Photochemistry of N-Heterocycles, 5[+]

A Comparison of Chemical and Photochemically Induced Reduction of Some 2(4),5-Dihydro-1,2,4-triazines and Aromatic 1,2,4-Triazines

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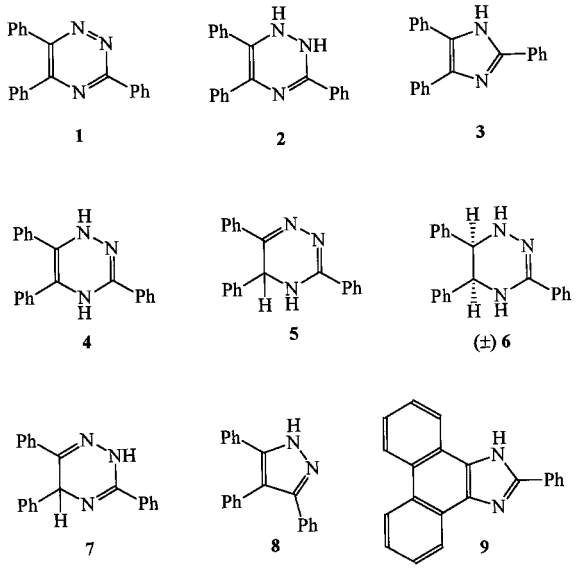
Chemical reduction (Zn/AcOH) of the arene **1** and of 2(4),5-dihydro-1,2,4-triazine **7** has been reinvestigated, resulting in the amendment of literature data concerning this reaction. Chemical, electrochemical, and photochemically induced reductions and ring contractions of 1,2,4-triazine derivatives have been compared. The first example of a triaryl-1,4-dihydrotriazine has been prepared. Some further evidence is presented that supports the proposed mechanism of the photochemically induced reduction and ring contraction of 1,2,4-triazines.

Introduction

In continuation of our earlier research, we have further investigated the photochemically induced reduction and ring contraction of 1,2,4-triazines. At the same time, we have reinvestigated some chemical reductions with the aim of gaining further evidence to support our proposed mechanism for the photochemically induced reductions. If the latter reactions take place as electron/proton-transfer reactions, their pathways can be expected to be similar to those of the chemical (zinc/acetic acid) and electrochemical reductions.

With the exception of our more recent studies on the photochemically induced reduction of 1,2,4-triazines,[1] the chemical[2,3a,4] and electrochemical[5,6] reductions of compounds of this type have been known for a long time. Various structures have been proposed for the first reduction products starting from the aromatic triazine **1**, namely 1,2-dihydro- (**2**),[4] 1,4-dihydro- (**4**),[5] 4,5-dihydro- (**5**),[3a] and 2,5-dihydro-1,2,4-triazine **7**.[1] Further electrochemical reduction leads to the tetrahydro derivative *rac*-**6**. The photochemically induced reduction[1] furnishes 2,5-dihydro-1,2,4-triazine **7**. In all cases, imidazoles are isolated as final products, apart from in the photochemically induced reactions, where pyrazoles are also formed.

The aim of our reinvestigation of the chemical reduction has been to assess whether the structures **2**, **4**, and **5** are correct, and whether they are indeed different from **7**.



Scheme 1. Starting materials and reduction products

Results and Discussion

On the basis of our earlier studies,[1] we proposed the following mechanism for the photochemically induced reduction and ring contraction (Scheme 2).

