207. Photo-*Emde* Degradation of 1,2,3,4-Tetrahydroquinolinium Salts

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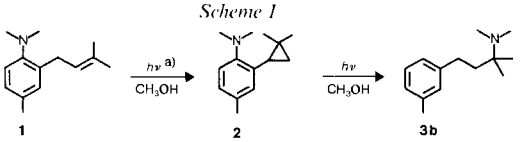
It is shown that 1,1-dimethyl-1,2,3,4-tetrahydroquinolinium ions undergo, under direct irradiation through quartz in CH_3OH and independent of the nature of the counterion (I^-, BF_4^-), a reductive cleavage of the N(1)–C(8a) bond (photo-*Emde* degradation). The corresponding *N,N*-dimethyl-3-phenylpropylamines are formed in high yields and without contamination by *Hofmann* degradation products of the tetrahydroquinolinium salts. Me groups at C(2) as well as substituents at C(6) (CH_3, Cl, CH_3O) favour the photo-*Emde* degradation. The aromatic Cl-substituent is reductively split off in the course of the photoreaction.

Scheme 1 shows an amazing overall photochemical reductive transformation of 2-(3′-methyl-2′-butenyl)-4,*N*,*N*-trimethylaniline (**1**) in CH_3OH which we observed in the course of our investigations of triplet di-π-methane rearrangements of allylbenzene derivatives with electron-donor and electron-acceptor substituents [1–3].

Scheme 1



1 **2** **3b**

a) Irradiations through quartz with a high-pressure Hg lamp.

Intermediate of these consecutive photoreactions is the expected di-π-methane-rearrangement product **2**, the formation of which can be repressed by addition of *trans*-piperylene. On the other hand, if **1** is irradiated in the presence of a 10-fold excess of benzonitrile which absorbs most of the incident light, the formation of **2** but not that of **3b** is observed. Direct irradiation of **2** in CH_3OH, however, yields **3b**. These observations indicate that the formation of **2** from **1** is the result of a triplet reaction, whereas the transformation of **2** seems to start from the singlet state. Since the reaction of phenylcyclopropane derivatives in their excited singlet state with nucleophiles such as alcohols and amines (*cf.* [4]) under ring-opening and uptake of the nucleophile is well-known, we assumed a similar, however, intramolecular photoreaction of **2** leading to the 1,2,3,4-tetrahydroquinolinium ion **4b** *(Scheme 2)*.

Models show that the geometrical prerequisite for such a reaction is optimal in the conformation displayed in *Scheme 2*. The formation of **3b** from **4b** should then be the

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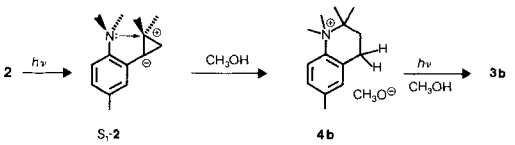
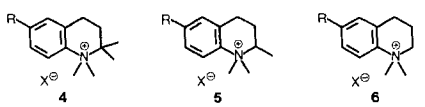
Scheme 2



result of a photochemical reductive cleavage of the N(1)–C(8a) bond in **4b**[4]). Similar photochemical reductions of anilinium ions have already been reported (*cf.* [6] [7]).

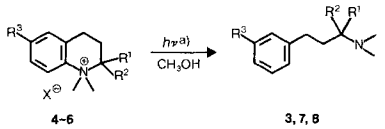


	R
a	H
b	CH_3
c	Cl
d	CH_3O

X = I, Cl, BF_4

To substantiate our hypothesis of the photochemical behaviour of **2**, we prepared a number of 1,1-dimethyl-1,2,3,4-tetrahydroquinolinium salts (**4–6**) by standard methods (see *Exper. Part*), and we report here on their photo-*Emde* degradation to yield the corresponding 3-aryl-*N*,*N*-dimethylpropylamines *(Scheme 3)*.

Scheme 3



R^1	R^2	R^3	Starting material No.	X	Irradiation time [h]	Product No.	Isolated[b]) yield [%]
CH_3	CH_3	H	**4a**	I	3.5	**3a**	74
CH_3	H	H	**5a**	I	7	**7a**	48
CH_3	H	H	**5a**	BF_4	6.5	**7a**	46
H	H	H	**6a**	I	45	**8a**	48
H	H	H	**6a**	BF_4	25.5	**8a**	32
CH_3	CH_3	CH_3	**4b**	I	3	**3b**	62
CH_3	CH_3	CH_3	**4b**	BF_4	2.5	**3b**	63[c])
CH_3	H	CH_3	**5b**	I	23	**7b**	59
H	H	CH_3	**6b**	I	13.5	**8b**	60
CH_3	H	Cl	**5c**	I	6	**7a** (R^3=H)	47[d])
H	H	Cl	**6c**	I	2.5	**8a** (R^3=H)	70[d])
CH_3	CH_3	CH_3O	**4d**	I	3	**3d**	69
CH_3	H	CH_3O	**5d**	I	6	**7d**	50
H	H	CH_3O	**6d**	I	8	**8d**	61

a) 150-W high-pressure Hg lamp through quartz; *ca.* 10^{-2} M solutions in CH_3OH.

b) Yields are not optimized. The products were characterized spectroscopically and **3b** and **8a** also by an independent synthesis (see *Exper. Part*).

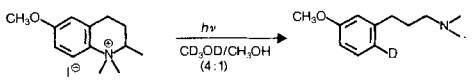
c) A 0.1 M solution of NaOMe was used.

d) Only the product free of the Cl substituent was detected.

4) We suggest for this type of reaction the expression photo-*Emde* degradation (*cf.* [5] for the corresponding ground-state reactions with Na(Hg)).

