**Photochemistry of N-Heterocycles. 7** [1])

# Light Induced Reductive Ring Contractions of Sixmembered Cyclic Iminium Ions [2])

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**Abstract.** Photochemically induced reductive ring contractions, previously observed for 2,5-dihydro-1,2,4-triazines, have also been verified for 1,4-dihydropyrimidines **2a**,**b**, the dihydro-1,2,4,5-tetrazine **9**, and dihydro-1,3,5-triazines **11a**,**b** giving rise to fivemembered fully unsaturated heterocycles (pyrroles **4a**,**b**, imidazoles **13a**,**b**, and triazole **10**, respectively). The 1,4-dihydropyrazines **15a**–**j** tend to decompose in acidified 2-propanol in the dark, but on irradiation they also undergo reductive ring contraction furnishing solely the 1,2,5-triarylpyrroles **16a**–**d** rather than the (*a priori* also possible) isomeric 1,3,4-triarylpyrroles **17a**–**d**. In contrast, the 3,6-diphenylpyrid-azine **18** gives the 4-isopropyl-analogue **19** in low yield upon irradiation in hydrogen chloride saturated 2-propanol.

Upon electronic excitation in acidified methanol, pyridine undergoes methylation [1a].

A similar reaction has been observed for quinoline and isoquinoline in ethanol containing hydrogen chloride [1b]. These reactions have been rationalized in terms of initial hydrogen atom transfer from the solvent to the excited protonated heterocycle followed by radical combination [1a,b].

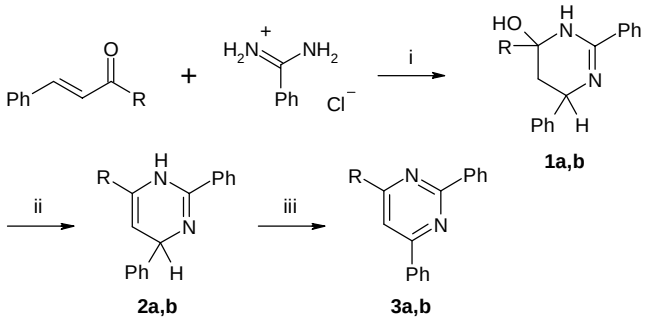
More recently, the photochemically induced ring contractions and reductions of 1,2,4-triazine derivatives, especially of 2,5-dihydro-3,5,6-triphenyl-1,2,4-triazinium chlorides [2], have been rationalized as being initiated by photoinduced electron transfer (PET) reactions from the solvent alcohol (as donor) to the excited cyclic iminium ions (as acceptors) similar to the well-known PET reactions in the 4,5-dihydro-3*H*-pyrrolium series [3]. It was therefore expected that suitable dihydropyrimidinium, dihydro-1,3,5-triazinium, and dihydro-1,2,4,5-tetrazinium salts also show analogous PET initiated photoreductive ring contractions. From the results reported here it will become evident that this expectation is met.

## Results and Discussion

### *1,4-Dihydropyrimidinium chlorides*

The preparation of the starting materials **2** will be commented briefly (Scheme 1). Although the first synthesis of 1,4-dihydropyrimidine **2a** was reported many years ago [4], the first reliable one with well reproducible results was published only in 1985 [5].

The dehydration of **1b** to **2b** was not described in the latter article. Compounds **2a** and **2b** are in equilibrium in solution with their 1,6-dihydro tautomers [6] and are very sensitive towards dehydrogenation to the fully unsaturated analogues **3a**,**b** [7] (Scheme 1). We found that the method of Weis [5] was not suitable for the synthesis of **2b**, but a slightly modified version proved to be successful. TLC monitoring showed that in the reaction of benzamidinium chloride with 1,3-diphenyl-2-propen-1-one using sodium methoxide in acetone solution, the formation of the aromatic pyrimidine **3b** could be avoided if the amount of the base did not exceed 70% of the equimolar amount.




**Scheme 1 a:** R = Me, **b:** R = Ph; i: NaOMe, acetone, 0–20 °C; ii: benzene, reflux, $N_2$; iii: benzene, reflux, air

[1]) Part 6.: See Z. Madarász, Cs. Hertelendi, J. Nagy, J. Fekete, M. Kajtár-Peredy, and J. Nyitrai; ACH – Models in Chemistry, **1999**, *136*, 393
[2]) Presented in part at the Fourth Conference on Iminium Salts, Stimpfach-Rechenberg (Germany), September 14–16, 1999

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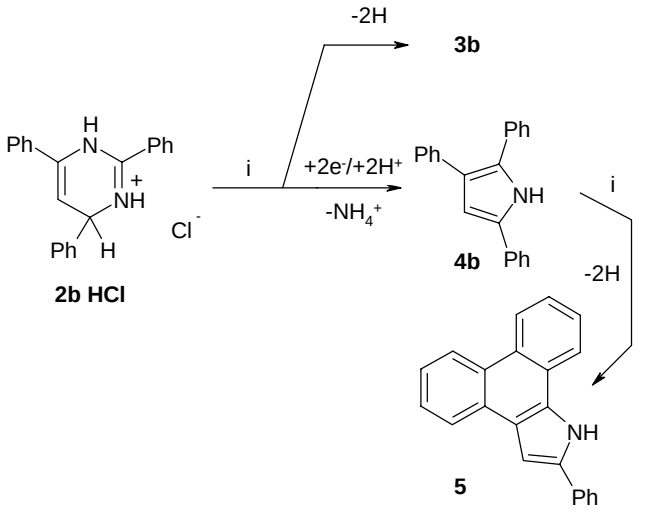
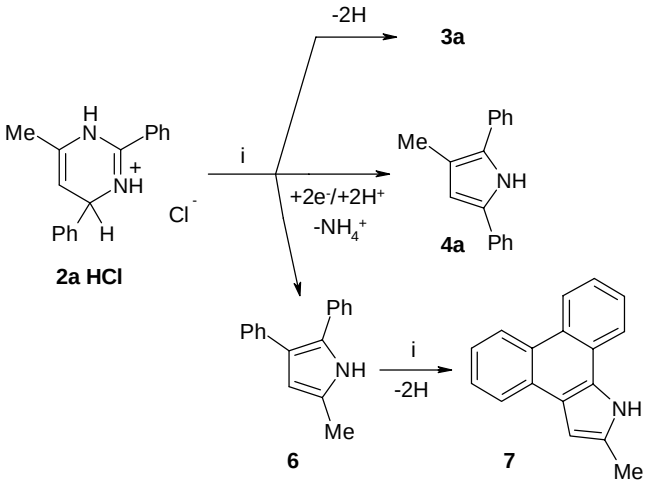
The base used also catalyzes the elimination of water from **1b** providing **2b**, but any excess of base in the presence of unreacted unsaturated ketone promotes a redox reaction furnishing the aromatic pyrimidine **3b**.

Irradiation ($\lambda \geq 280$ nm) of **2b**·HCl salt in 2-propanol gave the expected ring contracted pyrroles **4b** (16%) and **5** (19%) besides the aromatic pyrimidine **3b** (47%) (Scheme 2). The yields show that **3b** is insensitive to irradiation, and a considerable fraction of **4b** must have decomposed in the acidic 2-propanol through dark reactions.




**Scheme 2** i: h$\nu$, *i*-PrOH, HCl.

The irradiation of **2a**·HCl salt proved that either nitrogen atom of the dihydro-pyrimidine ring could be eliminated, because both of the *a priori* possible ring contracted products **4a** and **6** as well as the dehydrocyclized product **7** were isolated (Scheme 3). By increasing the excess of HCl to up to 5 moles per mole of pyrimidine **2a**, the yields of **4a**, **6** and **7** were also increased,

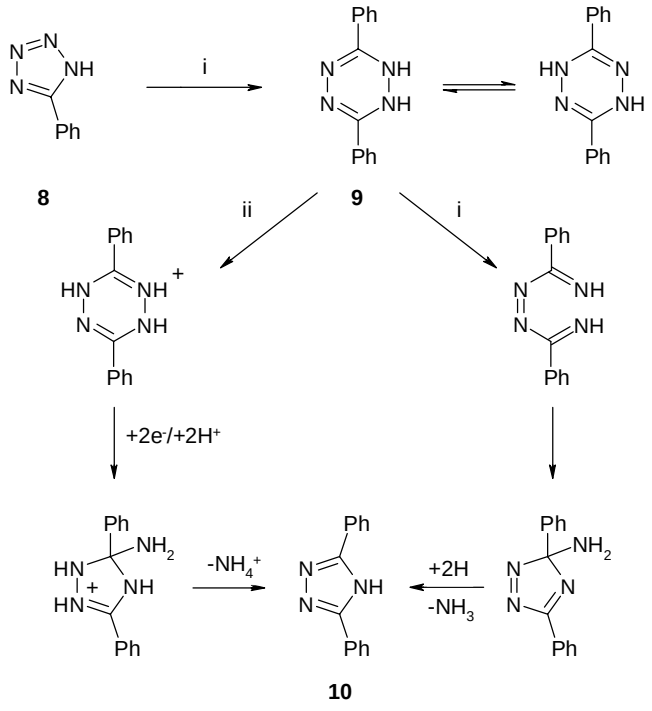



**Scheme 3** i: h$\nu$, *i*-PrOH, HCl.

while the necessary irradiation time could be decreased (the consumption of **2a**·HCl was monitored). When more than five fold molar quantities of HCl up to saturation were used only the aromatic pyrimidine **3a** could be isolated. Pyrrole **4a** was decomposed completely under these conditions.