It was also shown that the ratio of imidazoles formed by cleavage of the N(1)−N(2) bond is dependent on the structure of the triazine. The more alkyl substituents present at N(2) and N(4), the more the prototropic equilibrium is shifted towards the hypothetical intermediate **B**. The activation enthalpy must be lower for a nucleophilic attack on a protonated than on a non-protonated C=N bond, and hence only the *N*-ethylimidazole is formed in the reaction **14** → **11** + **15** (see Scheme 3, Table 1). On the other hand, in the reaction **10a** → **11** + **9** + **13** (see Scheme 3, Table 1) the activation enthalpies must be comparable for nucleophilic attack of N(2) and N(1) on the protonated C(6)=

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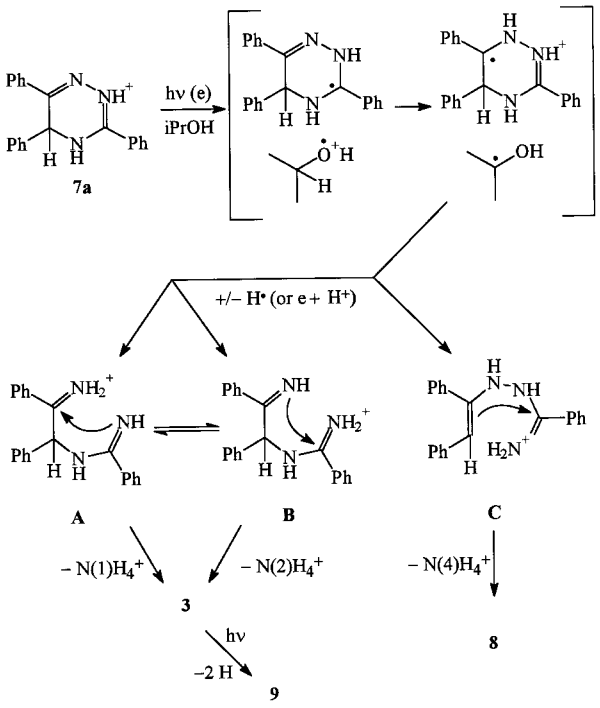
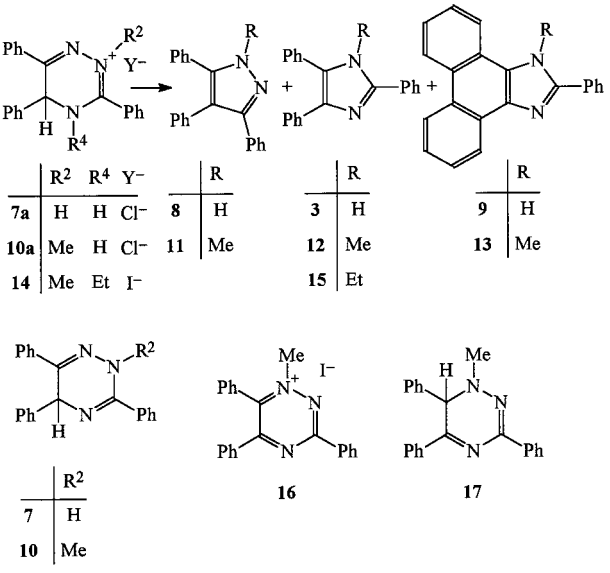


Scheme 2. Hypothetical mechanism of photochemically induced ring contractions

N(1) or C(3)=N(2) bonds, and hence non-methylated- and methylated imidazole **9** and **13** are formed simultaneously. In Scheme 3 and Table 1, various other examples of photochemically induced ring contractions of *N*-monosubstituted- and *N*,*N*′-disubstituted 1,2,4-triazines are presented, the product distributions from which are given in Table 2. The higher the degree of substitution of the formed amidine, the more the equilibrium is shifted in favour of the intermediate **B** and the larger the amount of product formed by extrusion of N(2).



