Photolysis of 2-Azidopyridines. The Behavior of 1-(2-Azido-6-chloropyrid-4-yl)-3-phenylurea, a Photoaffinity Labeling Reagent for Probing Cytokinin-binding Proteins

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The photolysis of 1-(2-azido-6-chloropyrid-4-yl)-3-phenylurea (**1**) was studied under various conditions. In alcohols or in hexane, complex mixtures of products were obtained. Methoxide anions or diethylamine gave rise in high yield to 1,3-diazepines resulting from ring enlargement of the intermediate nitrene with addition of one molecule of the nucleophile, and nucleophilic substitution of the chlorine atom. A similar reaction was observed in water, when Pyrex filtered light was used. However, with unfiltered light produced by a powerful lamp, the main reaction was photodechlorination. The reagent **1** is expected to bind covalently to cytokinin-binding proteins through different ways upon photolysis.

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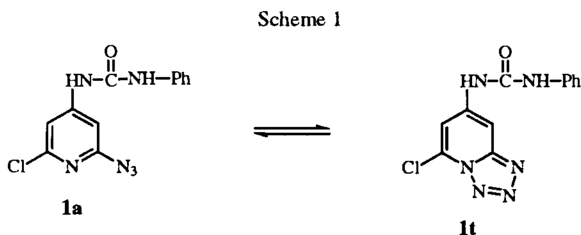
We have recently described the synthesis and the biological properties of 1-(2-azido-6-chloropyrid-4-yl)-3-phenylurea (**1**), a promising photoaffinity labeling reagent for cytokinin-binding proteins [1]. While aryl azides have been extensively used in photoaffinity labeling experiments [2], 2-azidopyridines had never been proposed before for this purpose. This can be explained probably from the limited knowledge of the photochemistry of this system, and moreover from the existence of the azido-tetrazole equilibrium [3] which generally lies on the side of the unphotolyzable tetrazole isomer. We have demonstrated that **1** exists mainly as the azido form **1a** (Scheme 1) in most solvents, except in water where the presence to a significant extent of the tetrazole form **1t** was suspected [1].

Scheme 1



A radiolabeled derivative of **1** has been used successfully for labeling a peptide from thylakoid membranes of *Pisum sativum* [4]. However we do not know how the photolyzed reagent **1** was covalently bound to the peptide. This information would be useful to identify the aminoacid(s) linked to the reagent, in order to map the binding site. With the goal of answering this question, we describe here the results of photolysis studies of the reagent **1** under various conditions.

Results and Discussion.

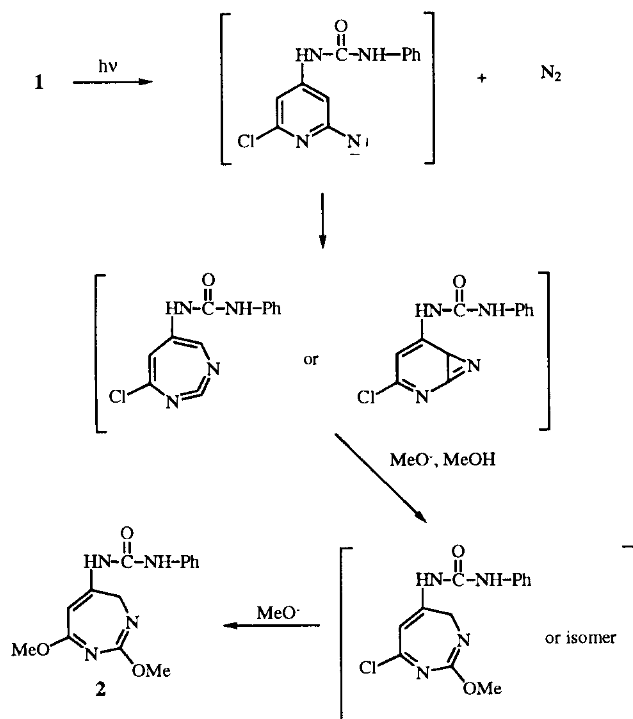
Photolysis in Alcohols.