Irradiation of the 1,2,3,4-tetrahydroquinolinium salts **4**–**6** in CH_3OH at 20° with a high-pressure Hg lamp through quartz led in all cases to the formation of the products of ring cleavage (**3**, **7**, and **8**) in high yields. No marked difference was observed in the photoreactivity of corresponding 1,2,3,4-tetrahydroquinolinium iodides and tetrafluoroborates (*cf.* **5a**, **6a**, and **4b**), in contrast to the photochemical behaviour of comparable anilinium salts where tetrafluoroborates proved to be unreactive under direct irradiation [6][5]). The Cl-substituted 1,2,3,4-tetrahydroquinolinium salts **5c** and **6c** (see *Scheme 4*) lost their Cl-substituent in the course of the photolysis in CH_3OH. The photochemically induced homolysis of aryl–Cl bonds in alcoholic media is well-documented (*cf.* [8]); however, we do not know whether the reductive cleavage of the C–Cl bond occurred in the starting material or in the product. The clean and facile photoreaction of **5c** and **6c** as compared to **5a** and **6a** suggests that ring cleavage, *i.e.* rupture of the N(1)–C(8a) bond, takes place easier than cleavage of the Cl–C(6) linkage.

Scheme 4



6d [6'-^{2}H]-**8d**

Pac and *Sakurai* [7b] have shown that the photodegradation of *N,N,N*-trimethylanilinium chloride and bromide occur from their excited triplet state since cleavage into benzene and Me_3N is sensitised by acetone, whereas direct excitation do not lead to product formation, in contrast to the photochemical behaviour of the corresponding iodide [6] [7]. We found that irradiation of 1,1,2,2,6-pentamethyl-1,2,3,4-tetrahydroquinolinium chloride (**4b**, X = Cl) as well as that of 6-methoxy-1,1-dimethyl-1,2,3,4-tetrahydroquinolinium iodide (**6d**, X = I) in acetone/H_2O 1:1 through a *Pyrex* filter which allowed only the excitation of acetone led also to a slow formation of the corresponding amines **3b** and **8d**, respectively. We, therefore, suppose that the photo-*Emde* degradation of the 1,2,3,4-tetrahydroquinolinium salts also occurs, at least partially, from their excited triplet states.

The result of the N(1)–C(8a) bond homolysis in the excited 1,2,3,4-tetrahydroquinolinium ions should be the formation of a substituted phenyl radical[6]). That the photolysis of the 1,2,3,4-tetrahydroquinolinium salts yields indeed the corresponding phenyl radicals rather than ionic species as in the case of 1,2,3,4-tetrahydroisoquinolinium salts (*cf.* [10]) and *N,N,N*-trialkyl-*N*-benzylammonium salts (*cf.* [11]) follows from the fact that irradiation of **6d** (X = I) in MeOD let to no D incorporation in the product **8d**, whereas irradiation in CD_3OD/CH_3OH 4:1 gave **8d**, specifically deuterated in position 6 of the aromatic ring (*Scheme 4*). This clearly shows that the CH_3 group in CH_3OH is the H-atom donor for the reductive cleavage of the 1,2,3,4-tetrahydroquinolinium salts.

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[5]) 4-Cyano-*N,N,N*-trimethylanilinium iodide, which itself is photochemically unreactive, shows a charge-transfer band at 290 nm (log ε 2.94) in its absorption spectrum ($CH_3OH/CHCl_3$). On this basis, *Walsh* and *Long* [6] postulated direct charge-transfer excitation to be responsible for the photochemical cleavage of anilinium salts with polarizable anions (*cf.*, however, [7b]).

[6]) Radical generation may occur by direct homolysis in the excited state (*cf.* [8]) or *via* CT-complex formation of excited **4**–**6** with electron-donor molecules such as CH_3OH (*cf.* [7a] [9]) and uptake of an electron from the donor with subsequent bond cleavage.

The photochemical cleavage of these compounds represents, beside their reductive cleavage with Na(Hg) [5] (*cf.* also [12]) as well as with H_2 in the presence of catalysts such as Pd and Pt [13] and their electrochemical reduction at Pb and Hg cathodes [14], a further efficient and unambiguous method of their degradation. However, in contrast to the *Emde* degradation with Na(Hg) (*cf.* [5] and *Exper. Part*) and its electrochemical variant, which often lead to *Hofmann* degradation products too (*cf.* [15]), attributable to the generation of an alkaline medium in the course of the reaction, the photo-*Emde* degradation takes place under neutral conditions and thus no *Hofmann*-degradation products are observed.

We thank Dr. *W. Bernhard* for mass spectra, Dr. *M. Cosandey* for NMR spectra, and *F. Nydegger* for elemental analyses. Support of this work by the *Schweizerische Nationalfonds zur Förderung der wissenschaftlichen Forschung* is gratefully acknowledged.

Experimental Part

General. Column chromatography (CC): silica gel (0.063–0.2 mm, *Woelm*). Flash chromatography (FC; *cf.* [16]): silica gel *60* (0.040–0.063 mm, *Merck*). Evaporation of solvents: rotatory evaporator at 20–40°/12 Torr. Bulb-to-bulb distillations: *Büchi* apparatus (model *GKR-50*); temp. of the oven/pressure (Torr). Capillary gas chromatography (cap. GC): *Carlo Erba* instruments (model *GI, Fractovap 2101 AC*, and *Fractovap 4160 HRGC*) on glass-capillary columns (20 m × 0.30 mm; *Brechbühler AG*) coated with OV-17; carrier gas: H_2. Anal. HPLC: *Siemens* instrument (model *S 111*) equipped with an UV detector (model *PM 2 DLC, Zeiss*); mobile phase: CH_3CN, stationary phase: *Lichrosorb RP 8*, detection at 220 nm. M.p.: *Büchi* apparatus (model *SMP-20*); not corrected. UV: *Perkin-Elmer* spectrophotometer (model *320*; 250–400 nm); λ_{max} and λ_{min} in nm ($\log \varepsilon$); IR: (film or KBr): *Perkin-Elmer* spectrophotometer (model *599*); band positions in cm^{-1}. ^{1}H-NMR: at 60 and 90 MHz on *Varian* instruments (model *T60* and *EM 390*); chemical shifts in ppm with respect to TMS (= O) as internal standard; coupling constants *J* in Hz. MS: *Du Pont* instrument (model *21-491*) at 70 eV; ions in *m/z* (rel. %).

1. Syntheses of Starting Materials and Compounds for Comparison. – 1.1. *Quaternization of the 1,2,3,4-Tetrahydroquinolines. – General.* The dimethylation at N(1) was performed with CH_3I (*ca.* 5 mol-equiv.) in H_2O in the presence of equimolar amounts of Na_2CO_3 at r.t. (*Method A; cf.* [17]) or with CH_3I (*ca.* 5 mol-equiv.) in boiling CH_3OH in the presence of equimolar amounts of 2,6-lutidine (= 2,6-dimethylpyridine; *Method B; cf.* [18]).