Scheme 3. *N*-Substituted starting materials and their products

All three reaction types (chemical, electrochemical, and photochemically induced electron transfer) must have very similar pathways. The electrochemical reduction of the aromatic triazine **1** has already been reinvestigated.[1c] In this case, the product of the first reduction step is the 2(4),5-dihydrotriazine **7** (the 2,5- and 4,5-dihydro compounds are in tautomeric equilibrium, this being shifted towards the 2,5-dihydro derivative in alcoholic solution[1a]). Pyrazole **8** is formed as a by-product rather than the 1,2-dihydrotriazine **2**. The 1,4-dihydrotriazine **4** would appear to be a short-lived intermediate; it has been detected but so far has eluded isolation. Consequently, there is no evidence to confirm its structure, although we also assumed its involvement in the photochemically induced reduction and ring contraction of aromatic triazine **1** to imidazole **3**. The second electrochemical reduction step furnished the imidazole **3** and the tetrahydro derivative *rac*-**6** (see Scheme 4).

Our reinvestigation of the chemical reduction revealed great similarities to the electrochemical reduction. The first reduction step gave after 1 h a mixture of 2,5-dihydrotriazine **7** (rather than the 1,2-dihydro derivative **2**, cf. ref.[4]!) (76%), imidazole **3** (17%), and pyrazole **8** (1%). After a prolonged reaction time, further reduction of the dihydrotriazine **7** occurred, furnishing more imidazole **3**. After 3 h, the product distribution was imidazole **3** (56%), 2,5-dihydrotriazine **7** (8%), and pyrazole **8** (1%).

The photochemical and chemical reductions leading to imidazoles must proceed through the same intermediates, these being formed by cleavage of the N(1)−N(2) bond. As can be seen in Table 2, the product distributions from photochemical and chemical reductions are essentially the same. Chemical reduction of 1-methyl-1,6-dihydro-1,2,4-triazine **17**, like the photochemical reduction,[1c] provided neither the corresponding imidazole **12**, nor pyrazole **11**; in fact **17** decomposed completely.

Metze and Scherowsky[4] treated the first chemical reduction product of the aromatic 1,2,4-triazine **1** with acetic anhydride, thereby producing a diacetyl derivative, which they believed to be the 1,2-diacetyl-1,2-dihydro-1,2,4-triazine **18**.[4] Analogous treatment of the actual intermediate dihydrotriazine **7** with acetic anhydride provided another *N*,*N*′-diacetyldihydrotriazine **19**. In the light of the arguments outlined below, its structure corresponds to 1,4-diacetyl-3,5,6-triphenyl-1,4-dihydro-1,2,4-triazine (see Scheme 5). Such 1,4-dihydrotriazines have been assumed to be intermediates in the electrochemical[5] and photochemical[1c] reactions, but it has not previously been possible to isolate them. Attempts to prepare *N*-unsubstituted or alkyl-substituted 3,5,6-triphenyl-1,4-dihydro-1,2,4-triazines have also been unsuccessful.[1c] Compound **19** represents the first example of a 1,4-dihydro-1,2,4-triazine tautomer in fixed form.

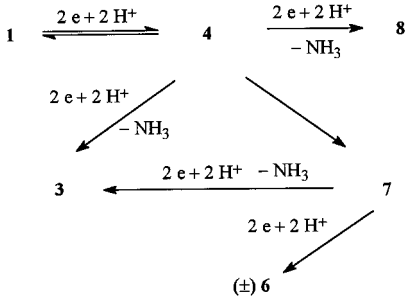
The 1,2-diacetyl and 1,4-diacetyl isomers could be distinguished on the basis of ^{15}N-NMR data, which was obtained by a two-dimensional heteronuclear multiple-bond correlation (HMBC) experiment.[7] The chemical shifts of N-1, N-2, and N-4 were found to be −175.1, −60.6, and −153.1, respectively (relative to nitromethane as an external

Table 1. Dependence of the products of various reductions on the structures of the starting materials