*Dihydro-3,6-diphenyl-1,2,4,5-tetrazinium chloride*

It has been known for a long time that irradiation of 5-phenyl-1*H*-tetrazole (**8**) in THF gives rise to the 1,2(4)-dihydrotetrazine **9** and 3,5-diphenyl-1*H*-triazole (**10**) (as products of a consecutive reaction of tetrazine **9**) [8a]. This ring contraction has been rationalized as a radical reaction probably *via* electron uptake by the excited heterocycle (see. *e.g.* ref. [8b] ). In this study it was found that raising the concentration of HCl in 2-propanol, the photoconversion of **9** was markedly accelerated and furnished the triazole **10** as a single product in good yield (50%). This result is again rationalized as an efficient PET induced reaction of an excited cyclic iminium salt (Scheme 4). In total, the transformation of **9**·HCl into **10** would require the addition of two electrons and one more proton as well as analogous steps like ring opening, ring reclosure and loss of ammonia as outlined for the neutral **9**. It is, however, not yet possible to say anything definite about the exact sequence of events.

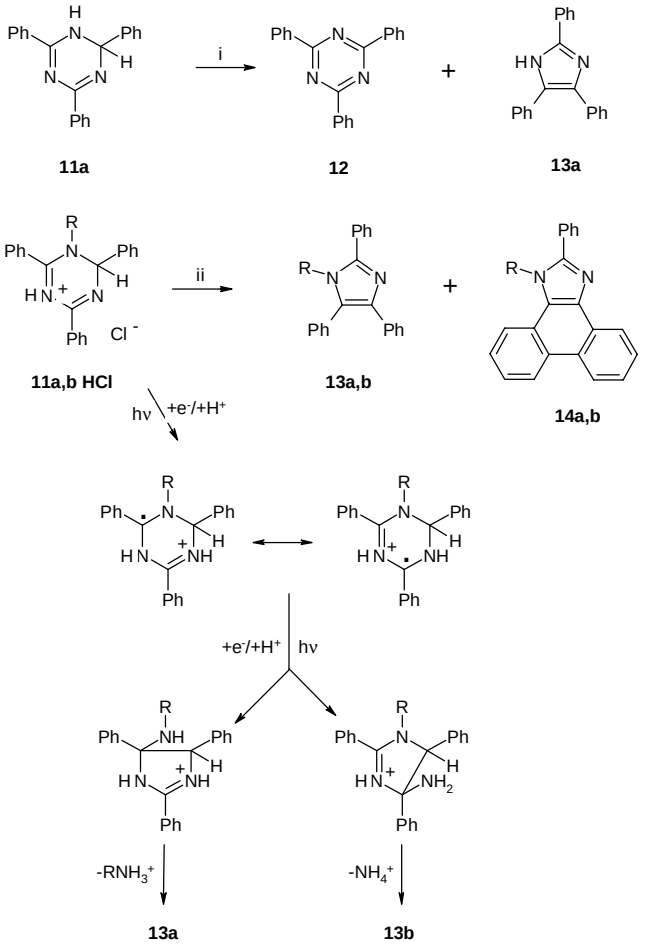



**Scheme 4** i: h$\nu$, THF, lit.[8]; ii: h$\nu$, *i*-PrOH, HCl.

*1,2-Dihydro-1,3,5-triazinium chlorides*

According to *Nyquist* irradiation of neutral 2,4,6-triphe-

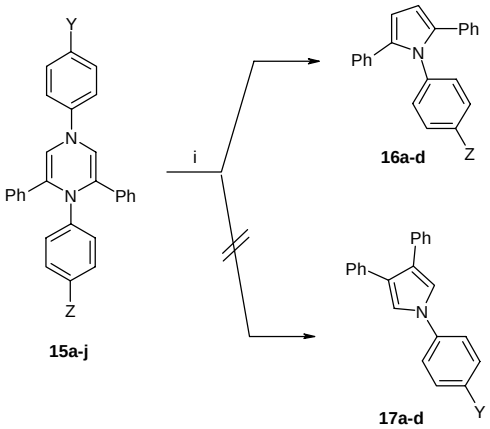
nyl-1,2-dihydro-1,3,5-triazine (**11a**) in benzene under reflux [9] gave the aromatic triazine **12** (54%) and the imidazole **13a** (15%) as main products. It had been observed earlier that the corresponding conjugate acid **11a**·HCl, being a cyclic iminium salt, on irradiation gave the corresponding ring contracted product **13a** in 29% and its cyclodehydrogenated analogue **14a** in 59% yield as determined by HPLC analysis (Scheme 5). Compound **11b** on irradiation in 2-propanol solution gave 36% of **13a** along with small amounts of **13b** and **14a**,**b** detectable only by HPLC.




**Scheme 5** **a:** R = H, **b:** R= Me; i: h$\nu$, benzene, reflux, lit. [9]; ii: h$\nu$, *i*-PrOH, HCl.

*1,4-Diaryl-1,4-dihydropyrazinium chlorides*

Irradiation of **15a**–**j** in 2-propanol furnished in all cases the corresponding 1,2,5-triarylpyrroles **16a**–**d** *via* reductive ring contraction by extrusion of solely Aryl-N(4) besides other decomposition products. Thus, **16a** was obtained from **15a**, **16b** from **15b**,**c**,**i**, **16c** from **15d**,**e**,**g**, and **16d** from **15f**,**h**,**j** (Scheme 6). Although the pyrroles **16a**–**d** themselves also decomposed under the conditions used for irradiation of **15a**–**j**, HPLC monitoring of their decomposition showed that pyrroles **16** disappeared much faster from the reaction mixture than compound **17a** (which also has to be regarded as *a priori* possible ring contraction product) was destroyed in a separate experiment under otherwise the same conditions. Attempts to isolate decomposition products have so far not been successful.

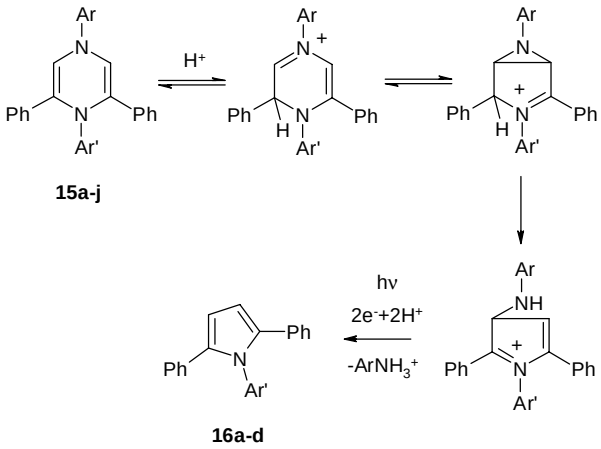



| 15 | a | b | c | d | e | f | g | h | i | j |
|---|---|---|---|---|---|---|---|---|---|---|
| Y | Cl | H | Me | H | Me | Me | $F_3C$ | $F_3C$ | $F_3C$ | H |
| Z | Cl | H | H | Me | Me | $F_3C$ | Me | $F_3C$ | H | $F_3C$ |

| 16 | a | b | c | d |
|---|---|---|---|---|
| Z | Cl | H | Me | $F_3C$ |

**Scheme 6** i: h$\nu$, *i*-PrOH, HCl

This experiment proved unambiguously that compounds **17a**–**d** could not have formed during the irradiations of dihydropyrazines **15**. In a dark control, the decomposition of compounds **15** in acidified 2-propanol showed a quite different pattern in the HPLC analysis than that observed in case of irradiation of the same compounds under otherwise the same conditions. This information allows us to propose a rationale for the ring contraction of 1,4-dihydropyrazines **15a**–**j** into the corresponding pyrroles **16a**–**d**. Of course, fully unsaturated sixmembered products may not be expected from these starting materials (see Scheme 7).