1.1.1. *1,1-Dimethyl-1,2,3,4-tetrahydroquinolinium Salts* (**6a**). – *Iodide (X = I).* By *Method B*, 1,2,3,4-tetrahydroquinoline gave 42% of **6a** (X = I) which was recrystallized from i-PrOH; m.p. 172.5° ([19]: 172–174°). UV (CH_3OH): λ_{max} 268 (2.52), 262 (2.62); λ_{min} 266 (2.47). IR: 1430/1425 ($(CH_3)_2N^+$). Anal. calc. for $C_{11}H_{16}IN$ (289.16): C 45.69, H 5.58, N 4.84; found: C 45.76, H 5.60, N 4.90.

Chloride (X = Cl). Prepared from **6a** (X = I) with AgCl and directly used in the *Emde* degradation (see *2.1*).

Tetrafluoroborate (X = BF_4). Prepared from **6a** (X = I) with $AgBF_4$ in MeOH and recrystallized from MeOH (47%); m.p. 107°. IR: 1435/1425 ($(CH_3)_2N^+$). Anal. calc. for $C_{11}H_{16}BF_4N$ (249.06): C 53.05, H 6.48, N 5.62; found: C 53.20, H 6.49, N 5.71.

1.1.2. *1,1,6-Trimethyl-1,2,3,4-tetrahydroquinolinium Salts* (**6b**). *Iodide (X = I).* By *Method B*, 6-methyl-1,2,3,4-tetrahydroquinoline (prepared from 6-methylquinoline *(Fluka AG)* with Na in boiling EtOH; *cf.* [20]; m.p. 32°) was dimethylated to yield 44% of **6b** (X = I); m.p. 230° (i-PrOH; [21]: 224°). UV (CH_3OH): λ_{max} 271 (2.30), 262 (2.43); λ_{min} 270 (2.28). IR: 1420/1415 ($(CH_3)_2N^+$). Anal. calc. for $C_{12}H_{18}IN$ (303.18): C 47.54, H 5.98, N 4.62; found: C 47.42, H 6.02, N 4.70.

Chloride (X = Cl). Prepared from **6b** (X = I) with AgCl and directly used in the *Emde* degradation (see *2.2*).

1.1.3. *6-Chloro-1,1-dimethyl-1,2,3,4-tetrahydroquinolinium Iodide* (**6c**, X = I). By *Method B*, 6-chloro-1,2,3,4-tetrahydroquinoline (prepared from 6-chloroquinoline with Sn in conc. HCl [22]) was dimethylated in 7% yield and the salt recrystallized from i-PrOH; m.p. 180° ([23]: 175°). UV (CH_3OH): λ_{max} 274 (2.43), 267 (2.55); λ_{min} 272 (2.38). IR: 1425/1415 ($(CH_3)_2N^+$), 1125 (C–Cl). Anal. calc. for $C_{11}H_{15}ClIN$ (323.60): C 40.83, H 4.67, N 4.33; found: C 40.91, H 4.68, N 4.36.

1.1.4. *6-Methoxy-1,1-dimethyl-1,2,3,4-tetrahydroquinolinium Iodide* (**6d**, X = I). By *Method A*, 6-methoxy-1,2,3,4-tetrahydroquinoline (prepared from 6-methoxyquinoline with Sn in conc. HCl) was dimethylated in 72%

yield and **6d** (X = I) recrystallized from i-PrOH; m.p. 218.5–219°. IR: 1425/1415 ($(CH_3)_2N^+$). Anal. calc. for $C_{12}H_{18}INO$ (319.18): C 45.16, H 5.68, N 4.39; found: C 45.21, H 5.69, N 4.50.

1.1.5. *1,1,2-Trimethyl-1,2,3,4-tetrahydroquinolinium Salts* (**5a**). – *Iodide (X = I).* By *Method B,* 2-methyl-1,2,3,4-tetrahydroquinoline (prepared from quinaldine *(Fluka AG)* with Na in boiling EtOH; *cf.* [20]) was dimethylated in 46% yield and **5a** (X = I) recrystallized from i-PrOH; m.p. 195–195.5° ([24]: 205°). UV (CH_3OH): λ_{max} 269 (2.62), 262 (2.67); λ_{min} 266 (2.57). IR: 1415/1395 ($(CH_3)_2N^+$). Anal. calc. for $C_{12}H_{18}IN$ (303.18): C 47.54, H 5.98, N 4.62; found: C 47.61, H 6.01, N 4.66.

Chloride (X = Cl). Prepared from **5a** (X = I) with AgCl and directly used in the *Emde* degradation (see *2.3*).

Tetrafluoroborate (X = BF_4). Prepared from **5a** (X = I) with $AgBF_4$ in CH_3OH and recrystallized from CH_3OH (62%); m.p. 152°. IR: 1425/1405 ($(CH_3)_2N^+$). Anal. calc. for $C_{12}H_{18}BF_4N$ (263.09): C 54.79, H 6.89, N 5.32; found: C 54.70, H 6.88, N 5.31.

1.1.6. *1,1,2,6-Tetramethyl-1,2,3,4-tetrahydroquinolinium Iodide* (**5b**, X = I). By *Method A,* 2,6-dimethyl-1,2,3,4-tetrahydroquinoline (prepared from 2,6-dimethylquinoline [25] with Na in boiling EtOH) was dimethylated in 60% yield and the salt recrystallized from i-PrOH; m.p. 183°. IR: 1410/1395 ($(CH_3)_2N^+$). Anal. calc. for $C_{13}H_{20}IN$ (317.21): C 49.22, H 6.36, N 4.42; found: C 49.66, H 5.79, N 4.52.