Photolysis of compound **1** in methanol or ethanol led to complex mixtures of products, as evidenced by hplc analyses. Moreover, the composition of these mixtures continued to evolve after the end of the irradiation, thus indicating that some primary products were unstable or reacted with the solvents. We did not attempt to separate and identify these products.

The only products described in the photolysis of aryl azides in alcohols have been correlated to the presence of electron-withdrawing substituents on the phenyl ring of the aryl azides [5]. Good yields of 2-aminoazepines have been obtained by photolysis of aryl azides in the presence of amines [6], through their addition to an intermediate presumed ketenimine, the efficiency of the reaction depending upon the nature of the ring substituents [6,7]. In a similar reaction, in the presence of methoxide ions, 2- or 4-azidopyridines have given in good yield 2-methoxy-1,3-diazepines or 5-methoxy-1,4-diazepines respectively [8,9].

With the aim of characterizing the corresponding 2-methoxy-1,3-diazepine in the photolysis mixture of **1** in methanol, we tried to obtain this product selectively by photolysis in the presence of methoxide ions. In fact, the 2,4-dimethoxy-1,3-diazepine **2** was obtained as the major product whose formation is tentatively explained in Scheme 2. As it has been previously observed in the photolysis of 2-azido-6-substituted pyridines [8], the ring expansion of the intermediate 2-pyridylnitrenes led selectively to the formation of a 1,3-diazepine rather than a 1,2-diazepine. The structure of **2** was determined by hrms and nmr (^{1}H and ^{13}C) spectroscopy. In the ^{1}H nmr spectra, only two protons could be exchanged with deuterium in deuterium oxide demonstrating that there were no intracyclic NH in this compound. Homonuclear ^{1}H nuclear Overhauser effect studies (NOEDIFF) then showed that the ethylenic proton was proximate to one NH proton and

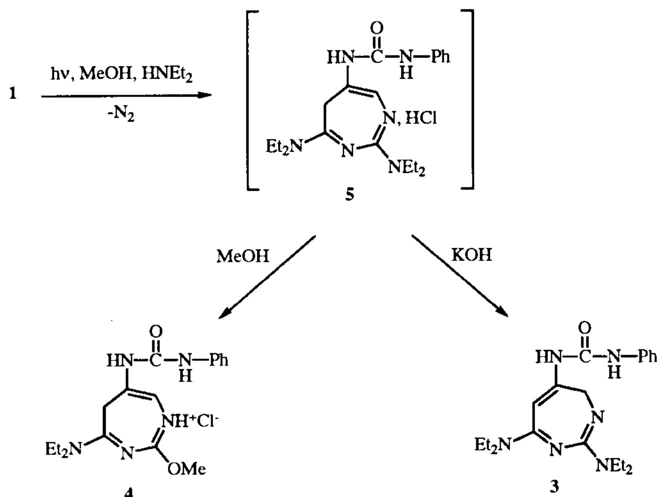
Scheme 2



to one methyl protons group. This result is compatible with the proposed 7*H*-diazepine structure rather than with the 5*H*-tautomeric form proposed by Sawanishi and Tsuchiya [8] for similar compounds. Heteronuclear long-distance correlation (HMBC) indicated that the ethylenic proton was correlated with 4-C (δ 153.8 ppm), 6-C, 7-C and a C-methyl while the methylene protons were correlated with 2-C (δ 159.2 ppm), 5-C and 6 C. These results were also in agreement with the structure proposed for **2**. Hplc monitoring of the reaction did not allow us to detect any intermediate on the way from **1** to **2**. This means, in particular, that substitution of the chlorine atom by a methoxy group is a very fast reaction. As expected, a peak with the same retention time as **2** was found in the chromatogram of the products mixture from the photolysis in methanol without methoxide.

