Synthesis and Photochemical Degradation of *N*-Arylmethyl Derivatives of the Herbicide 3-Amino-1,2,4-triazole

Abderrahman Er-Rhaimini and René Mornet*

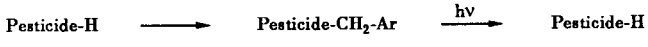
Laboratoire de Chimie Organique Fondamentale et Appliquée,
UFR des Sciences de l'Environnement,
2 Boulevard Lavoisier, 49045 Angers Cedex, France

Received April 7, 1992

Reaction of an arylmethyl halide with 3-amino-1,2,4-triazole (**1**) allows the preparation of the three *N*-arylmethyl derivatives of **1** bearing the substituent on the heterocyclic nitrogen atoms. In basic medium (methoxide anion in DMF or methanol, or in benzene by phase transfer catalysis), the isomers **3** and **5** substituted at N-1 and N-2 respectively are obtained, while the isomer **4** is isolated from neutral medium (DMF). The isomers **3** and **4** may be also prepared by cyclization of appropriate formylguanidinium derivatives. 3-Arylmethylamino-1,2,4-triazoles **2** may be obtained through reaction of 3-chloro-1,2,4-triazole (**6**) with arylmethylamines. Photolysis of the *N*-arylmethyl-3-amino-1,2,4-triazoles **2-5** in methanol or water-methanol mixture, induces homolytic and heterolytic cleavage of the arylmethyl-C-N bond giving rise to 3-amino-1,2,4-triazole (**1**). Thus, compounds **2-5** with arylmethyl groups able to absorb solar light may be considered as potential photoactivatable herbicides.

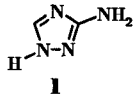
J. Heterocyclic Chem., **29**, 1561 (1992).

We have recently reported on a new concept of potential photoactivatable pesticides [1], resulting from the replacement of the hydrogen atom of an OH or NH groups in the molecule of a known pesticide, by an arylmethyl substituent. The arylmethyl pesticide derivative, upon photolysis, liberates the active unsubstituted molecule:

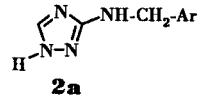


The photolysis of arylmethyl compounds has been studied [2], and we have shown that *N*-arylmethyl derivatives of *N*-heterocycles, like adenine as an example [3], may be photolyzed with elimination on the *N*-arylmethyl substituent, in a way similar as in more simple arylmethyl derivatives.

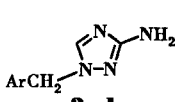
We now describe our studies on *N*-arylmethyl derivatives of 3-amino-1,2,4-triazole (**1**) (AT), a herbicide of heterocyclic structure. Series of the four isomers **2-5** have been synthesized by arylmethylation of AT or by cyclization methods. The photochemical behaviour of some of these compounds is also reported.



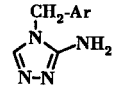
1



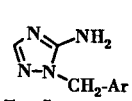
2a



3a,b

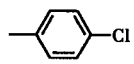


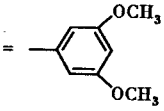
4a,b

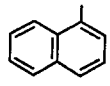


5a-d

a Ar = 

b Ar = 

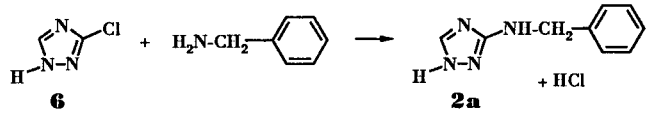
c Ar = 

d Ar = 

Unequivocal methods have been first attempted for the syntheses of the arylmethyl derivatives of AT **2-5**.

3-Benzylamino-1,2,4-triazole (**2a**) was a known compound [4,5]. We prepared it by nucleophilic substitution of benzylamine on 3-chloro-1,2,4-triazole (**6**) at 180°, without any solvent [4] (Scheme I).