1.1.7. *6-Chloro-1,1,2-trimethyl-1,2,3,4-tetrahydroquinolinium Iodide* (**5c**, X = I). By *Method B,* 6-chloro-2-methyl-1,2,3,4-tetrahydroquinoline (prepared from 6-chloro-2-methylquinoline [25] with Na in boiling EtOH) was dimethylated in 20% yield and the salt recrystallized from i-PrOH; m.p. 224°. IR: 1415/1400 ($(CH_3)_2N^+$). Anal. calc. for $C_{12}H_{17}ClIN$ (337.63): C 42.69, H 5.08, N 4.15; found: C 42.84, H 5.15, N 4.22.

1.1.8. *6-Methoxy-1,1,2-trimethyl-1,2,3,4-tetrahydroquinolinium Iodide* (**5d**, X = I). By *Method A,* 6-methoxy-2-methyl-1,2,3,4-tetrahydroquinoline (prepared from 6-methoxy-2-methylquinoline [25] with Sn in conc. HCl) was dimethylated in 71% yield and the salt recrystallized from i-PrOH; m.p. 186°. IR: 1410/1395 ($(CH_3)_2N^+$). Anal. calc. for $C_{13}H_{20}INO$ (333.21): C 46.84, H 6.05, N 4.20; found: C 46.82, H 6.15, N 4.11.

1.1.9. *1,1,2,2-Tetramethyl-1,2,3,4-tetrahydroquinolinium Iodide* (**4a**, X = I). – 1.1.9.1. *2,2-Dimethyl-1,2-dihydroquinoline* (*cf.* [26]). For 8 d, *N*-(1',1'-dimethyl-2'-propynyl)aniline (16.0 g; m.p. 49.5° [26] [27]) was heated in a bomb tube in decane (80 ml) at 205°. The org. bases were extracted with dil. HCl, liberated with conc. NaOH, and, after drying, distilled at 50–52°/0.15 Torr. FC (hexane/$CHCl_3$ 1:2) yielded 4.3 g (27%) of the desired compound [26].

1.1.9.2. *2,2-Dimethyl-1,2,3,4-tetrahydroquinoline.* The dihydro compound (see above; 2.3 g, 0.014 mol) in THF (35 ml) was added to a soln. of $LiAlH_4$ (2.0 g, 0.05 mol) in THF (35 ml). The mixture was boiled during 6 h and then decomposed by addition of H_2O (8 ml) and 15% KOH soln. (2 ml). The mixture and the precipitate were thoroughly washed with Et_2O. Distillation (150°/0.3 Torr) of the residue of the Et_2O extracts yielded 1.8 g (78%) of pure tetrahydro compound. IR: 1390/1370 ($(CH_3)_2C$). ^{1}H-NMR (CCl_4): 6.9–6.1 (*m*, 4 arom. H); 3.20 (*s*, NH); 2.73 (*t*, $J \approx 7$, 2 H–C(4)); 1.66 (*t*, $J \approx 7$, 2 H–C(3)); 1.19 (*s*, 2 CH_3–C(2)).

1.1.9.3. *Iodide* **4a**. The tetrahydro compound was dimethylated *(Method A)* to yield 28% of **4a** (X = I); m.p. 187° (i-PrOH). IR: 1410/1400 ($(CH_3)_2N^+$). 1385/1365 ($(CH_3)_2C$). Anal. calc. for $C_{13}H_{20}IN$ (317.21): C 49.22, H 6.36, N 4.42; found: C 48.84, H 6.23, N 4.25.

1.1.10. *1,1,2,2,6-Pentamethyl-1,2,3,4-tetrahydroquinolinium Salts* (**4b**). – 1.1.10.1. *2,2,6-Trimethyl-1,2-dihydroquinoline* (*cf.* [26] [28]). For 9 d, *N*-(1',1'-dimethyl-2'-propynyl)-4-methylaniline (14.5 g; m.p. 36.5° [26] [27]) was heated in decane (45 ml) at 205°. Workup (see *1.1.9.1*) and distillation (75°/0.06 Torr) yielded 3.5 g (24%) of pure dihydro compound [26] [28].

1.1.10.2. *2,2,6-Trimethyl-1,2,3,4-tetrahydroquinoline.* The dihydro compound (see above; 3.2 g, 0.018 mol) was reduced with Na (4.2 g, 0.183 mol) in boiling EtOH (80 ml) to yield after workup and distillation (110°/0.02 Torr) 2.5 g (78%) of pure tetrahydro compound[7]). IR: 3385 (NH). 1390/1370 ($(CH_3)_2C$). ^{1}H-NMR (CCl_4): 6.8–6.0 (*m*, 3 arom. H); 3.20 (*s*, NH); 2.70 (*t*, $J \approx 7$, 2 H–C(4)); 2.10 (*s*, CH_3–C(6)); 1.62 (*t*, $J \approx 7$, 2 H–C(3)); 1.13 (*s*, 2 CH_3–C(2)).

1.1.10.3. *Iodide* **4b** (X = I). The tetrahydro compound was dimethylated *(Method A)* to yield 53% of **4b** (X = I); m.p. 159° (i-PrOH). IR: 1410/1400 ($(CH_3)_2N^+$); 1385/1365 ($(CH_3)_2C$). Anal. calc. for $C_{14}H_{22}IN$ (331.23): C 50.77, H 6.69, N 4.23; found: C 50.66, H 6.78, N 4.24.

1.1.10.4. *Tetrafluoroborate* (X = BF_4). Prepared from **4b** (X = I) with $AgBF_4$ in EtOH. Two recrystallizations from $CHCl_3$/hexane yielded 46% of colourless **4b** (X = BF_4); m.p. 103–105°.

1.1.11. *6-Methoxy-1,1,2,2-tetramethyl-1,2,3,4-tetrahydroquinolinium Iodide* (**4d**, X = I). – 1.1.11.1. *6-Methoxy-2,2,-dimethyl-1,2-dihydroquinoline* (*cf.* [26]). For 8 d, *N*-(1',1'-dimethyl-2'-propynyl)-4-methoxyaniline

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[7]) The reduction was also performed with *Raney*-Ni in hexane/EtOH 1:1 to yield the tetrahydro compound in 88% yield.

(18.9 g; [26] [27]) was heated in decane (50 ml) at 205°. Workup (see *1.1.9.1*) and distillation yielded 4.1 g (23%) of the pure dihydro compound [26].