A result similar to that found with the methoxide ions was observed when **1** was photolyzed in methanol in the presence of diethylamine, giving the 2,4-bis(diethylamino)-7*H*-1,3-diazepine **3** (Scheme 3). However, if the hydrochloric acid produced by the reaction was not neutralized (*e.g.* by potassium hydroxide) before isolation of the product, the protonated molecule **5** underwent a solvolysis reaction resulting in the substitution of a diethylamino group by a methoxy group. In this case, the 5*H*-diazepine **4** was isolated as a hydrochloride, instead of **3**. ^{1}H and ^{13}C nmr spectra of **3** were found very similar to the corresponding spectra of **2** with the 7-H methylene signal at lower field (δ 1.90 ppm vs 2.94 ppm). The 5*H* tautomeric structure was attributed to **4** by ^{1}H nOe experiments which allowed to determine the position of the methoxy and diethylamino groups together with that of the protonation. Indeed, presaturation of the NH^{+} proton (δ 11.44 ppm) led to strong signal enhancements at δ 6.81 and 3.85 ppm (7-H and 2-OCH_3 respectively).

Scheme 3



The 5*H*-diazepine structure of **4** strongly suggested that its bis(diethylamino) precursor **5** had the same 5*H*-structure and that the 7*H*-diazepine **3** resulted from the isomerization of **5** upon treatment by potassium hydroxide. A similar process might have occurred which would explain the obtention of **2** in the presence of the basic methoxide ions.

Photolyses of **1** in methanol solutions containing methanethiol or sodium thiomethoxide gave rise to unstable 1,3-diazepines which were only partially characterized by ^{1}H nmr and were not purified.

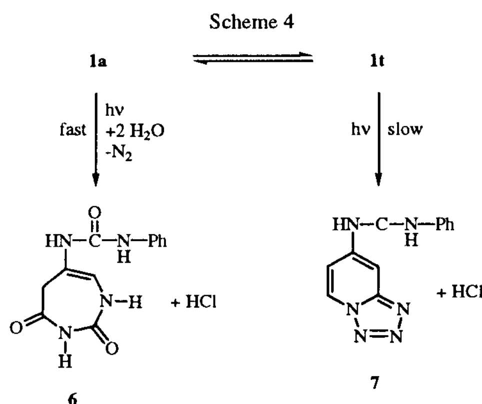
Photolysis in Water Solution.

Because of the low solubility of compound **1** in water, the photolyses were driven on saturated solutions (17.5 µ*M*), at a concentration close to those used in photoaffinity labeling experiments. When a Pyrex filtered uv light from a 400 w medium-pressure mercury vapor lamp was used, the 5*H*-1,3-diazepine-2,4-dione **6** was obtained almost exclusively (Scheme 4). The scheme of formation of this product was expected to be similar to those proposed for the 1,3-diazepines **2** or **3**, including the addition of one molecule of water to an intermediate carbodiimide or azirine, and substitution of the chlorine atom by a hydroxyl group. By comparing the ^{1}H nmr spectrum of **6** to those of the above diazepines **2-4**, two additional N-H signals appeared, which vanished after deuterium oxide addition. One of these signals was a doublet (J = 4 Hz) and was attributed to the 1-NH coupled with the 7-H

ethylenic proton which also gave a doublet (turned to a singlet in deuterium oxide). Assignments of the ^{13}C resonances were completed through an HMQC experiment which particularly showed that the 5-C resonance was masked by the signal of dimethyl sulfoxide.

Few examples of photolysis of aryl azides in the presence of water are known. Photolysis of *o*- and *p*-substituted phenyl azides in tetrahydrofuran-water mixtures yielded 5-substituted 3*H*-azepine-2-ones, products of ring enlargement of the phenyl nitrene, with addition of water to an intermediate [6,10]. The formation of these azepinones was correlated with the presence of electron-withdrawing groups in *o*- and *p*-position to the azido group. There was no example of obtention of corresponding cyclic ureas from the photolysis of 2-azidopyridines in water.