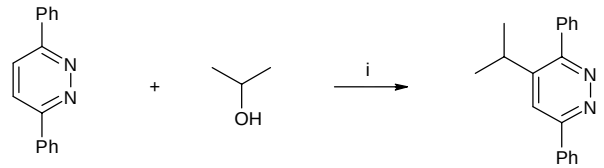



**Scheme 7**

This reaction may be related to the photoreductive ring contraction observed earlier [10] with 1,4-diacetyl-1,4-dihydro-3,5,6-triphenyl-1,2,4-triazine giving rise to 3,4,5-triphenylpyrazole.

*3,6-Diphenylpyridazine*

When this compound (**18**) was irradiated in 2-propanol saturated with HCl, the only product we were able to isolate (in low yield) proved to be **19**, the 4-isopropyl derivative of **18**, which must have formed similarly to the reported photoinduced alkylation of other N-heterocycles [11] (Scheme 8). This example demonstrates that fully unsaturated electron poor azaheterocycles – in contrast to their dihydro analogues – may prefer other reactions than photoreductive ring contractions upon irradiation in acidified reducing solvents.




**18** **19**

**Scheme 8** i: h$\nu$, *i*-PrOH, HCl

## Conclusions

The monohydrochlorides of dihydropyrimidines **2a**,**b**, of dihydro-1,2,4,5-tetrazine **9** and of 1,2-dihydro-1,3,5-triazines **11a**,**b** undergo, similarly to the hydrochlorides of 2(4),5-dihydro-1,2,4-triazines, photoreductive ring contractions upon irradiation in 2-propanol containing HCl. These reactions belong to the family of PET initiated reactions of other cyclic iminium salts with reducing solvents [3]. The 1,4-dihydropyrazines **15a**–**j** gave also ring contracted products, but by a rather different pathway than that observed with the abovementioned cyclic iminium salts. In any case, as a prerequisite for successful ring contraction, a total of two electrons and one proton has to be transferred to the protonated heterocycles. The initial single electron transfer may later be supplemented by light induced or dark reductions, *e.g.* H-atom transfer from the 2-hydroxypropyl radical logically formed from 2-propanol. That such solvent derived radicals are indeed formed is evident from the alkylations of heterocycles related to those used in this study, namely hydroxyethylation of 4-methyl-3,5,6-triphenyl-4,5-dihydro-1,2,4-triazinium chloride at C(6) [2] or the introduction of an isopropyl group at C(4) of 3,6-diphenylpyridazine (**18**).

The formation of fully unsaturated products (**3a**,**b**, **12**) under reducing (!) conditions from their dihydro-precursors deserves a comment. This dehydrogenation may be in part due to the presence of residual oxygen and the result of a redox dismutation: The neutral starting materials serve as reductants themselves. In principle, any radical species present could abstract a hydrogen atom from the neutral starting materials. Since the fully unsaturated products are less light sensitive than their precursors under the conditions employed, they may accumulate.

Cyclodehydrogenated products **5**,**7**, and **14a**,**b** are most likely formed from the corresponding vicinal diphenyl compounds **4b**, **6**, **13a**,**b** by the well known dehydrogenative cyclization of stilbene like compounds documented also for the heterocyclic series [12a] and observed in the transformation of **13b** into **14b** previously [12b].

Since the systems investigated in this study have in common that they react as iminium ions but still are structurally different, an unifying rationale satisfactory in all cases will not be possible. The suggested rationales have at present to be regarded as tentative but do rest on reasonable assumptions. This study has contributed to the general knowledge of the reactivity of iminium ions and – from the section of study subjects chosen – has demonstrated the photoreductive ring contraction to be fairly general for cyclic iminium ions derived from dihydroazaarenes.

The authors are grateful to Miss K. Ófalvi for recording the IR and NMR spectra, and to Dr. József Balla and Mr. W. van Hoof (Duisburg) for the recording of mass spectra. We are also indebted to Dr. Jenö Fekete and Ms. Zs. Romvári for HPLC measurements and to graduate students Mr. S. Marokházi and Ms. A. Arany for their fruitful contributions. Thanks are also due to Mrs. H. Medzihradszky–Schweiger and staff for the performing micro-analyses. Z. Madarász is indebted to the German Academic Exchange Service (DAAD) for a fellowship. Financial assistance by OTKA (Hungarian Scientific Research Fund; grant T 016261 and T 14978) and Fonds der Chemischen Industrie is gratefully acknowledged.

## Experimental

Melting points were determined with a hot-stage melting point apparatus and are uncorrected. – IR spectra were obtained on Specord 75 (Zeiss, GDR) and Perkin–Elmer 283 instruments. – $^1$H NMR spectra were recorded with Bruker CW 80, Bruker DRX 300 and 500 spectrometers (80, 300 and 500 MHz, respectively), $^{13}$C NMR spectra were obtained on Bruker spectrometers (75.5, 125.75 MHz), with TMS as internal reference in $CDCl_3$, unless stated otherwise. Special measurements (DEPT, HETCOR) were used in any doubtful cases. – Mass spectra (EI) were measured with Varian MAT 311 A spectrometer using direct insertion system at 70 eV. – Column and thin-layer chromatography were carried out on Merck Kieselgel 60 (0.063–0.2 mm) and Merck Kieselgel 60 $F_{254}$ Alufolien, respectively. For preparative TLC Merck PSC

ready-for-use plates (Kieselgel 60 $F_{254}$, 20 × 20 cm, 2 mm) were used, unless stated otherwise. TLC spots were detected by UV, and/or $I_2$. – HPLC parameters were as follows: Perkin–Elmer 200 LC high pressure pump, eluent: methanol/water/phosphoric acid (80:20:0.5), flow rate 0.5 ml/min, Perkin Elmer ISS 200 automatic sample supplier, volume of sample 20$\mu$l, Nova Pak C-18 Waters column (3.9×300 mm), Perkin Elmer 235 C Diode Array Detector using $\lambda$ = 240 nm wavelength. In case of 1,3,5-triazine derivatives a Waters 660 apparatus was used with Waters 6000A high pressure pump, 440 absorbance detector ($\lambda$ = 240 nm), Resolve™ C-18 column (3.9×150mm), eluent: acetonitrile/0.045M sodium acetate buffer (60:40).

**Synthesis of Starting Materials and Authentic Samples of Products**

For the synthesis of compounds **1a**,**b** and *2,4-diphenyl-6-methyl-1,4(6)-dihydropyrimidine* (2a) see ref. [5]. *2,4-Diphenyl-6-methylpyrimidine* (**3a**) [6c], *2,4,6-triphenylpyrimidine* (**3b**) [6a; 7], *2,5-diphenyl-3-methylpyrrole* (**4a**) [13], *2,3,5-triphenylpyrrole* (**4b**) [14], *3,6-diphenyl-1,2-dihydro-1,2,4,5-tetrazine* (**9**) and *3,5-diphenyl-1,2,4-triazole* (**10**) [8a], *2,4,6-triphenyl-1,3,5-triazine* (**12**) [16], *1-(4-chlorophenyl)-2,5-diphenylpyrrole* (**16a**) and *1,2,5-triphenylpyrrole* (**16b**) [13], as well as *1-(4-methylphenyl)-2,5-diphenylpyrrole* (**16c**) [18] were prepared according to the published procedures.

*2,4,6-Triphenyl-1,4(6)-dihydropyrimidine* (**2b**) *and 2,4,6-Triphenylpyrimidine* (**3b**)

Sodium methoxide (prepared from 0.23 g of sodium and 25 ml of dry methanol) was added in 2.5 ml portions every 0.5 h at 0 °C to a mixture of benzamidinium chloride (1.6 g, 10 mmol) and 1,3-diphenyl-2-propen-1-one (1.5 g, 10 mmol) in 35 ml acetone. The mixture was allowed to warm up to room temperature and stirred overnight. The inorganic salts were filtered off. The filtrate was concentrated to dryness and the residue was dissolved in hot methanol (15 ml). The insoluble aromatic pyrimidine **3b** was filtered off and the product crystallized out on cooling to give **2b** (2.4 g, 77%), *m.p.* 112 °C (dec.). – IR (KBr): $\nu$/cm$^{-1}$ = 3 420 (NH), 1 620, 1 590, 1 550, 1 510. – $^1$H NMR ( DMSO-$D_6$): $\delta$/ppm = 5.4 and 5.7 (2 × d, $J$ = 4.7 Hz, 2H, 4(6)-H and 5-H), 7.2–8.2 (m, 15H, Ph-H). – MS (70 eV): *m/z* (%) = 310 (52.1) [M$^+$], 309 (55.6), 233 (100), 206 (17.8), 105 (57.0), 104 (79.7), 103 (60.5), 102 (60.5), 77 (9).