1.1.11.2. *6-Methoxy-2,2-dimethyl-1,2,3,4-tetrahydroquinoline.* The dihydro compound (see above; 8.0 g, 0.042 mol) was reduced with Na (8.8 g, 0.38 mol) in boiling EtOH (190 ml) to yield, after workup and distillation, 6.2 g (76%) of the pure tetrahydro compound. IR: 3370 (NH); 1385/1365 ($(CH_3)_2C$). ^{1}H-NMR (CCl_4): 6.6–6.0 (*m*, 3 arom. H); 3.63 (*s*, CH_3O–C(6)); 3.10 (*s*, NH); 2.70 (*t*, $J \approx 7$, 2 H–C(4)); 1.63 (*t*, $J \approx 7$, 2 H–C(3)); 1.13 (*s*, 2 CH_3–C(2)).

1.1.11.3. *Iodide* **4d**. The tetrahydro compound was dimethylated *(Method A)* to yield 80% of the salt; m.p. 182–182.5° (i-PrOH). IR: 1410/1400 ($(CH_3)_2N^+$); 1385/1360 ($(CH_3)_2C$). Anal. calc. for $C_{14}H_{22}INO$ (347.23): C 48.43, H 6.38, N 4.03; found: C 48.60, H 6.49, N 3.95.

1.2. N,N,*4-Trimethyl-2-(3'-methyl-2'-butenyl)aniline* (**1**). For 50 min, *N*-(1',1'-dimethylallyl)-4-methylaniline (2.5 g, 14.3 mmol; [26]) was boiled in aq. 0.1N H_2SO_4 (380 ml) to yield, after workup, 2.45 g (98%) of 4-methyl-2-(3'-methyl-2'-butenyl)aniline [26]. *N,N*-Dimethylation was performed with CH_3I/K_2CO_3 in acetone at r.t. Crude **1** (2.5 g, 94%) was purified by CC (benzene) to yield 1.32 g (46%) of pure **1**.

1.3. *2,*N,N-*Trimethyl-4-(3'-tolyl)-2-butanamine* (**3b**). A mixture of 4-(3'-tolyl)-2-butanone (2.5 g, 15.4 mmol; prepared by standard methods (*cf.* [29]) through alkylation of ethyl acetoacetate with 3-methylbenzyl bromide and hydrolysis and decarboxylation of the product), and dimethyl ammonium perchlorate (2.24 g, 15.4 mmol) in benzene (20 ml) were boiled in an apparatus with a H_2O separator (*cf.* [30]). After 16 h, no further separation of H_2O could be observed. The colourless solid was filtrated after cooling and recrystallized from i-PrOH/hexane to yield 2.80 g (63%) of the desired *N,N*-dimethyliminium perchlorate; m.p. 76° (not sharp). IR (Nujol): 1666 ($>C=\overset{+}{N}<$); 758 (4 adjac. arom. H); 618 (ClO_4^-). ^{1}H-NMR ($CDCl_3$): 7.3–6.8 (*m*, 4 arom. H); 3.57, 3.46 (2*s*, $C=\overset{+}{N}(CH_3)_2$); 3.1–2.7 (*m*, 2 H–C(3), 2 H–C(4)); 2.48 (*s*, 3 H–C(1)); 2.31 (*s*, CH_3–C(3')).

To a suspension of the iminium salt (2.4 g, 8.28 mmol) in Et_2O (10 ml) were added 10.4 mmol of CH_3MgI in Et_2O (6 ml; *cf.* [31]). The mixture was stirred for 6 h at r.t. The hydrolytic workup yielded 89% of the starting ketone and 6% (100 mg) of **3b** which was distilled (135–140°/11 Torr). UV (hexane): λ_{max} 248 (3.11); λ_{min} 234 (2.94). IR: 2820/2780 ($(CH_3)_2N$); 1382/1364 ($(CH_3)_2C$); 788 (3 adjac. arom. H). ^{1}H-NMR: 7.1–6.7 (*m*, 4 arom. H); 2.8–2.4, 1.8–1.4 (*AA'XX'*, 2 H–C(4) and 2 H–C(3), resp.); 2.29 (*s*, CH_3–C(3')); 2.19 (*s*, $(CH_3)_2N$–C(2)); 1.01 (*s*, 3 H–C(1), CH_3–C(2)). MS: 205 (31, M^+), 190 (51), 105 (42), 91 (15), 87 (18), 86 (100, $(CH_3)_2C=\overset{+}{N}(CH_3)_2$), 58 (20), 42 (34), 31 (13), 27 (48).

2. *Emde* Degradation of 1,1-Dimethyl-1,2,3,4-tetrahydroquinolinium Chlorides for Comparison (*cf.* [32]). – 2.1. *Degradation of* **6a** *(X = Cl)* (*cf.* [33]). The salt (0.9 g, 5.0 mmol) was dissolved in 70% EtOH and Na(Hg) (freshly prepared from 0.6 g (26 mmol) of Na and 11.4 g (57 mmol) of Hg; *cf.* [34]) cautiously added. The mixture was stirred at r.t. for 1 h and then heated for 1.5 h at 95–100°. Workup and distillation (85°/0.02 Torr) yielded an oil (0.45 g, 50%) which contained according to cap. GC 42% of **8a** and 57% of *1-methyl-1,2,3,4-tetrahydroquinoline.* Amine **8a** was separated by formation of its hydrogen oxalate in EtOH and recrystallization of the salt from EtOH. Decomposition of the hydrogen oxalate with 3N NaOH gave pure **8a** (0.2 g, 23%) identical with an authentic sample[8]). IR: 2810/2760 ($(CH_3)_2N$). ^{1}H-NMR (CCl_4): 7.2 (br. *s*, 5 arom. H); 2.7–2.4 (*m*, 2 H–C(3)); 2.3–1.9 (*m* + *s*, 2 H–C(1), $(CH_3)_2N$–C(1)); 1.9–1.4 (*m*, 2 H–C(2)).

1-Methyl-1,2,3,4-tetrahydroquinoline. ^{1}H-NMR (CCl_4): 7.0–6.4 (*m*, 4 arom. H); 3.20 (*t*, $J \approx 7$, 2 H–C(2)); 2.80 (*s*, CH_3–N(1)); 2.60 (*t*, $J \approx 7$, 2 H–C(4)); 2.1–1.4 (*m*, 2 H–C(3)).

