,* J. Amer. chem. Soc. *62,* 1879 (1940).