*2,4,6-Triphenyl-1,4(6)-dihydropyrimidinium Chloride* (**2b**·HCl)

Compound **2b** (0.8 g, 2.6 mmol) was dissolved in methanol (25 ml) and this solution was saturated with dry HCl gas. After evaporation of the solvent, the residue was triturated with dry ether to give the title compound (0.75 g, 83.8%), *m.p.* 212–215 °C. – IR (KBr): $\nu$/cm$^{-1}$ = 3 100–2 300 (br, NH$^+$), 1 550. – $^1$H NMR ( DMSO-$D_6$): $\delta$/ppm = 5.7 and 5.8 (2 × d, $J$ = 4.7 Hz, 2H, 4(6)-H and 5-H), 7.3–8.2 (m, 15H, Ph-H). – UV (ethanol): $\lambda_{max}$/nm (log $\varepsilon$) = 202.4 (4.58), 242.7 (4.42), 326.8 (3.25).

| | | | | | |
|---|---|---|---|---|---|
| $C_{22}H_{19}ClN_2$ | Calcd.: | C 76.18 | H 5.52 | Cl 10.22 | N 8.08 |
| (376.86) | Found: | C 76.34 | H 5.73 | Cl 10.60 | N 7.78. |

*2-Phenylphenanthro[9,10-b]pyrrole* (**5**)

2,4,5-Triphenylpyrrole (**4b**, 295 mg, 1.0 mmol) and iodine (127 mg, 0.5 mmol) were dissolved in 2-propanol (150 ml) and irradiated in a Pyrex immersion well reactor using a Philips HPK 125 high pressure mercury lamp at ambient temperature for 90 h. The solvent was removed and the residue was taken up in ethyl acetate (50 ml). This solution was washed with 10% aqueous sodium thiosulfate (15 ml), than with 5% aqueous sodium hydrogen carbonate (15 ml), and dried over $MgSO_4$. The residue was purified by column chromatography using hexane/acetone (10:4) to give 86.3 mg of **5** (30.0%), *m.p.* 171–173 °C. – IR (KBr): $\nu$/cm$^{-1}$ = 3 425 (NH), 730 ($\gamma$ CH). – $^1$H NMR (DMSO-$D_6$): $\delta$/ppm = 7.2–7.8 (m, 8H, ar-H), 8.04 (m, 2H, ar-H), 8.32 (m, 1H, ar-H), 8.6–8.8 (m, 3H, ar-H), 12.09 (brs, 1H, NH). – $^{13}$C NMR DMSO-$D_6$): $\delta$/ppm = 100.34, 121.66, 123.48, 123.77, 124.00, 124.29, 124.79, 125.06, 126.87, 127.02, 129.00 (arom. CH); 121.57, 126.66, 127.69, 128.33, 129.79, 132.51, 135.97 (arom. C). – MS (70 eV): *m/z* (%) = 293 (100%, M$^+$), 291 (8.2, M–2H$^+$),189 (11.4, M–PhCNH$^+$).

*5-Methyl-2,3-diphenylpyrrole* (**6**)

A mixture of ethyl 2-methyl-4,5-diphenylpyrrol-3-carboxylate [7] (2.37 g, 7.8 mmol), sulfuric acid, (5.1 ml), and water (2.1 ml) was stirred at 100 °C for 3h. The solution was cooled to 15 °C and neutralized by saturated sodium carbonate solution. The red sulfate of the title compound was filtered off, washed with hexane and suspended in ethyl acetate. To this suspension 10% aqueous NaOH was added until pH = 12. The aqueous layer was extracted with ethyl acetate (2× 20 ml). The combined organic phase was dried over $MgSO_4$. The residue was purified by column chromatography using hexane/acetone (10:2) to give 0.86 g (46.2%) of **6**. The product decomposes on standing and also on preparative TLC plate. – IR (KBr): $\nu$/cm$^{-1}$ = 3 490 (NH), 3 110, 3 080, 2 980, 1 600, 1 510, 1 500, 1 430, 1 420, 1 060, 920, 715, 665. – $^1$H NMR ($CDCl_3$): $\delta$/ppm = 2.34 (d, 3H, $J$ = 1.0 Hz, $CH_3$), 6.10 (dq, 1H, $J$ = 2.9 Hz and 1.0 Hz, 4-H), 7.15–7.35 (m, 10H, Ph-H), 7.92 (brs, 1H, NH). – MS (70 eV): *m/z* (%) = 233 (100%, M$^+$), 232 (34.0, M–H$^+$), 217(8), 189 (3.0), 128 (3.0). – HRMS ($C_{17}H_{15}N$): calcd.: 233.1204, found: 233.1214.

*2-Methylphenanthro[9,10-b]pyrrole* (**7**)

5-Methyl-2,3-diphenylpyrrol (**6**) (231 mg, 1.0 mmol) and 2.16 M methanolic HCl (0.46 ml, 1.0 mmol) were dissolved in 2-propanol (150 ml) and this solution was irradiated in a Pyrex immersion well reactor using a Philips HPK 125 high pressure mercury lamp at ambient temperature for 30 h and the solvent removed. The residue was purified by column chromatography using hexane–acetone 10:4 eluent to give 100.3 mg of 7 (43.5%) colourless foam, *m.p.* 143–144 °C. – IR (KBr): $\nu$/cm$^{-1}$ = 3 020 (NH), 2 980, 2 920, 1 460, 1 250, 1 080, 780, 690. – $^1$H NMR ($CDCl_3$): $\delta$/ppm = 2.5 (d, 3H, $J$ = 1.0 Hz, $CH_3$), 6.68 (dq, 1H, $J$ = 1.0 Hz and 2.2 Hz, 3-H), 7.40–7.55 (m, 4H, 5-, 6-, 9-, 10-H), 7.83–8.63 (m, 4H, 4-, 7-, 8-, 11-H), 8.55 (brs, 1H, NH). – MS (70 eV): *m/z* (%) = 231 (100%, M$^+$), 228 (5.0), 202 (10.0), 189 (4.0), 116 (11.0), 115 (6.0), 114 (3.0). – HRMS ($C_{17}H_{13}N$): calcd.: 231.1048, found: 231.1028.

*2,4,6-Triphenyl-1,2-dihydro-1,3,5-triazine* (**11a**)

According to the method of *Swamer, Reynolds,* and *Hauser* [16] 51.5 g (0.5 mol) of benzonitrile were treated with 11.5 g (0.48 mol) of sodium hydride in 50 ml of benzene for 5 h at reflux temperature. The crude product **11a**, being contaminated with the aromatic triazine **12**, could be purified by repeated recrystallization from ethanol to give 12.1g (23%), *m.p.* 176 °C (ref. [16] 171–172 °C)). – UV (ethanol): $\lambda_{max}$/nm (lg $\varepsilon$) = 246 (4.37), 334 (3.29). – IR (KBr): $\nu$/cm$^{-1}$ = 3 180, 3 040, 3 010, 1 600, 1 565, 1 500, 1 490, 1 480, 1 345, 1 270, 735, 690.

| | | | | | | |
|---|---|---|---|---|---|---|
| $C_{21}H_{17}N_3$ | Calcd.: | C | 81.00 | H | 5.50 | N 13.50 |
| (311.37) | Found: | C | 80.91 | H | 5.51 | N 13.50. |

From the residues of filtration, *2,4,6-triphenyl-1,3,5-triazine* (**12**), being less soluble in ethanol than **11a**, may be obtained in 6% yield, *m.p.* 243 °C (ref. [16] 228–229 °C).