2.2. *Degradation of* **6b** *(X = Cl).* As described under *2.1*, 0.9 g (4.3 mmol) of the salt yielded, after workup, 0.45 g (50%) of an amine mixture containing according to cap. GC 34% of **8b** and 65% of *1,6-dimethyl-1,2,3,4-tetrahydroquinoline.* Amine **8b** was purified *via* hydrogen-oxalate formation to yield 0.13 g (20%) of pure **8b**. IR: 2810/2760 ($(CH_3)_2N$). ^{1}H-NMR (CCl_4): 7.7–7.2 (*m*, 4 arom. H); 2.7–2.3 (*m*, 2H–C(3), 2H–C(1)); 2.28 (*s*, CH_3–C(3')); 2.13 (*s*, $(CH_3)_2N$–C(1)); 1.9–1.5 (*m*, 2H–C(2)).

1,6-Dimethyl-1,2,3,4-tetrahydroquinoline. ^{1}H-NMR (CCl_4): 6.6–6.2 (*m*, 3 arom. H), 3.20 (*t*, $J \approx 6$, 2H–C(2)); 2.80 (*s*, CH_3–N(1)); 2.50 (*t*, $J \approx 6$, 2H–C(4)); 2.30 (*s*, CH_3–C(6)); 2.2–1.4 (*m*, 2H–C(3)).

2.3. *Degradation of* **5a** *(X = Cl).* Degradation and workup according to *2.1* gave, after distillation (100°/0.2 Torr), 66% (0.60 g) of a mixture of 38% **7a** and 61% of *1,2-dimethyl-1,2,3,4-tetrahydroquinoline.* Amine **7a** was purified *via* its hydrogen oxalate to yield 0.14 g (28%) of pure **7a** (*cf.* [35]). IR: 2810/2770 ($(CH_3)_2N$). ^{1}H-NMR (CCl_4): 7.1 (br. *s*, 5 arom. H); 2.7–2.3 (*m*, 2 H–C(4), H–C(2)); 2.15 (*s*, $(CH_3)_2N$–C(2)); 1.9–1.0 (*m*, 2 H–C(3)); 0.90 (*d*, J = 6.6, 3 H–C(1)).

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[8]) Prepared by dimethylation ($CH_2O/NaBH_3CN$) of 3-phenylpropylamine *(Fluka AG)* in CH_3CN.

1,2-Dimethyl-1,2,3,4-tetrahydroquinoline. ^{1}H-NMR (CCl_4): 7.0–6.4 (*m*, 4 arom. H); 3.5–3.1 (*m*, H–C(2)); 2.80 (*s*, CH_3–N(1)); 2.8–2.5 (*m*, 2 H–C(4)); 2.1–1.4 (*m*, 2 H–C(3)); 1.20 (*d*, *J* = 7.0, CH_3–C(2))[9].

3. Photo-*Emde* Degradation. – The 1,1-dimethyl-1,2,3,4-tetrahydroquinolinium salts **4**–**6** were irradiated in CH_3OH (250 ml; unless otherwise stated) with a high-pressure Hg immersion lamp (type *TQ 150*, Quarzlampenges., Hanau) in a 400 ml photoreactor (*H. Mangels*, Roisdorf) through quartz at r.t. The soln. was stirred by a N_2 stream. All analyses for reactants and products were performed with the *Siemens* HPLC system using CH_3CN as mobile phase.

3.1. N,N-*Dimethyl-3-phenylpropylamine* (**8a**). – 3.1.1. *From* **6a** (*X* = BF_4). The salt (0.8 g, 3.2 mmol) was photolyzed for 25.5 h. Basic workup (1N NaOH) yielded, after distillation (110°/0.01 Torr), 0.24 g (44%) **8a**, 73% pure (cap. GC). The amine was purified *via* the hydrogen oxalate. It was identical with that described under *2.1*.

3.1.2. *From* **6a** (*X* = *I*). The salt (0.8 g, 2.8 mmol) was irradiated for 45 h to yield 0.30 g (67%) of crude **8a** (cap. GC: 73% pure). Formation of the hydrogen oxalate led to pure **8a**.

3.1.3. *From* **6c** (*X* = *I*). The salt (0.8 g, 2.5 mmol) was irradiated for 2.5 h and yielded, after distillation (150°/0.03 Torr), 0.25 g (51%) of **8a** (cap. GC: 92%). The 3′-Cl-substituted amine could not be detected.

3.2. N,N-*Dimethyl-3-(3′-tolyl)propylamine* (**8b**) *from* **6b** (*X* = *I*). The salt (1.0 g, 3.3 mmol) was irradiated for 13.5 h to yield, after distillation (120°/0.02 Torr), 0.40 g (69%) of crude **8b** (cap. GC: 89%). The purified **8b** (*via* hydrogen oxalate) was identical with that described under *2.2*.

3.3. *3-(3′-Methoxyphenyl)*-N,N-*dimethylpropylamine* (**8d**). – 3.3.1. *From* **6d** (*X* = *I*). The salt (0.9 g, 2.8 mmol) was irradiated for 8 h to yield, after distillation (120°/0.015 Torr), 0.40 g (78%) of crude **8d** (cap. GC: 78%). Formation of the hydrogen oxalate gave pure **8d**. IR: 2800/2760 ($(CH_3)_2N$). ^{1}H-NMR (CCl_4): 7.2–6.3 (*m*, 4 arom. H); 3.75 (*s*, CH_3O–C(3′)); 2.6–2.3 (*m*, 2 H–C(3)); 2.3–2.0 (*m* + *s*, 2 H–C(1), $(CH_3)_2N$–C(1)); 1.9–1.4 (*m*, 2 H–C(2)). ^{13}C-NMR (25.2 MHz; $CDCl_3$): 159.5 (*s*, C(3′)); 143.1 (*s*, C(1′)); 129.1 (*d*, C(5′)); 120.6 (*d*, C(6′)); 113.9 (*d*, C(2′)); 110.0 (*d*, C(4′)); 58.8 (*t*, C(1)); 54.9 (*q*, CH_3O–C(3′)); 44.9 (*q*, $(CH_3)_2N$–C(1)); 33.4, 28.6 (2*t*, C(2), C(3)). MS: 194 (7, M^+ + 1), 193 (43, M^+), 122 (13, **i**[10])), 121 (7, **ii**[10])), 91 (6), 71 (17, CH_2=CH$\overset{+}{N}$$(CH_3)_2$), 58 (100, CH_2=$\overset{+}{N}$$(CH_3)_2$).