Scheme 4



When no Pyrex filter was used for the photolysis of **1**, the product **6** was again obtained, but the major product was identified as 1-(tetrazolo[1,5-*a*] pyrid-7-yl)-3-phenylurea (**7**), a photoreduction product (Scheme 4). Photoreduction of haloarenes may result from various mechanisms [11], including photoinduced electron transfer as a competitive pathway for photosubstitution reaction [12]. Such photodechlorinations have been also observed in azaheterocyclic compounds like chloropyrimidines [13]. In water, the azido-tetrazole equilibrium was suspected to be largely in favor of the tetrazole form **1t** [1]. The quantum yields of photolysis of aryl azides are generally high [14], and it is likely that the main way for the photolysis of **1a** is the transformation of the azide group into the nitrene, rather than photodechlorination. On the other hand, while the tetrazolo[1,5-*a*]pyridine system is inert to photolysis under the conditions used [1], the tetrazole form **1t** appears to be prone to react essentially through the chlorine atom. Thus, making the assumption that **1t** is the major isomer in water, the photolysis of **1** may be easily explained by Scheme 4. A pyrex filter cuts the light from the mercury vapor lamp below 290 nm, and the solution can absorb only the radiations at 297 nm (5% of the lamp energy), 312 nm (8%) and 313 nm (15%) [15], and with a low

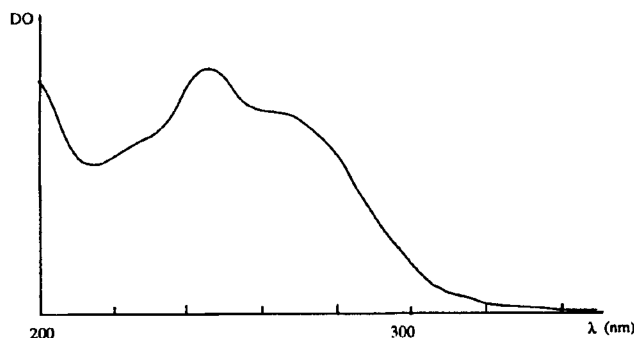


Figure 1. The uv Spectrum of Compound **1** in water.

efficiency in consideration of the weak absorbance of **1** at these wavelengths (Figure 1). Under these conditions, the mixture of isomers **1a** and **1t** is photolyzed slowly, and while the quantum yield of photolysis of **1t** is lower than that of **1a**, **1t** isomerizes to **1a** as fast as this compound disappears. Contrarily, with unfiltered light, a high flux density of photons reaches the sample and is absorbed. Then, the photolysis of **1t** is faster than its isomerization to **1a** and the amount of the tetrazole **7** produced is closely related to that of **1t** at the initial equilibrium. Control experiments have been done using the 400 w lamp without filter, the sample being set in quartz tubes at various distances from the lamp. As expected, the relative amount of **7** decreased when the sample was taken away from the lamp, while the flux density of photons reaching the sample also decreased.

Photolysis in Hexane.

Compound **1** was photolyzed very slowly in hexane, and produced a complex mixture whose components have not been identified. However, reverse phase hplc analyses of this mixture did not allow us to detect products less polar than **1** which would have resulted from insertion of the intermediate nitrene in C-H bonds of the solvent, a possible reaction of aryl nitrenes.

Photoaffinity Labeling Potentiality of **1**.

Only the azido isomer **1a** is expected to bind to cytokinin-binding proteins [1], and to undergo photolysis with covalent binding ability with surrounding molecules, provided the flux density of the absorbed light is moderate. Thus, the azido-tetrazole equilibrium which exists in water should not be detrimental to photoaffinity labeling. Covalent attachment of the reagent **1** (from the form **1a**) to its protein binding sites may occur through different ways upon photolysis. While insertion reactions of the photogenerated nitrene in C-H, O-H, S-H or N-H bonds [16] have not been demonstrated, some of the many products observed in alcohols may result from such reactions. Furthermore, if the binding sites contain nucleophilic group like amines (*e.g.* lysine) alcohols (*e.g.* serine or

tyrosine) and probably thiols (*e.g.* cysteine), the covalent attachment may also be obtained through two different consecutive reactions, an addition of the nucleophile to an intermediate azirine or carbodiimide, and the substitution of the chlorine atom. Water may be a competitive nucleophile in these reactions. An enlargement of the pyridine ring is expected to occur, leading to 2,4-disubstituted 1,3-diazepines. However, as it has been shown with the formation of **4**, it should be taken into account that solvolysis reactions may further occur in slightly acidic conditions, resulting in the breakage of the bond between the 2-C of the diazepine and the nucleophilic atom of the bound amino acid. Thus, while the extent of the diazepines formation is unknown, a partial loss of labeling of the protein might be observed related to this solvolytic reaction, during the purification process of the labeled protein.