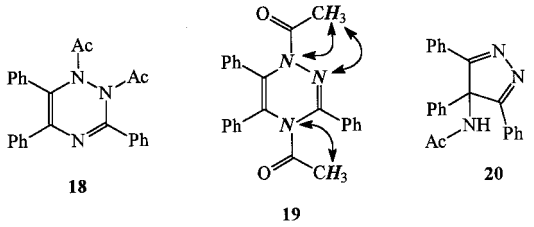
Starting material	Photochemical reduction		Chemical reduction	
	Pyrazoles	Imidazoles	Pyrazoles	Imidazoles
1	**8**	**9**	**8**	**3**
7a or **7**	**8**	**9**	–	**3**
10a or **10**	**11**	**9** and **13**	–	**3** and **12**
14	**11**	**15**	–	**15**
16	–	**3**	**11**	**3**
17	–	–	–	–

Table 2. Dependence of product distributions on the structures of starting materials

Starting material	Ratio of imidazole/pyrazole	Ratio of imidazoles formed by extrusion of N(2)/N(1)	
	Photochemical reduction	Photochemical reduction	Chemical reduction
7a or **7**	0.49	Not determined	Not determined
10a or **10**	0.93	0.86	0.81
14	2.08	∞	∞
16	∞	0	0



Scheme 4. Hypothetical mechanism of chemical and electrochemical reductions



Scheme 5. Proposed[4] and determined structures of diacetyl derivatives; its ring contracted product

standard), values in accordance with ^{15}N correlation charts. No cross-peaks could be detected between the aromatic proton and the ^{15}N signals; the *N*-1-(acetyl)methyl signal at $\delta = 2.56$ shows cross-peaks with the N-1 and N-2 signals, while the *N*-4-(acetyl)methyl signal at $\delta = 2.35$ shows a cross-peak only with the N-4 signal. These observations corroborate the 1,4-diacetyl structure. In the case of the 1,2-diacetyl alternative, both N-1 and N-2 would show cross-peaks with the two methyl signals, while N-4 might not appear due to the lack of polarization transfer (the closest methyl hydrogen atoms are five bonds away from N-4).

Chemical and photochemical reduction of compound **19** resulted in a mixture of pyrazole **8** (40%), imidazole **3**, and dihydrotriazine **7**, of which only the first compound could be isolated; the latter two minor products could only be detected by TLC. The 1,4-dihydro compound **19** was found to be unstable under acidic conditions; on leaving a solution of this compound in acidic propan-2-ol to stand for an extended period, it underwent conversion to compound **20** (see Scheme 5), which, upon chemical or photochemical reduction, was transformed exclusively into pyrazole **8**.

These results support the following hypothesis: While the imidazoles formed in the course of chemical, electrochemical, and photochemically induced reductions of various 1,2,4-triazines stem from a common mechanism with common intermediates, the pyrazoles formed from 2,5-dihydro-1,2,4-triazines in photochemically induced reactions and from aromatic 1,2,4-triazines in chemical and electrochemical reductions stem from two different pathways with different mechanisms.

Conclusions

Reinvestigation of the chemical reduction (Zn/AcOH) of 3,5,6-triphenyl-1,2,4-triazine (**1**) has shown that the 2,5-dihydro derivative **7** is formed rather than the 1,2-dihydro compound **2**. The 2,5-dihydro-1,2,4-triazine **7** has been shown to be the intermediate of the reaction leading to the imidazole **3**. Besides imidazole **3**, a small amount of pyrazole **8** is also formed.

The ratio of the N(2)/N(1) extrusion proved to be independent of whether the reaction was carried out chemically or photochemically, thus proving the mechanistic similarity of these two types of ring-contraction reactions.

The first representative of a 1,4-dihydrotriazine, **19**, has been prepared and its structure has been verified by ^{15}N-NMR measurements. In acidic propan-2-ol, it undergoes conversion to 4-acetylamino-4*H*-pyrazole **20**.