*1-Methyl-2,4,6-triphenyl-1,2-dihydro-1,3,5-triazine* (**11b**)

This compound was prepared according to the procedure described by *Smith et al.* [17] from 5.1 g (38 mmol) of *N*-methylbenzamidine with 2.0 g (19 mmol) of benzaldehyde in 17 ml of refluxing toluene in 33% yield, *m.p.* 174–176 °C (ref. [17] 169–170 °C). – UV (ethanol): $\lambda_{max}$/nm (lg $\varepsilon$) = 250 (4.34), 336 (3.46); in presence of 1 eq. HCl: 276 (4.25), 336 (3.81). – IR (KBr): $\nu$/cm$^{-1}$ = 1 610, 1 570, 1 565, 1 520, 1 505, 1 475, 1 450, 1 410, 1 360, 1 330, 1 300, 1 285, 1 210, 1 130, 780, 765, 720, 695. – $^1$H NMR ($CDCl_3$): $\delta$/ppm = 3.00 (s, 3H, $CH_3$), 6.03 (s, 1H, 2-H), 7.27–7.67 (m, 13H, Ph-H), 8.23–8.34 (m, 2H, Ph-H).

*2,4,5-Triphenylimidazole* (**13a**)

This compound was prepared according to ref. [19] in 60% yield, *m.p.* 281°C (ref. [19] 270 °C). – UV (ethanol): $\lambda_{max}$/nm (lg $\varepsilon$) = 300 (4.40), 224 (4.32). – IR (KBr) $\nu$/cm$^{-1}$ = 3 400, 3 050, 1 600, 1 580, 1 500, 1 480, 1 455, 1 440, 1 410, 1 390, 1 125, 1 065, 1 020, 960, 910, 760, 730, 710, 700, 690, 665, 600. – $^1$H NMR (DMSO-$D_6$): $\delta$/ppm = 7.23 – 7.70 (m, 13H), 8.00 – 8.23 (m, 2H), 12.70 (br, 1H, NH).

| | | | | | | |
|---|---|---|---|---|---|---|
| $C_{21}H_{16}N_2$ | Calcd.: | C | 85.11 | H | 5.44 | N 9.45 |
| (296.35) | Found: | C | 85.16 | H | 5.36 | N 9.48. |

*1-Methyl-2,4,5-triphenylimidazole* (**13b**)

By adaption of the method by *Davidson*, *Weiss* and *Jellin* [19] 3.3 g (10 mmol) of *N*-desyl-*N*-methylbenzamide were treated with 15.4 g (0.2 mol) of ammonium acetate in 100 ml of glacial acetic acid for 1h at reflux temperature. The precipitate was crystallized from hexane to give 1.70 g (55%) of colourless crystals, *m.p.* 144 –151 °C (ref. [20] 143.5–144.5 °C). – UV (ethanol): $\lambda_{max}$/nm (lg $\varepsilon$) = 282 (4.33), 220 (sh, 4.3). – IR (KBr): $\nu$/cm$^{-1}$ = 3 055, 1 600, 1 500, 1 480, 1 465, 1 445, 1 440, 1 430, 1 385, 1 070, 1 025, 960, 920, 790, 780, 770, 750, 725, 715, 705, 700. – $^1$H NMR ($CDCl_3$): $\delta$/ppm = 3.50 (s, 3H), 7.10 – 7.90 (m, 15H).

*2-Phenylphenanthro[9,10-d]imidazole* (**14a**)

By adaption of the procedure from ref. [19], 2.1 g (10 mmol) of 9,10-phenanthrenequinone, 1.6 g (15 mmol) of benzaldehyde and 15.4 g (0.2 mol) of ammonium acetate in 100 ml of acetic acid were kept at reflux for 1 h. The precipitate obtained upon addition of 150 ml of water was crystallized from acetone to give 1.20 g (41%) of pale brown crystals, *m.p.* 332–334 °C (ref. [21] 314 °C). – UV (ethanol): $\lambda_{max}$/nm (lg $\varepsilon$) = 224 (4.42), 259 (4.76), 308 (4.32), 342 (4.03), 358 (4.00). – IR (KBr): $\nu$/cm$^{-1}$ = 3 130, 3 050, 1 610, 1 470, 1 455, 1 375, 1 100, 1 070, 1 055, 1 030, 955, 910, 765, 745, 705, 695, 685. – $^1$H NMR (DMSO-$D_6$): $\delta$/ppm = 7.50 – 7.93 (m, 7H), 8.26 (m, 6H), 13.5 (br, 1H, NH).

| | | | | | | |
|---|---|---|---|---|---|---|
| $C_{21}H_{14}N_2$ | Calcd.: | C | 85.69 | H | 4.79 | N 9.52 |
| (294.36) | Found: | C | 85.73 | H | 4.71 | N 9.50. |

*1-Methyl-2-phenylphenanthro[9,10-d]imidazole* (**14b**)

A sample of 300 mg (0.97 mmol) of **13b** in 110 ml of ethanol was irradiated through a quartz cooling sleeve with the full emission of a HPK 125 W high pressure mercury burner for 7 h. Repeated crystallization of the concentration residue gave 35 mg (9%) of pale yellow crystals, *m.p.* 186–188 °C (ref. [12b] 188–190 °C). – UV (ethanol): $\lambda_{max}$/nm (lg $\varepsilon$) = 231 (4.44), 257 (4.80), 283 (4.29), 302 (sh, 4.23), 338 (3.75), 355 (3.70).

**Preparation of 1,4-Diaryl-2,5-diphenyl-1,4-dihydropyrazines 15a–j (General Procedure)**

*N,N-Diphenacylarylamines*

In most cases these intermediates were synthesized by step-by-step alkylation of the aromatic amines with phenacyl bromide as follows: A solution of phenacyl bromide (10 mmol) and aromatic amine (20 mmol) in ether or ethanol (depending on the solubility of aromatic amine) was stirred overnight at ambient temperature. The amine hydrobromide was filtered off and the filtrate was concentrated to dryness. The residue was crystallized from an appropriate solvent. The mixture of *N*-phenacylamine (10 mmol), $KHCO_3$ (20 mmol), and tetrabutylammonium hydrogen sulfate was kept at 80 °C for 1 h. After being cooled to room temperature the reaction mixture was triturated with water (50 ml), the insoluble organic material was filtered off and dissolved in $CH_2Cl_2$. The aqueous layer was extracted with $CH_2Cl_2$ (3 × 15 ml). The combined $CH_2Cl_2$ solutions were dried ($MgSO_4$), filtered and concentrated to give *N,N*-diphenacylamine.

In case of 4-trifluoromethylaniline the corresponding *N,N*-diphenacylamine was prepared in a different way. Phenacyl bromide (40 mmol), 4-trifluoromethylaniline (20 mmol), and sodium carbonate (20 mmol) were thoroughly mixed and kept at 80–90 °C for 1.5 h. The cooled mixture was taken up in $CH_2Cl_2$ (350 ml), washed with water (3 × 100 ml), dried ($MgSO_4$), and filtered. The residue was triturated with hot methanol (600 ml) to give *N,N*-diphenacyl-4-trifluoromethylaniline as white yellow crystals in 19% yield, *m.p.* 232–234 °C. – $^1$H NMR ($CDCl_3$): $\delta$/ppm = 4.97 (s, 4H, $CH_2$), 6.53 + 7.39 (AB, $J$ = 8.5 Hz, 4H, ar-H), 7.50–7.68 (m, 6H, Ph-H), 8.00–8.04 (m, 4H, Ph-H).

*1,4-Diaryl-2,5-diphenyl-1,4-dihydropyrazines* **15a–j**

*p*-Toluenesulfonic acid monohydrate (0.5 mmol) was refluxed in toluene (50 ml) under a Stark–Dean trap for 1 h. *N,N*-diphenacylarylamine (10.0 mmol) and arylamine (10.0 mmol) were added to this dry mixture and refluxed until the diphenacylamine had been consumed (TLC monitoring using $CH_2Cl_2$/hexane/acetone 5:5:0.5).The insoluble catalyst was filtered off, the filtrate was concentrated to dryness and the