EXPERIMENTAL

Melting points were taken on a Kofler hot stage and are uncorrected. ^{1}H (270 MHz) and ^{13}C (67.5 MHz) nmr spectra were recorded in dimethyl sulfoxide-d_6 on a Jeol GSX 270 WB spectrometer with tetramethylsilane as an internal standard (δ in parts per million). J values are given in Hz. ^{13}C nmr signals were assigned interlocking DEPT, HMQC and HMBC experiments. The mass spectra were obtained from VG Autospec or VG Analytical ZAB SPEC TOF apparatus. The uv spectra were recorded on a Lambda 2 spectrometer. The tlc analyses were carried out on pre-coated plates of silica gel 60 F_{254} (Merck) and hplc analyses were run on a Waters apparatus using Merck Lichrospher® RP 18 columns and water-methanol mixtures as eluent; the wavelength of detection was 254 nm.

The photolysis experiments were done according to previous specifications [1].

Photolysis of **1** in the Presence of Methoxide Ions.

A solution of **1** (100 mg, 0.35 mmole) in 350 ml of methanol containing sodium methoxide (50 mg, 0.93 mmole) was photolyzed with a 400 w lamp in a 400 ml reactor equipped with a Pyrex filter, while nitrogen was bubbled through the solution. The reaction, monitored by hplc, was completed after about 40 minutes. Evaporation of the solvent under reduced pressure gave a solid residue which was dissolved in dichloromethane and then washed with water. The organic layer was dried over magnesium sulfate and the solvent was evaporated. The resulting residue was chromatographed through a silica gel column with dichloromethane-methanol (90:10) as the eluent. The fraction collected (R_f = 0.29 with the above eluent) was evaporated and the solid residue was then recrystallized in methanol giving 65 mg (64%) of white crystals identified to 1-(2,4-dimethoxy-7*H*-1,3-diazepin-6-yl)-3-phenylurea (**2**), mp 206°; ^{1}H nmr: δ 2.94 (s, 2 H, 7-CH_2), 3.64 (s, 3 H, 4-OCH_3), 3.68 (s, 3 H, 2-OCH_3), 6.67 (s, 1 H, 5-H), 6.94 (t, 1 H, 4'-H phenyl, J = 7.3), 7.25 (t, 2 H, 3'-H and 5'-H phenyl, J = 7.3), 7.39 (d, 2 H, 2'-H and 6'-H phenyl, J = 7.3), 8.24 and 8.60 (2 s, 2 H, 2 NH urea); significant {^{1}H}-^{1}H nOe's were 5-H to 4-OCH_3 (3%), 5-H to NH (δ 8.24) (7%) and 4-OCH_3 to 5-H (5%); ^{13}C nmr: δ 35.9 (7-C), 53.1 (4-OCH_3), 55.4 (2-OCH_3), 114.7 (6-C), 118.2 (2'-C and 6'-C phenyl), 121.8 (4'-C phenyl), 122.2 (5-C), 128.7 (3'-C and 5'-C phenyl), 139.6 (1'-C phenyl), 153.2 (C=O), 153.8 (4-C), 159.2 (2-C); ms: (70 eV, electron impact) m/z 288 (M^+, 74.2%), 195 (15), 169 (100), 154 (20.2), 140 (27.8), 119 (28.9), 93 (51.9), 77 (38.7); hrms: Found: 288.1220 (molecular ion); $C_{14}H_{16}O_3N_4$ requires 288.1222.

Photolysis of **1** in the Presence of Diethylamine.