Experimental Section

General: Melting points were determined with a hot-stage melting-point apparatus and are uncorrected. – IR spectra were obtained

with a Specord 75 (Zeiss, Jena) instrument. − ^{1}H-NMR spectra were recorded with Bruker CW 80 and Bruker DRX 500 spectrometers (80 and 500 MHz, respectively) and ^{13}C-NMR spectra with a Bruker DRX 500 spectrometer (125.75 MHz), using $CDCl_3$ solutions with TMS as internal reference, unless stated otherwise. Special measurements (DEPT, HETCOR) were used in any cases of uncertainty. ^{15}N-NMR spectra were recorded with a Bruker DRX 500 spectrometer (50.7 MHz) in $CDCl_3$ solution with nitromethane as external reference. − Mass spectra (EI) were measured with a Varian MAT 312 spectrometer using a 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 with UV and/or by exposure to I_2.

Synthesis of Starting Materials and Authentic Products: For the synthesis of compounds **1**, **3**, **7**, **8**, **9**, **10**, **11**, **12**, and **13**, see ref.[1a] Compounds **14**, **15**, and **16** were prepared according to ref.[1c]

Reductions with Zn/AcOH. − Reduction of 3,5,6-Triphenyl-1,2,4-triazine (1): (a) A mixture of the aromatic triazine **1** (1.0 g, 3.2 mmol), zinc powder (1.5 g, 23 mmol), and acetic acid (15 mL) was refluxed for 1 h. The unreacted zinc powder was then filtered off, the clear filtrate was concentrated to dryness in vacuo, and the residue was triturated with aqueous ammonia solution (20%, 15 mL) to give a solid crystalline mixture. This was separated into three components by column chromatography (CH_2Cl_2/acetone, 10:2): 2,4,5-triphenylimidazole (**3**) (163.3 mg, 17%), 3,5,6-triphenyl-2,5-dihydro-1,2,4-triazine (**7**) (759 mg, 76%), and 3,4,5-triphenylpyrazole (**8**) (7.5 mg, 1%). − (b) Work-up of the same reaction mixture after 3 h of reflux gave 2,4,5-triphenylimidazole (**3**) (526 mg, 56%), 3,5,6-triphenyl-2,5-dihydro-1,2,4-triazine (**7**) (84.1 mg, 8%), and 3,4,6-triphenylpyrazole (**8**) (6.6 mg, 1%). − Products **3**, **7** and **8** were found to be completely identical (IR, NMR, m.p., TLC) to authentic samples; see ref.[1a]

Reduction of 3,5,6-Triphenyl-2,5-dihydro-1,2,4-triazine (7): A mixture of the dihydrotriazine **7** (1.0 g, 3.2 mmol), zinc powder (1.5 g, 23 mmol), and acetic acid (15 mL) was refluxed until the starting material had been consumed (4 h). Subsequent work-up and chromatographic separation was carried out as described above following the reduction of the aromatic triazine **1**. The isolated product was identified as 2,4,5-triphenylimidazole (**3**) (612.4 mg, 65%).

Reduction of 2-Methyl-3,5,6-triphenyl-2,5-dihydro-1,2,4-triazine (10): Methyldihydrotriazine **10** (0.92 g, 2.8 mmol) was reduced with Zn/AcOH as described for the reduction of **7**. After a reaction time of 2 h, 2,4,5-triphenylimidazole (**3**) (315.5 mg, 38%) and 1-methyl-2,4,5-triphenylimidazole (**12**) (268.0 mg, 31%) were isolated. − Products **3** and **12** were found to be completely identical (IR, NMR, m.p., TLC) to authentic samples; see ref.[1a]

Reduction of 4-Ethyl-2-methyl-3,5,6-triphenyl-1,2,4-triazinium Iodide (14): A mixture of compound **14** (0.15 g, 0.3 mmol), zinc powder (0.15 g, 2.3 mmol), and acetic acid (5 mL) was refluxed until the starting material had been completely consumed (12 h). After conventional work-up and separation by preparative TLC (hexane/dioxane/triethylamine, 4:2:1), only 2-ethyl-2,4,5-triphenylimidazole (**15**) could be isolated (28 mg, 26%); the 1-methylpyrazole **11** could also be detected in the reaction mixture by TLC, but could not be recovered.