**Table 1** Yields and analytical data of 1,4-diaryl-2,5-diphenyl-1,4-dihydropyrazines (**15 a**–**j**)

| Compound | | | Reaction time (h) | Yield (%) | Melting point (°C) | Elemental Analysis and/or ref. | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Y | Z | | | | Calcd. / Found | C | H | N |
| **15a** | Cl | Cl | 5 | 31.4 | 203–206 | | | | [26] |
| **15b** | H | H | 5 | 44.0 | 207–208 | | 87.05 | 5.70 | 7.25 |
| | | | | | | | 86.94 | 5.90 | 7.56 |
| **15c** | Me | H | 4 | 25.8 | 206–209 | | 86.97 | 6.04 | 6.99 |
| | | | | | | | 86.72 | 6.26 | 6.91 |
| **15d** | H | Me | 5 | 41.0 | 132–136 | | 86.97 | 6.04 | 6.99 [27] |
| | | | | | | | 86.63 | 6.29 | 7.38 |
| **15e** | Z | Me | 5.5 | 24.7 | 167–170 | | 86.92 | 6.32 | 6.76 [27] |
| | | | | | | | 86.66 | 6.44 | 6.73 |
| **15f** | Me | $CF_3$ | 1.25 | 28.9 | 155–160 | | 76.92 | 4.91 | 5.98 |
| | | | | | | | 77.19 | 5.07 | 5.94 |
| **15g** | $CF_3$ | Me | 3 | 52.0 | 232–234 | | 76.92 | 4.91 | 5.98 |
| | | | | | | | 76.73 | 4.99 | 5.99 |
| **15h** | $CF_3$ | $CF_3$ | 1.5 | 67.6 | 222–223 | | 68.96 | 3.83 | 5.36 |
| | | | | | | | 70.11 | 4.17 | 4.77 |
| **15i** | $CF_3$ | H | 4 | 37.5 | 227–228 | | 76.65 | 4.63 | 5.74 |
| | | | | | | | 76.47 | 6.69 | 6.19 |
| **15j** | H | $CF_3$ | 1.5 | 30.5 | 175–179 | | 76.65 | 4.63 | 6.17 |
| | | | | | | | 76.61 | 4.90 | 5.74 |

residue was crystallized from an appropriate amount of ethanol/benzene (1:1). For yields, *m.p.*'s and analytical data see Table 1.

*1,4-Bis(4-chlorophenyl)-2,6-diphenyl-1,4-dihydropyrazine* (**15a**)

IR (KBr): $\nu$/cm$^{-1}$ = 3 082, 3 051, 1 645, 1 593, 1 489, 1 445, 1 363, 1 326, 1 234, 1 090, 1 030, 795, 732, 690. – $^1$H NMR ($CDCl_3$): [3]) $\delta$/ppm = 6.74 (d, 2 H, 2'-, 6'-H), 6.98 (d, 2H, 3'-, 5'-H), 7.08 (d, 2H, 2'''-, 6'''-H), 7.26 (t, 2H, 4''-H), 7.32 (d, 2H, 3'''-, 5'''-H), 7.38 (t, 4H, 3''-, 5''-H), 7.46 (s, 2H, 3-, 5-H), 7.68 (d, 4 H, 2''-, 6''-H). – $^{13}$C NMR ($CDCl_3$): [3]) $\delta$/ppm = 117.7* (C-2''', C-6'''), 117.7* (C-2', C-6'), 124.1 (C-2'', C-6''), 125.0 (C-3, C-5), 125.3 (C-4', C-4'''), 126.8 (C-1''), 127.3 (C-4''), 128.6 (C-3', C-5'), 129.3 (C-3'', C-5''), 129.8 (C-3''', C-5'''), 136.4 (C-2, C-6), 140.9 (C-1'''), 148.9 (C-1').

*1,2,4,6-Tetraphenyl-1,4-dihydropyrazine* (**15b**)

IR (KBr): $\nu$/cm$^{-1}$ = 3 032, 1 648, 1 593, 1 489, 1 446, 1 363, 1 343, 1 326, 1 244, 1 183, 1 054, 1 028, 847, 751, 732, 690. – $^1$H NMR ($CDCl_3$): $\delta$/ppm = 6.79 (t, 1H, 4'-H), 6.82 (d, 2H, 2'-, 6'-H), 7.04 (t, 1H, 4'''-H), 7.17 (d, 2H, 2'''-, 6'''-H), 7.26 (t, 2H, 4''-H), 7.36 (s, 8H, 3'-, 3''-, 3'''-, 5'-, 5''-, 5'''-H), 7.57 (s, 2H, 3-, 5-H), 7.74 (d, 4H, 2''-, 6''-H).

*1,2,6-Triphenyl-4-(p-tolyl)-1,4-dihydropyrazine* (**15c**)

IR (KBr): $\nu$/cm$^{-1}$ = 3 028, 2 859, 1 593, 1 513 1 490, 1 327, 1 241, 1 151, 806, 751, 690. – $^1$H NMR ($CDCl_3$): $\delta$/ppm = 2.23 (s, 3H, $CH_3$), 6.66 (d, 2H, 2'''-, 6'''-H), 6.71 (t, 1H, 4'-H), 6.85 (d, 2H, 3'''-, 5'''-H), 6.96 (t, 2H, 2'-, 6'-H), 7.07 (t, 2H, 4''-H), 7.10–7.30 (m, 8H, 3-, 3'-, 3''-, 5-, 5'-, 5''-H), 7.68 (d, 4H, 2''-, 6''-H). – $^{13}$C NMR ($CDCl_3$): $\delta$/ppm = 20.4 ($CH_3$), 116.4* (C-2''', C-6'''), 117.5* (C-2', C-6'), 120.1 (C-4'), 124.0, 125.4, 125.8, 126.6, 128.7, 128.9 (C-2'', C-6''), 129.9 (C-3'', C-5''), 132.7 (C-4'''), 137.3 (C-2, C-6), 140.5 (C-1'''), 151.0 (C-1').

*2,4,6-Triphenyl-1-(p-tolyl)-1,4-dihydropyrazine* (**15d**)

IR (KBr): $\nu$/cm$^{-1}$ = 3 033, 1 648, 1 595, 1 580, 1 501, 1 480, 1 445, 1 360, 1 336, 1 245, 1 131, 1 051, 849, 810, 762, 751, 711, 684. – $^1$H NMR ($CDCl_3$): $\delta$/ppm = 2.16 (s, 3H, $CH_3$), 6.76 (d, 2H, 2'-, 6'-H), 6.84 (d, 2H, 3'-, 5'-H), 7.05 (t, 1H, 4'''-H), 7.14 (d, 2H, 2'''-, 6'''-H), 7.23 (t, 2H, 4''-H), 7.31–7.37 (m, 6H, 3''-, 3'''-, 5''-, 5'''-H), 7.51 (s, 2H, 3-, 5-H), 7.72 (d, 4H, 2''-, 6''-H). – $^{13}$C NMR ($CDCl_3$): $\delta$/ppm = 21.0 ($CH_3$), 116.9 (C-2''', C-6'''), 117.1* (C-2', C-6'), 123.5 (C-4'''), 124.6* (C-2'', C-6''), 125.4 (C-3, C-5), 127.2** (C-1''), 127.3 (C-4''), 129.5 (C-3'', C-5''), 129.7 (C-3', C-5'), 129.8** (s, C-4'), 130.2 (C-3''', C-5'''), 137.6 (C-2, C-6), 142.9 (C-1'''), 148.6 (C-1').

*2,6-Diphenyl-1,4-bis(p-tolyl)-1,4-dihydropyrazine* (**15e**)

IR (KBr): $\nu$/cm$^{-1}$ = 3 027, 2 918, 2 859, 1 609, 1 593, 1 566, 1 506, 1 444, 1 360, 1 335, 1 243, 1 132, 1 051, 810, 754, 692. – $^1$H NMR ($CDCl_3$): $\delta$/ppm = 1.99 (s, 3H, $CH_3$), 2.09 (s, 3H, $CH_3$), 6.69 (d, 2H, 2'''-, 6'''-H) 6.78 (d, 2 H, 2'-, 6'-H), 6.88 (d, 2H, 3'''-, 5'''-H), 7.10–7.30 (m, 10H, 3-, 3'-, 3''-, 4''-, 5-, 5'-, 5''-H), 7.74 (d, 4 H, 2''-, 6''-H). – $^{13}$C NMR ($CDCl_3$): $\delta$/ppm = 20.4 ($CH_3$), 20.6 ($CH_3$), 117.1* (C-2', C-6'), 117.5* (C-2''', C-6'''), 124.4 (2C, C-2'', C-6''), 125.7, 126.2, 126.7, 127.8, 128.2, 129.4 (2C, C-3'', C-5''), 129.5 (C-3', C-5'), 130.1** (C-4'), 132.7** (C-4'''), 137.7 (C-2, C-6), 140.8 (C-1'''), 149.00 (C-1').