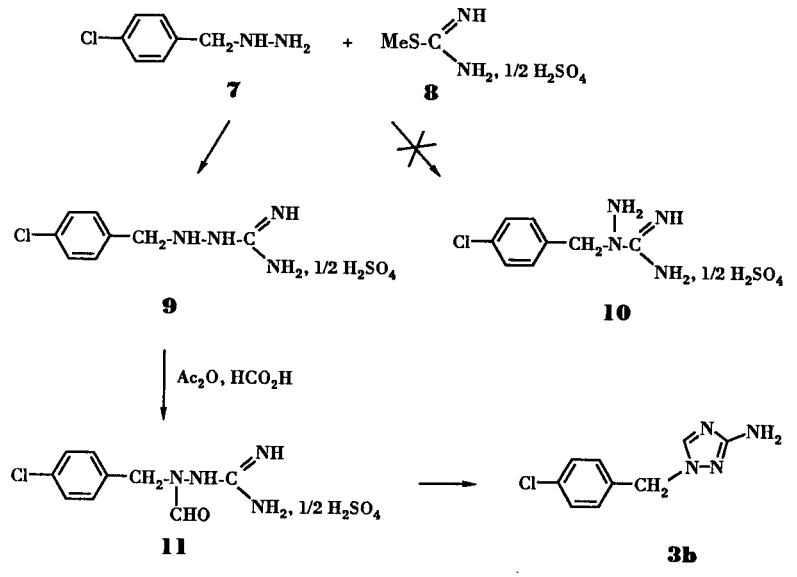
Scheme I



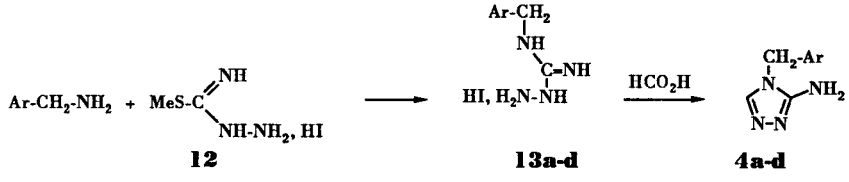
6 **2a**

3-Amino-1-(4-chlorobenzyl)-1,2,4-triazole (**3b**) was synthesized from 4-chlorobenzylhydrazine (**7**), according to Scheme II. Condensation of **7** with *S*-methylisothiourea sulfate (**8**) could give rise to two products, **9** or its isomer **10**. Literature gave examples of the formation of the two types of compounds [6a-g], depending on the hydrazine used. We only obtained the product **9**, its structure being ascertained by the absence of reaction with benzaldehyde, while its isomer **10** would have reacted to give an hydrazone [6a,g]. Cyclization of **9** to the substituted triazole **3b** by heating in formic acid [7] gave mainly an *N*-formyl derivative of **3b**, and we preferred to accomplish the reaction in two steps. Treatment of **9** by formic acid-acetic anhydride mixture gave rise to the mono *N*-formyl derivative **11**. Formylation of the nitrogen atom linked to the chlorobenzyl group was evidenced by comparing the chemical shifts of the methylene group, which increased largely ($\Delta\delta = 0.7 \times 10^{-6}$) in the ^{1}H nmr spectra from **9** to **11**. This compound **11** was cyclized to give the expected substituted triazole **3b**, by heating to reflux in ethanol.

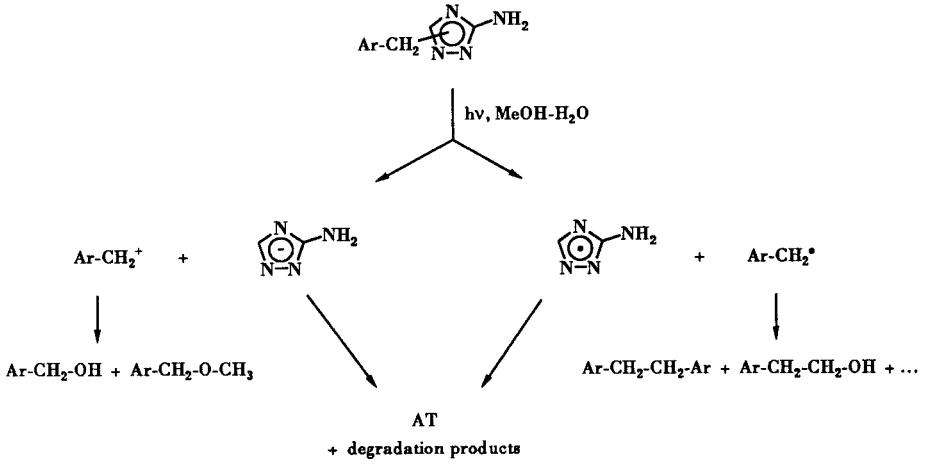
Scheme II



Scheme III



Scheme IV

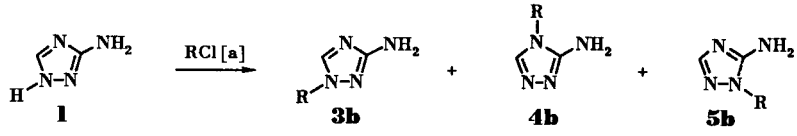


The 4-substituted 3-amino-1,2,4-triazoles **4a-d** were prepared by a known method [8] (Scheme III). *S*-Methylisothiosemicarbazide hydroiodide (**12**) [9] was condensed with an arylmethylamine to produce the corresponding 1-amino-2-arylmethylguanidine hydroiodide **13a-d**. These compounds **13a-d**, upon heating with formic acid cyclized to give the expected compounds **4a-d**.