Reduction of 1-Methyl-3,5,6-triphenyl-1,2,4-triazinium Iodide (16): A mixture of compound **16** (0.5 g, 1.1 mmol), zinc powder (0.75 g, 11.5 mmol), and acetic acid (10 mL) was refluxed until the starting material had been completely consumed (1 h). After conventional work-up and separation by preparative TLC, 2,4,5-triphenylimidazole (**3**) (114.2 mg, 35%) and 1-methyl-3,4,5-triphenylpyrazole (**11**) (64.3 mg, 19%) were isolated.

Reduction of 1-Methyl-3,5,6-triphenyl-1,6-dihydro-1,2,4-triazine (17): Compound **17** (0.1 g, 0.3 mmol) was treated with Zn/AcOH as described above. After reflux of the reaction mixture for 4 h, the starting material had completely decomposed, but none of the expected products could be detected.

Preparation and Transformations of 1,4-Diacetyl-3,5,6-triphenyl-1,4-dihydro-1,2,4-triazine (19) and 4-Acetylamino-3,4,5-triphenyl-4*H*-pyrazole (20). − 1,4-Diacetyl-3,5,6-triphenyl-1,4-dihydro-1,2,4-triazine (19): A mixture of dihydrotriazine **7** (1.0 g, 3.2 mmol) and acetic anhydride (20 mL) was refluxed for 2 h. The mixture was then poured into 50 mL of cold water. The separated oil crystallized after cooling for several hours. The product was separated from the aromatic triazine by-product **1** by column chromatography (hexane/acetone, 10:2) and recrystallized from ethanol (10 mL) to afford crystals of **19** (0.72 g, 57%); m.p. 224−225°C. − IR (KBr): $\tilde{\nu}$ = 3070 cm^{-1}, 3030, 2990, 2930, 1700, 1660, 1600, 1500, 1450, 1390, 1290, 1270, 1230, 980, 950, 930, 760, 700, 560. − ^{1}H NMR (500 MHz): δ = 2.35 [s, 3 H, N(4)−$COCH_3$], 2.56 [s, 3 H, N(1)−$COCH_3$], 6.65−7.39 (m, 13 H, aromatic H), 7.82−7.83 (m, 2 H, aromatic H). − ^{13}C NMR (125.75 MHz): δ = 14.24 [N(4)−CO*C*H$_3$], 23.19 [N(1)−CO*C*H$_3$], 95.73, 106.90 (C-5 and C-6), 127.28, 127.72, 127.75, 127.93, 128.20, 128.40, 129.40, 130.05, 134.11, and 135.51 (aromatic C atoms), 154.25 (C-3), 166.13 [N(4)−*C*OCH$_3$], 169.50 [N(1)−*C*OCH$_3$]. − ^{15}N NMR: δ = −60.6 (N-2), −153.1 (N-4), −175.1 (N-1). − $C_{25}H_{21}N_3O_2$ (395.5): calcd. C 75.93, H 5.35, N 10.63; found C 75.76, H 5.16, N 10.67.

Reduction of 1,4-Diacetyl-3,5,6-triphenyl-1,4-dihydro-1,2,4-triazine (19): A mixture of compound **19** (0.2 g, 0.5 mmol), zinc powder (0.3 g, 4.6 mmol), and acetic acid (10 mL) was refluxed until the starting material had been completely consumed (5 h). After conventional work-up and separation by preparative TLC (hexane/dioxane/triethylamine, 4:2:1), 3,4,5-triphenylpyrazole (**8**) (70.0 mg, 47%) was isolated.