3.3.2. *From* **6d** (*X* = *I*) *in* CH_3OD. The salt (0.27 g, 0.85 mmol) was irradiated in 30 ml of CH_3OD in a half-cylindrical quartz cuvette for 6.5 h. the usual workup led to 0.11 g (69%) of **8d** (GC: 92%). Neither in the IR nor in the ^{1}H-NMR an incorporation of D was recognizable.

3.3.3. *From* **6d** (*X* = *I*) *in Acetone*/H_2O *1:1*. The salt (0.20 g, 0.6 mmol) was dissolved in acetone/H_2O (40 ml) and irradiated in the half-cylindrical quartz cuvette for 6.5 h through a *Pyrex* filter. The usual workup showed that 15% of **8d** had been formed.

3.3.4. N,N-*Dimethyl-3-((3′-methoxy[6′-*$^2H_1$*]phenyl)propylamine [6′-*$^2H_1$*]*-**8d**) *from* **6d** (*X* = *I*) *in* CD_3OD/CH_3OH 4:1. Irradiation of the salt (0.18 g, 0.56 mmol) in CD_3OD/CH_3OH (15.6 ml) for 2.5 h yielded, after usual workup, 68 mg (62%) of [6′-$^2H_1$]-**8d**. IR: 2860/2780 ($(CH_3)_2N$); 2210/2070 (C–D). ^{1}H-NMR (CCl_4): identical with that of **8d** (see *3.3.1*) with the exception of the arom. region (7.3–7.0 (*m*, 1 arom. H); 6.6–6.5 (*m*, 2 arom. H)) where less than 4 H were found by integration. ^{13}C-NMR ($CDCl_3$): identical with that of **8d** (see *3.3.1*) with the exception of the signal for C(6′) at 120.5 which appeared as a d superimposed by a *t* (^1J(C,D)). MS[10])[11]: 195 (5, M_D^+ + 1), 194 (71, M_D^+), 193 (95, M^+), 123 (19, $\mathbf{i}_D$). 122 (35, $\mathbf{ii}_D$ + **i**), 121 (17, **ii**), 92 (14), 71 (15), 58 (54). Calc. D-content according to MS 56%.

3.4. N,N-*Dimethyl-4-phenyl-2-butanamine* (**7a**). – 3.4.1. *From* **5a** (*X* = BF_4). The salt 1.0 g (3.8 mmol) was irradiated for 6.45 h and yielded, after distillation (130°/0.02 Torr), 0.37 g (55%) of **7a**, 84% pure (cap. GC). The crude **7a** was purified *via* its hydrogen oxalate. It was identical with the amine from the *Emde* degradation (*cf. 2.3*).

3.4.2. *From* **5a** (*X* = *I*). The salt (0.80 g, 2.6 mmol) was irradiated for 7 h. Workup and distillation (130°/0.02 Torr) yielded 310 mg (68%) of crude **7a** (GC: 76%). It was purified *via* its hydrogen oxalate and was identical with the amine from the *Emde* degradation (*cf. 2.3*).

3.4.3. *From* **5c** (*X* = *I*). The salt (0.50 g, 1.5 mmol) was irradiated for 6 h to yield, after workup and distillation (120°/0.02 Torr), 0.23 g (88%) of **7a**, 80% pure (cap. GC). Formation of the hydrogen oxalate yielded pure **7a** which was identical in all aspects with the amine obtained from the irradiation of **5a** (X = I).

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[9]) We were not able, also by varying the degradation conditions, to suppress the formation of the demethylation product (*cf.*, however, [36]).

[10]) 

i ii

[11]) M_D *etc.* marks the deuterated species.

3.5. N,N-*Dimethyl-4-(3'-tolyl)-2-butanamine* (**7b**) *from* **5b** (*X* = *I*). The salt (0.90 g, 2.8 mmol) was irradiated for 23 h. Workup and distillation (110°/0.09 Torr) yielded 0.36 g (67%) of **7b** (GC: 90%) which was further purified by hydrogen oxalate formation. IR: 2880/2780 ($(CH_3)_2N$). ^{1}H-NMR (CCl_4): 7.1–6.6 (*m*, 4 arom. H), 2.7–2.3 (*m*, 2 H–C(4), H–C(2)); 2.28 (*s*, CH_3–C(3')); 2.15 (*s*, $(CH_3)_2$N–C(2)); 1.9–1.1 (*m*, 2 H–C(3)); 0.88 (*d*, *J* = 6.6, 3 H–C(1)).

3.6. *4-(3'-Methoxyphenyl)*-N,N-*dimethyl-2-butanamine* (**7d**) *from* **5d** (*X* = *I*). The salt (0.90 g, 2.7 mmol) was irradiated for 6 h. Workup and distillation (150°/0.02 Torr) yielded 0.31 g (55%) of **7d**, 90% pure (cap. GC) (*cf.* [37]). IR: 2820/2780 ($(CH_3)_2N$). ^{1}H-NMR (CCl_4): 7.2–6.5 (*m*, 4 arom. H); 3.72 (*s*, CH_3O–C(3')); 2.8–2.4 (*m*, 2 H–C(4), H–C(2)); 2.20 (*s*, $(CH_3)_2$N–C(2)); 2.0–1.4 (*m*, 2 H–C(3)); 0.95 (*d*, *J* = 6.3, 3 H–C(1)).

3.7. *2*,N,N-*Trimethyl-4-phenyl-2-butanamine* (**3a**) *from* **4a** (*X* = *I*). The salt (0.8 g, 2.5 mmol) was irradiated for 3.5 h. Workup and distillation (130°/0.035 Torr) yielded 0.40 g (83%) of **3a** (cap. GC: 90% pure) which was transformed into the hydrogen oxalate for purification. IR: 2870/2780 ($(CH_3)_2N$); 1380/1360 ($(CH_3)_2C$). ^{1}H-NMR (CCl_4): 7.1 (br. *s*, 5 arom. H); 2.7–2.4 (*m*, 2 H–C(4)); 2.20 (*s*, $(CH_3)_2$N–C(2)); 1.8–1.3 (*m*, 2 H–C(3)); 1.05 (*s*, CH_3–C(2), 3 H–C(1)).