1-(4-Diethylamino-2-methoxy-5*H*-1,3-diazepin-6-yl)-3-phenylurea (**4**).

The photolysis of **1** (100 mg, 0.35 mmole) was carried out in methanol (350 ml) in the presence of diethylamine (1 g, 13.7 mmoles) according to the conditions described for the photolysis in the presence of methoxide ions. After 40 minutes of photolysis, the solvent was evaporated under reduced pressure and the resulting mixture was chromatographed through a silica gel column with dichloromethane-methanol (90:10) as the eluent. The appropriate fractions were gathered giving 34 mg (27%) of **4** in a pure state (tlc and hplc), mp 174°; ^{1}H nmr: δ 1.15 and 1.24 (2 t, 6 H, 2 CH_2CH_3, J = 7.2), 3.50 (s, 2 H, 5-H), 3.60 and 3.76 (2 q, 4 H, 2 CH_2CH_3, J = 7), 3.85 (s, 3 H, 2-OCH_3), 6.81 (s, 1 H, 7-H), 6.97 (t, 1 H, 4'-H phenyl, J = 7), 7.26 (t, 2 H, 3'-H and 5'-H phenyl, J = 7.5), 7.39 (d, 2 H, 2'-H and 6'-H phenyl, J = 7.5), 9.39 and 9.65 (2 s, 2 H, 2 NH urea), 11.44 (s, 1 H, 1-NH^+); ^{13}C nmr: δ 11.9 and 14.8 (2 CH_2CH_3), 34.2 (5-C), 44.9 and 45.0 (2 CH_2CH_3), 109.2 (7-C), 118.0 (2'-C and 6'-C phenyl), 118.8 (6-C), 122.1 (4'-C phenyl), 128.8 (3'-C and 5'-C phenyl), 139.2 (1'-C phenyl), 152.8 (C=O), 154.9 (4-C), 155.4 (2-C); uv (methanol): λ max 241.7 nm (ε 20 800); ms: (fab^+) m/z 330 (MH^+-HCl, 36%), 281 (37), 237 (23), 221 (52), 207 (46), 147 (100) and 136 (41); hrms: (fab^+) Found: 330.1936 (MH^+-HCl); $C_{17}H_{24}N_5O_2$ requires 330.1930.

1-[2,4-Bis(diethylamino)-7*H*-diazepin-6-yl]-3-phenylurea (**3**).

This compound was obtained similarly to the urea **4**, from **1** (94 mg, 0.33 mmole) and diethylamine (7 g, 96 mmoles) in methanol (350 ml). At the end of the photolysis (monitored by hplc), potassium hydroxide (40 mg, 0.7 mmole) was introduced into the solution, under magnetic stirring. After complete dissolution of potassium hydroxide, the solvent was evaporated under reduced pressure and the residue was taken with dichloromethane (20 ml) and washed with water. The organic layer was dried over magnesium sulfate and the solvent was then removed by evaporation giving 112 mg (92%) of orange crystals identified to **3**, which was not further purified because of its unstability, mp 75-80° dec; ^{1}H nmr: δ 0.95 to 1.15 (m, 12 H, CH_2CH_3), 1.90 (s, 2 H, 7-CH_2), 3.22 to 3.50 (m, 8 H, CH_2CH_3), 6.51 (s, 1 H, 5-H), 6.92 (t, 1 H, 4'-H phenyl, J = 7.5), 7.23 (t, 2 H, 3'-H and 5'-H phenyl, J = 7.5), 7.41 (d, 2 H, 2'-H and 6'-H phenyl, J = 7.5), 8.25 and 8.67 (2 s, 2 H, 2 NH urea); ^{13}C nmr: δ 12.1 and 15.2 (2 CH_2CH_3 4-diethylamino), 13.2 and 14.0 (2 CH_2CH_3 2-diethylamino), 33.0 (7-CH_2), 42.1 (2 CH_2CH_3 2-diethylamino), 42.7 and 42.9 (2 CH_2CH_3 4-diethylamino), 113.0 (6-C), 118.0 (2'-C and 6'-C phenyl), 121.5 (4'-C), 124.4 (5-C), 128.7 (3'-C and 5'-C phenyl), 139.9 (1'-C phenyl), 152.1 (4-C), 153.5 (C=O), 156.2 (2-C); uv (methanol): λ max 243 nm (ε 20 150); ms (ci-ammonia) m/z 371 (MH^+, 6%), 278 (36), 252 (33), 237 (71), 211 (79), 193 (82), 168 (49), 154 (73), 137 (67), 125 (55), 111 (98); hrms (fab^+) Found: 371.2576 (MH^+); $C_{20}H_{30}N_6O$ requires 371.2559.