*1-(4-Trifluoromethylphenyl)-2,6-diphenyl-4-(p-tolyl)-1,4-dihydropyrazine* (**15f**)

IR (KBr): $\nu$/cm$^{-1}$ = 3 081, 3 053, 3 032, 2 921, 2 859, 1 609, 1 566, 1 515, 1 491, 1 324, 1 283, 1 239, 1 166, 1 129, 1 101,

[3]) Henceforth single-primed locants refer to 1-aryl, double-primed locants to 2,6-diaryl, triple-primed locants to 4-aryl protons and carbons. Assignments of carbon resonances starred by the same number of asterisks are mutually interchangeable

1 070, 1 048, 858, 824, 807, 798, 771, 755, 690. – $^1$H NMR ($CDCl_3$): $\delta$/ppm = 2.09 (s, 3H, $CH_3$), 6.71 (d, 2H, 2'''-, 6'''-H), 6.90 (d, 2H, 3'''-, 5'''-H), 6.96 (d, 2H, 3'-, 5'-H), 7.05 – 7.30 (m, 10H, 2'-, 3-, 3''-, 4''-, 5-, 5''-, 6'-H), 7.60 (d, 4H, 2''-, 6''-H). – $^{13}$C NMR ($CDCl_3$): $\delta$/ppm = 20.6 ($CH_3$), 115.8 (C-2', C-6'), 118.0 (C-2''', C-6'''), 123.9 (C-2'', C-6''), 124.3 (C-3', C-5'), 126.4, 127.0, 128.5, 129.3 (C-3'', C-5''), 130.2 (C-3''', C-5'''), 133.7 (C-4'''), 136.6 (C-2, C-6), 140.5 (C-1'''), 153.6 (C-1').

*4-(4-Trifluoromethylphenyl)-2,6-diphenyl-1-(p-tolyl)-1,4-dihydropyrazine* (**15g**)

IR (KBr): $\nu$/cm$^{-1}$ = 3 060, 3 031, 2 925, 1 611, 1 582, 1 569, 1 506, 1 447, 1 363, 1 323, 1 248, 1 196, 1 154, 1 117, 1 071, 1 045, 1 008, 824, 812, 753, 690. – $^1$H NMR ($CDCl_3$): $\delta$/ppm = 2.15 (s, 3H, $CH_3$), 6.75 (d, 2H, 2', 6'-H), 6.84 (d, 2H, 3', 5'-H), 7.15 (d, 2H, 2'''-, 6'''-H), 7.27 (t, 2H, 4''-H), 7.38 (t, 4H, 3''-, 5''-H), 7.39 (s, 2H, 3-, 5-H), 7.57 (d, 2H, 3'''-, 5'''-H), 7.73 (d, 4H, 2''-, 6''-H). – $^{13}$C NMR ($CDCl_3$): $\delta$/ppm = 20.6 ($CH_3$), 114.5 (C-2''', C-6'''), 117.5 (C-2', C-6'), 123.3 (C-3, C-5), 123.8 (C-4''', $J_{CF}$ 32.7 Hz), 124.7 (C-2'', C-6''), 127.0 (C-3''', C-5''', $J_{CF}$ 3.6 Hz), 127.5 (C-4''), 129.2 (C-3'', C-5''), 129.4 (C-3', C-5'), 130.06 (C-1''), 130.10 (C-4'), 136.7 (C-2, C-6), 144.3 (C-1'''), 147.1 (C-1').

*1,4-Bis(4-trifluoromethylphenyl)-2,6-diphenyl-1,4-dihydropyrazine* (**15h**)

IR (KBr): $\nu$/cm$^{-1}$ = 3 060, 3 036, 1 611, 1 570, 1 515, 1 491, 1 364, 1 324, 1 249, 1 197, 1 165, 1 119, 1 072, 1 043, 1 008, 824, 756, 693. – $^1$H NMR ($CDCl_3$): $\delta$/ppm = 6.83 (d, 2H, 2'-, 6'-H), 7.20 (d, 2H, 2'''-, 6'''-H), 7.27 (d, 2H, 3'-, 5'-H), 7.31 (t, 2H, 4''-H), 7.42 (t, 4H, 3''-, 5''-H), 7,54 (s, 2H, 3-, 5-H), 7.60 (d, 2H, 3'''-, 5'''-H), 7.71 (d, 4H, 2''-, 6''-H). – $^{13}$C NMR ($CDCl_3$): $\delta$/ppm = 115.5 (C-2''', C-6'''), 116.1 (C-2', C-6'), 122.1 (C-4', $J_{CF}$ 32.3 Hz), 124.5 (C-2'', C-6''), 124.6 (C-3, C-5), 125.1 (C-4''', $J_{CF}$ 33.1 Hz), 126.2 (C-3', C-5', $J_{CF}$ 3.7 Hz), 127.4 (C-3''', C-5''', $J_{CF}$ 3.7 Hz), 128.0 (C-4'’), 128.4 (C-1''), 129.6 (C-3'', C-5''), 136.0 (C-2, C-6), 144.4 (C-1'''), 152.4 (C-1').

*4-(4-Trifluoromethylphenyl)-1,2,6-triphenyl-1,4-dihydropyrazine* (**15i**)

IR (KBr): $\nu$/cm$^{-1}$ = 3 059, 1 611, 1 595, 1 582, 1 569, 1 519, 1 492, 1 447, 1 364, 1 323, 1 300, 1 247, 1 196, 1 163, 1 116, 1 071, 1 047, 1 009, 824, 759, 748, 690. – $^1$H NMR ($CDCl_3$): $\delta$/ppm = 6.79 (t, 1H, 4'-H), 6.82 (d, 2H, 2'-, 6'-H), 7.03 (t, 2H, 3'-, 5'-H), 7.17 (d, 2H, 2'''-, 6'''-H), 7.29 (t, 2H, 4''-H), 7.39 (t, 4H, 3''-, 5''-H), 7.46 (s, 2H, 3-, 5-H), 7.58 (d, 2H, 3'''-, 5'''-H), 7.74 (d, 4H, 2''-, 6''-H). – $^{13}$C NMR ($CDCl_3$): $\delta$/ppm = 114.7 (C-2''', C-6'''), 116.9 (C-2', C-6'), 120.5 (C-4'), 123.7 (C-3, C-5), 124.1 (C-4''', $J_{CF}$ 32.3 Hz), 124.6 (C-2'', C-6''), 127.1 (C-3''', C-5''', $J_{CF}$ 3.7 Hz), 127.6 (C-4''), 128.8 (C-3', C-5'), 129.2 (C-3'', C-5''), 129.6 (C-1''), 136.6 (C-2, C-6), 144.3 (C-1'''), 149.4 (C-1').

*1-(4-Trifluoromethylphenyl)-2,4,6-triphenyl-1,4-dihydropyrazine* (**15j**)

IR (KBr): $\nu$/cm$^{-1}$ = 3 057, 1 611, 1 598, 1 581, 1 515, 1 500, 1 446, 1 360, 1 327,1 269, 1 243, 1 194, 1 163, 1 114, 1 072, 1 048, 1 008, 826, 750, 690, 677, 664. – $^1$H NMR ($CDCl_3$): $\delta$/ppm = 6.89 (d, 2H, 2'-, 6'-H), 7.12 (t, 1H, 4'''-H), 7.20 (d, 2H, 2'''-, 6'''-H), 7.25 – 7.32 (m, 4H, 3'-, 4''-, 5'-H), 7.38 – 7.45 (m, 6H, 3''-, 3'''-, 5''-, 5'''-H), 7.63 (s, 2H, 3-, 5-H), 7.71 (d, 4H, 2''-, 6''-H). – $^{13}$C NMR ($CDCl_3$): $\delta$/ppm = 115.6 (C-2', C-6'), 117.1 (C-2''', C-6'''), 121.5 (C-4', $J_{CF}$ 32.7 Hz), 123.89 (C-2'', C-6''), 123.94 (C-4'''), 125.1 (C-1''), 125.8 (C-3, C-5), 125.9 (C-3', C-5', $J_{CF}$ 3.6 Hz), 127.2 (C-4''), 129.3 (C-3'', C-5''), 129.9 (C-3''', C-5'''), 136.2 (C-2, C-6), 142.3 (C-1'''), 153.2 (C-1').

**Synthesis of 1,2,5-Triarylpyrroles (General Method)**

A mixture of 1,4-diphenylbutane-1,4-dione (2.38 g, 10 mmol) and 10 mmol of 4-substituted aniline in acetic acid (10 ml) was heated at 70 – 80 °C for 1 h. The solvent was removed from the clear solution formed, and the residue was triturated with ether. The product was filtered off and recrystallized from acetic acid. The syntheses of compounds **16a**,**b** [13] and **16c** [18] have been reported.