3.8. *2*,N,N-*Trimethyl-4-(3'-tolyl)-2-butanamine* (**3b**). – 3.8.1. *From* **4b** (*X* = *I*). The salt (0.90 g, 2.7 mmol) was irradiated for 3 h. Workup and distillation (120°/0.03 Torr) yielded 0.45 g (80%) of **3b**, 77% pure (CGC). The amine was purified *via* its hydrogen oxalate and was identical in all aspects with the sample from *1.3*.

3.8.2. *From* **4b** (*X* = BF_4). The salt (30 mg, 0.1 mmol) was irradiated in CH_3OH (10 ml) in a quartz cuvette for 1 h to yield 84% of **3b** (cap. GC). A by-product (15% yield) was shown (cap. GC) not to be *1,2,2,6-tetramethyl-1,2,3,4-tetrahydroquinoline* (prepared in 90% yield by methylation of 2,2,6-trimethyl-1,2,3,4-tetrahydroquinoline; *cf. 1.1.10.2*). The structure of the by-product the amount of which raised up to 35% when the irradiation was performed in 0.1N CH_3ONa (63% yield of **3b**) was not determined.

3.8.3. *From* **4b** (*X* = *Cl*) *in Acetone*/H_2O *1:1*. The salt (0.25 g, 1.0 mmol) was dissolved in 40 ml of acetone/H_2O and irradiated in the half-cylindrical quartz cuvette for 40 min through a *Pyrex* filter. After workup, cap. GC analysis showed that **3b** had been formed to an extent of 5%.

3.9. *4-(3'-Methoxyphenyl)-2*,N,N-*trimethyl-2-butanamine* (**3d**) *from* **4d** (*X* = *I*). The salt (1.0 g, 2.9 mmol) was irradiated for 3 h. Workup and distillation (150°/0.02 Torr) yielded 0.43 g (83%) of **3d** (cap. GC: 83% pure) which was purified *via* its hydrogen oxalate. IR: 2860/2785 ($(CH_3)_2N$); 1385/1365 ($(CH_3)_2C$). ^{1}H-NMR (CCl_4): 7.3–6.4 (*m*, 4 arom. H); 3.74 (*s*, CH_3O-C(3')); 2.7–2.3 (*m*, 2 H–C(4)); 2.19 (*s*, $(CH_3)_2$N–C(2)); 1.8–1.3 (*m*, 2 H–C(3)); 1.00 (*s*, CH_3–C(2), 3 H–C(1)).

4. Irradiations of 4,*N*,*N*-Trimethyl-2-(3'-methyl-2'-butenyl)aniline (1). – 4.1. *In CH_3OH.* The aniline (0.15 g, 0.74 mmol) was irradiated for 21 h in 80 ml. The soln. showed at that time a composition (cap GC; in the order of increasing t_R) of 39% of *2-(2',2'-dimethylcyclopropyl)-4*,N,N-*trimethylaniline* (**2**), 36% of **1** and 24% of **3b**. The reaction was repeated 3 times to yield in total 0.55 g (92%) of the mixture of amines. Amines **2** and **3b** were prepurified by CC (benzene) and then separated by prep. GC on *Carbowax* (2 m, 170°).

2: UV (hexane): λ_{max} 288 (3.27), 252 (3.83), 219 (4.22); λ_{min} 270 (2.85), 231 (2.95). IR: 3062 (C–H, cyclopropane), 2780 ($(CH_3)_2N$). ^{1}H-NMR (CCl_4): 6.82 (*m*, H–C(3), H–C(5)); 6.64 (*d*, *J* = 8, H–C(6)); 2.67 (*s*, $(CH_3)_2$N–C(1)); 2.23 (*s*, CH_3–C(4)); 2.04 (*dd*, *J*(1',3'*cis*) = 8.4, *J*(1',3'*trans*) = 6.0, H–C(1')); 1.28 (*s*, CH_3–C(2') *trans* to arom. ring); 0.83 (*s*, CH_3–C(2') *cis* to arom. ring); 0.73 (*dd*, *J*(3',1'-*cis*) = 8.4 *J*(3',3') = 8.1, H–C(3') *trans* to arom. ring); 0.67 (*dd*, *J*(3',3') = 8.1, *J*(3',1'*trans*) = 6.0, H–C(3') *cis* to arom. ring). MS: 203 (100, M^+), 188 (31), 146 (83). Anal. calc. for $C_{14}H_{21}N$ (203.33): C 82.70, H 10.41, N 6.89; found: C 82.53, H 10.33, N 7.01.

Amine **3b** was identical with the authentic sample (see *1.3*).

4.2. *In CH_3OH in the Presence of (E)-1,3-Pentadiene.* Aniline **1** (7.5 mg, 0.037 mmol) and (*E*)-1,3-Pentadiene (25 mg, 0.37 mmol) were irradiated in CH_3OH (4 ml) in a quartz cuvette. Neither after 4.5 nor 24 h could the formation of **2** or **3b** be detected (cap. GC).

4.3. *In CH_3OH in the Presence of Benzonitrile.* Aniline **1** (7.5 mg, 0.037 mmol) and benzonitrile (38 mg, 0.37 mmol; E_T = 76.8 kcal/mol [38]) were irradiated in CH_3OH (4 ml) in a quartz cuvette. After 19 h, the soln. showed the following composition (cap. GC): 7.2% of **2**, 64.3% of **1**, and several by-products formed in small amounts. Neither of these products was identical with **3b**.

4.4. *Photoreaction of* **2** *in CH_3OH.* Compound **2** (7.5 mg, 0.037 mmol) was irradiated in CH_3OH (**4** ml) in a quartz cuvette. After 5 (20) h, the soln. showed the following composition (cap. GC): 72% (41%) of **2**, 22% (50%) of **3b**, and 6% (8.5%) of an unknown by-product.

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