Photolysis of **1** in Water.

With a Pyrex Filter.

A saturated solution of **1** (100 mg, 0.35 mmole) in pure water (20 l) was photolyzed (400 w lamp and Pyrex filter) in successive runs in a 2 l reactor under magnetic stirring and with bubbling of nitrogen. The reaction was monitored by uv spectroscopy and it was completed after 20 minutes. Photolysis products were concentrated on a Lichroprep® RP 8 column (310 x 25 mm) and then eluted with methanol. Evaporation of the solvent from the fraction containing the product gave a residue which was dissolved in acetone and chromatographed through a silica gel column with dichloromethane-methanol (90:10) as the eluent. 80 mg (88%) of pure (tlc) 1-(1,3,5*H*-1,3-diazepin-2,4-dion-6-yl)-3-phenylurea (**6**) was isolated, mp 203-210° dec; ^{1}H nmr: δ 3.15 (s, 2 H, 5-CH_2), 6.51 (d, 1 H, 7-H, J = 4), 6.95 (t, 1 H, 4'-H phenyl, J = 7), 7.25 (t, 2 H, 3'-H and 5'-H phenyl, J = 7), 7.38 (d, 2 H, 2'-H and 6'-H phenyl, J = 7), 8.11 and 8.56 (2 s, 2 H, 2 NH urea), 8.98 (d, 1 H, 1-NH, J = 4), 10.06 (s, 1H, 3-NH); ^{13}C nmr: δ 39.6 (5-C), 109.9 (7-C), 118.1 (2'-C and 6'-C phenyl), 120.9 (6-C), 121.9 (4'-C phenyl), 128.7 (3'-C and 5'-C phenyl), 139.4 (1'-C phenyl), 151.9 (2-C), 152.5 (C=O), 169.0 (4-C); uv (water): λ max 251 nm; ms: (ci-methane) m/z 261 (MH^+, 21%), 289 ([$M+C_2H_6^+$], 5.6), 218 (8.1), 142 (24.3), 120 (100), 99 (32.4), 94 (71.5); (ci-ammonia) m/z 261 ([MH^+], 71%), 278 ([$M+NH_4^+$], 27.5), 218 (21.7), 142 (53.6), 119 (24.6), 99 (26.1), 94 (100); hrms (fab^+) Found: 261.0986 (MH^+); $C_{12}H_{13}N_4O_3$ requires 261.0987.

Without a Pyrex Filter.

The photolysis was carried out in conditions similar as above, but without the Pyrex filter, from **1** (100 mg, 0.35 mmole) in water (20 l). Every 2 l fractions were photolyzed for 15 minutes. The resulting solutions were pumped through a Lichroprep RP 18 column. Elution by methanol gave a yellow solid mixture which was triturated several times with methanol yielding 40 mg (44%) of a solid which was found identical with an authentical sample of 1-(tetrazolo[1,5-*a*]pyrid-7-yl)-3-phenylurea (**7**) [1] (mp, ^{1}H nmr, ei-ms and uv spectrum); ^{13}C nmr: δ 96.3 (6-C), 111.5 (8-C), 118.8 (2'-C and 6'-C phenyl), 122.7 (4'-C phenyl), 126.3 (5-C), 128.9 (3'-C and 5'-C phenyl), 138.8 (1'-C phenyl), 143.4 (7-C), 149.2 (C=N), 152.2 (C=O).

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