Irradiation of 1,4-Diacetyl-3,5,6-triphenyl-1,4-dihydro-1,2,4-triazine (19): A solution of **19** (0.35 g, 0.88 mmol) in 150 mL of propan-2-ol was irradiated for 10 h under nitrogen at ambient temperature in a Pyrex immersion well reactor using a high-pressure mercury lamp (Philips HPK 125). No reaction was detected by TLC. This experiment was repeated in the presence of 1 equiv. of a hydrogen chloride solution in propan-2-ol, but again, after 13 h of irradiation, no reaction was detected. When the reaction was carried out in the presence of 10 equiv. of the alcoholic hydrogen chloride solution, the starting material was consumed after 30 h of irradiation. The resulting solution was concentrated to dryness under reduced pressure and the residue was triturated with aq. ammonia solution. The solid material was filtered off and following separation by preparative TLC (hexane/dioxane/triethylamine, 4:2:1), 3,4,5-triphenylpyrazole (**8**) (120.0 mg, 46%) was isolated.

Acidic Transformation of 1,4-Diacetyl-3,5,6-triphenyl-1,4-dihydro-1,2,4-triazine (19). − Preparation of 4-Acetylamino-3,4,5-triphenyl-4*H*-pyrazole (20): A solution of **19** (0.3 g, 0.75 mmol) in 30 mL of propan-2-ol containing 3 equiv. of hydrogen chloride was stirred at ambient temperature for 4 d, until the starting material had been consumed. The solution was then concentrated to dryness under reduced pressure and the residue was triturated with aq. ammonia solution. The solid material was filtered off and recrystallized from methanol to give 0.22 g of **20** (83%) as white crystals; m.p. 325°C.

− IR (KBr): $\tilde{\nu}$ = 3250 cm^{-1} (br.), 1680, 1530, 1525, 1505, 1490, 1445, 1275, 760, 680. − ^{1}H NMR ([D$_6$]DMSO, 500 MHz): δ = 1.94 (s, 3 H, N−COCH$_3$), 7.27−7.46 (m, 11 H, aromatic H), 7.81−7.83 (m, 4 H, aromatic H), 9.52 (s, 1 H, NH). − ^{13}C NMR ([D$_6$]DMSO, 125.75 MHz): δ = 22.37 (N−CO*C*H$_3$), 78.65 (C-4), 125.00, 127.56, 128.85, 128.95, 129.61, and 131.16 (aromatic CH groups), 128.95 and 132.17 (C-1 atoms), 169.56 (C-3 and C-5), 174.06 (N−*C*OCH$_3$) (the ^{13}C assignments were corroborated by DEPT). − MS; *m/z* (%): 353 (100) [M$^+$], 310 (4) [M$^+$ − CH$_3$CO], 296 (16) [M$^+$ − CH$_3$CONH + H], 295 (2) [M$^+$ − CH$_3$CONH], 248 (13), 233 (7), 178 (5), 105 (64), 104 (86) [C$_6$H$_5$C≡NH$^+$], 103 (10) [C$_6$H$_5$C≡N$^+$], 77 (30) [C$_6$H$_5^+$], 44 (30), 43 (42) [CH$_3$C=O$^+$]. − $C_{23}H_{19}N_3O \cdot H_2O$ (371.4): calcd. C 74.37, H 5.70, N 11.31; found C 74.45, H 5.74, N 11.47.

Reduction of 4-Acetylamino-3,4,5-triphenyl-4*H*-pyrazole (20): A mixture of compound **20** (0.1 g, 0.3 mmol), zinc powder (0.15 g, 2.3 mmol), and acetic acid (5 mL) was refluxed until the starting material had been consumed (2 h). After conventional work-up, 3,4,5-triphenylpyrazole (**8**) (80.0 mg, 89%) was isolated.

Irradiation of 4-Acetylamino-3,4,5-triphenyl-4*H*-pyrazole (20): A solution of **20** (0.1 g, 0.3 mmol) in 150 mL of propan-2-ol was irradiated as described for **19**, in the presence of 1 equiv. of a hydrogen chloride solution in propan-2-ol. The starting material was consumed within 24 h of irradiation. After conventional work-up, 3,4,5-triphenylpyrazole (**8**) (76.0 mg, 85%) was isolated.

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