*1-(p-Chlorophenyl)-2,5-diphenylpyrrole* (**16a**) [13]

Oil, $^1$H NMR ($CDCl_3$): $\delta$/ppm = 6.50 (s, 2H, pyrrole 3-, 4-H), 6.97 + 7.08 (AB, $J$ = 8.3 Hz, 4H, ar-H), 7.09 (d, $J$ = 6.5 Hz, 2H, Ph-H), 7.20 – 7.25 (m, 8H, Ph-H). – MS (70 eV): *m/z* (%) = 329 (100) [$M^+$], 294 (16) [$M^+$ – Cl], 191 (40.8) [$M^+$ – $ClC_6H_4N$=CH], 165 (13.6), 139 (12.3), 77 (19.6), 51 (11.8), 44 (25.8).

*1-(p-Trifluoromethylphenyl)-2,5-diphenylpyrrole* (**16d**)

This compound was obtained in 28.9% yield, *m.p.* 209 – 211 °C (ethanol). – IR (KBr): $\nu$/cm$^{-1}$ = 2 900, 1 680, 1 592, 1 448, 1 400, 1 384, 1 376, 1 368, 1 352, 1 224, 1 180, 992, 776, 736, 696. – $^1$H NMR (acetone-$d_6$): $\delta$/ppm = 6.50 (s, 2H, pyrrole 3-, 4-H), 7.08 (d, 4H, 2''-, 6''-H), 7.19 – 7.28 (m, 6H, 3''-, 4''-, 5''-H), 7.28 (d, 2H, 2'-, 6'-H), 7.66 (d, 2H, 3'-, 5'-H). – $^{13}$C NMR (acetone-$d_6$): $\delta$/ppm = 111.5 (C-2', C-6'), 126.8 (C-3', C-5', $J_{CF}$ 4.8 Hz), 127.6 (C-4''), 129.0* (C-2'', C-6''), 129.7* (C-3'', C-5''), 130.7 (C-3, C-4), 134.0** (C-1''), 136.9** (C-2, C-5), 143.5 (C-1').

*1-(p-Chlorophenyl)-3,4-diphenylpyrrole* (**17a**)

According to the literature [22] a solution of dimethyl 1-(*p*-chlorophenyl)-3,4-diphenyl-2,5-dicarboxylate (2.9 g, 6.5 mmol) and KOH (10.7 g, 0.19 mole) in ethanol (110 ml) was refluxed for 4 h. The solution was acidified at 0 ° C with sulfuric acid (32.3 ml, 0.61 mole), and diluted with ethanol (105 ml). The resulting mixture was refluxed for 8 h and after cooling it was neutralized by slow addition of solid NaOH (40.6 g, 1.02 mole). This mixture was poured onto crushed ice (600 g). The product was filtered off, washed with water, and recrystallized from acetic acid to give **17a** in 47.6% yield (1.02 g), *m.p.* 147 – 149 °C (ref. [22] 145 – 146 °C). – IR (KBr): $\nu$/cm$^{-1}$ = 3 060, 1 605, 1 542, 1 505, 1 448, 1 400, 1 250, 1 080, 1 060, 945, 840, 795, 776, 700. – $^1$H NMR ($CDCl_3$): $\delta$/ppm = 7.16 (s, 2H, pyrrole 2-H, 5-H), 7.20 – 7.24 (m, 2H, ar-H), 7.26 – 7.31 (m, 8H, ar-H), 7.40 – 7.44 (m, 4H, ar-H). – MS (70 eV): *m/z* (%) = 329 (100) [$M^+$], 191 (58.1) [$M^+$ – $ClC_6H_4N$=CH], 165 (11.25).

*3,6-Diphenylpyridazine* (**18**)

This compound was prepared according to the method described by *Paal and Schulze* [23] starting from *(E)*-1,4-diphenylbut-2-en-1,4-dione and hydrazine hydrate in 27.5% yield.

All physical properties (*m.p.*, IR, NMR) proved to be completely identical with those reported in the literature [24].

*Irradiations of Iminium Salts*

Irradiation has been carried out in a Pyrex immersion well reactor using Philips HPK 125 high pressure mercury lamp. Unless stated otherwise, 1.5 mmol of starting material was dissolved in 150 ml of 2-propanol and the solution acidified as listed. During irradiation the reaction mixture was maintained between 20–30 °C and was purged with dry nitrogen. Unless stated otherwise, samples (1 ml) were taken from the reaction mixture at appropriate intervals and assayed for product composition by HPLC under the conditions described above. Calibrations were made using authentic samples.

*Irradiation of* **2a**·HCl

HPLC-monitoring revealed that the irradiation time required for complete conversion was dependent on the amount of hydrochloric acid present: 48 h in absence of added HCl, but 35, 29, 27 and 26 h, respectively, in the presence of 1, 2, 5 and 10 equivalents, respectively, of added HCl. The reaction mixtures were concentrated to dryness *in vacuo* and the residues were taken up in dichloromethane (50 ml each), washed with 10% aqueous ammonia (3×15 ml), and dried over $MgSO_4$. The residue was subjected to silica gel chromatography using hexane/acetone (4:1) and compounds **3a**, **4a**, **6**, and **7** were isolated in quantities suitable to allow for identification. The exact amounts of products could, however, not be determined in this experiment due to inevitable losses and partial decomposition during separation.

*Irradiation of* **2b**·HCl

According to HPLC-monitoring the reaction was complete after 16 h. The reaction mixture was concentrated to dryness *in vacuo*. The residue was taken up in ethyl acetate (50 ml), washed with 10% aqueous ammonia (3×15 ml), and dried over $MgSO_4$. The residue was purified by column chromatography using hexane/acetone (4:1) to give 143 mg of **3b** (46.7%), 42.2 mg of **4b** (15.5%), and 5.2 mg of **5** (19.3%).

*Irradiation of* **9**·HCl

The solution of **9** was saturated with dry HCl gas and irradiated for 30 h. The work-up was similar to that described above. The isolated pure product (52%) proved to be completely identical (IR, *m.p.*, NMR) with an authentic sample of compound 10 [15].

*Irradiation of* **11a**·HCl

Compound **11a** was irradiated in ethanol in presence of 1 eq. HCl. HPLC analysis showed the following product distribution after 2 h irradiation and 99.8% conversion of **11a**: 29% of **13a**, 59% of **14a**.

*Irradiation of* **11b**·HCl

Compound **11b** was irradiated in ethanol in presence of 2 eq. HCl. After 2 h irradiation to 99.8% conversion, HPLC-analysis showed the following product distribution: 36.2% **13a** and 5.8% **13b**. Compounds **14a**,**b** were present also but in very low quantity.

*Irradiation of* **15a**–**j** *in Presence of HCl*

Quantities of 1.0–1.5 mmol of starting materials were dissolved in 100–150 ml of 2-propanol and purged with $N_2$. Equimolar amounts of HCl were introduced by adding the appropriate quantities of 2-propanol saturated with dry HCl (11.17 mol/L). Samples (1 ml) were taken every 10 h. Irradiation times were kept between 30–130 h, dark reactions were run for 30 h. Products observed (with retention times given in parentheses) were **16a** (17.17 min), **16b** (9.02 min), **16c** (14.85 min), and **16d** (29.73 min), respectively (see Table 2).

*Irradiation of* **18**

A 1.0 mmol sample (232.30 mg) of starting material was suspended in 2-propanol (150 ml). This mixture was saturated with dry HCl gas at 0 °C and was allowed to warm up to room temperature. The clean solution was irradiated until the starting material had disappeared (monitored by TLC, hexane/acetone 10:3). After conventional work up the crude product was purified by using TLC ready-plates by using hexane/acetone (10:4) to give 39.4 mg (14.5%) of *4-isopropyl-3,6-diphenylpyridazine* (**19**), *m.p.* 110 °C (ref. [25] 110 °C). – $^1$H NMR ($CDCl_3$): $\delta$/ppm = 1.25 (d, $J$ = 7.2 Hz, 6H, $CH_3$), 3.20 (sept, 1H, CH), 6.54 (s, 1H, 5-H), 7.10–7.70 (m, 8H, ar-H), 8.12–8.17 (m, 2H, ar-H). For literature NMR data see ref. [25].

**Table 2** Decomposition of triarylpyrroles **15a** and **16a**. Percentages of material still present after the times listed.

| Time (h) | Dark reaction of **16a** | Dark reaction of **17a** | Irradiation of **16a** | Irradiation of **17a** |
|---|---|---|---|---|
| 1 | 77% | 95% | | |
| 10 | | 88% | | 18% |
| 30 | 40% | | not detectable | 8% |

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