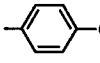
None of the 3-amino-2-arylmethyl-1,2,4-triazoles **5** were prepared by a cyclization method. Only the methyl-substituted analogue of **5** had been obtained in such a way [10], but the method used for the preparation of this compound could not be applied easily to other analogues because their precursors **10** were hardly available [6a]. The compounds **5a,b** were obtained by direct alkylation of AT in

Table I

Alkylation of AT under Basic Conditions



Reaction conditions	Compound No.	3b	4b	5b
MeOH, MeO^-		42%	15%	43%
DMF, MeO^-		48%	trace	52%
Benzene, OH^- [b]		52%	trace	48%

[a] R = Cl-  -CH_2. [b] Phase transfer catalysis, $Et_3N^+CH_2$-C_6H_5, Cl^- as catalyst.

the presence of a base, in mixtures containing their isomers **3a,b** and **4a,b** from which they were separated.

Four different conditions of alkylation of AT were first studied, using 4-chlorobenzyl chloride as the alkylating agent, in order to evaluate this way of synthesis for the *N*-arylmethyl derivatives of AT **2-5**. In basic conditions, sodium methoxide was used as the base, in methanol or dimethylformamide (DMF) solution. Phase transfer catalysis was also used, with sodium hydroxide as the base and water-benzene as solvents, benzyltriethylammonium chloride being the phase transfer catalyst. Alkylation in neutral conditions were driven in DMF. The mixtures of products obtained were analyzed by ^1H nmr and hplc. While the product **2b** of alkylation on the exocyclic amino was absent from the mixtures of products, three alkylation derivatives were present, **3b**, **4b**, and a third product which was expected to be **5b**. The proportions of the different isomers obtained in basic medium are reported in Table I. The amounts of **3b** and **5b** were found to be equivalent and the isomer **4b** competed significantly with them only when methanol was used as the solvent.

In neutral DMF solution, a mixture of the above three isomers was obtained, together with unreacted AT and unidentified dialkylated species. The main monoalkylated product in the mixture was **4b**.

Similar results had been found in methylation of AT [10], both in neutral and basic medium.

From the above studies on the arylmethylation of AT, we concluded that the isomers **4** might be obtained by reaction in neutral medium in DMF. Compounds **4a-d** were prepared by this method in 30-35% yields after purification by recrystallization. Arylmethylation of AT in basic medium was achieved with 4-chlorobenzyl chloride, using the three conditions used in preliminary essays (Table I). Both the isomers **3b** and **5b** were isolated, with a small amount of **4b** when methanol was used as the solvent. Their separation and purification were achieved by a combination of dissolutions and recrystallizations in various solvents. Thus alkylation of AT, either in neutal or in basic solution, appears to be a general method for providing all the three products **3-5** of alkylation on the heterocyclic nitrogen atoms.

Table II

NMR Spectra of *N*-Arylmethyl Derivatives of AT

Solvent	DMSO-d_6			$CDCl_3$		CF_3CO_2H	
Compound No.	δ CH	δ NH_2	δ CH_2	δ CH	δ CH_2	δ CH	δ CH_2
2a	7.70	6.90 [a]	4.40 [b]	insoluble		8.30	4.70
3a	8.13	5.22	5.10	7.67	5.08	8.75	5.37
3b	8.08	5.22	5.10	7.70	5.07	8.92	5.38
4a	7.97	5.83	5.00	insoluble		8.05	5.22
4b	7.92	5.82	5.00	insoluble		8.08	5.23
4c	8.08	5.88	5.00	7.85	4.85	8.08	5.20
4d	7.90	5.98	5.53	insoluble		7.75	5.65
5a	7.37	6.27	5.10	7.52	5.12	8.23	5.38
5b	7.37	6.32	5.10	7.52	5.08	8.22	5.35

[a] δ NH. [b] Doublet, J = 6.5 Hz.

Identification of the compounds **2-5**, and their quantitative determination in the mixtures of the reaction products, were based mainly on their ^{1}H nmr spectra (Table II). Exocyclic *N*-alkylation product **2a** was easily characterized by considering the doublet splitting of the methylene signal, resulting from NH-CH_2 coupling. In the spectra of compounds **3-5** recorded in DMSO-d_6, the chemical shifts of the CH_2, NH_2 and triazole CH protons, followed the same variations as in the methyl substituted analogues [10]: $\delta(CH_2)$: δ **(3)** # δ **(5)** > δ **(4)**, $\delta(NH_2)$: δ **(5)** > δ **(4)** > δ **(3)**, and δ (triazole CH): δ **(3)** > δ **(4)** > δ **(5)**.

The triazole C-H proton also exhibited a larger chemical shift in the isomer **3** than in the isomers **4** and **5**, like in the methyl analogues [10], in spectra recorded in trifluoroacetic acid solutions.

The uv spectra of the compounds **2-5** were not useful to determine the position of the arylmethyl substitution on AT. The uv absorption bands of the aminotriazole chromophore which occur at 210-230 nm [10] were superimposed with the bands of the aryl groups, and could not be measured.

The four *N*-benzyl derivatives of AT **2a-5a** were photolyzed in 10^{-3} *M* methanol or aqueous methanol (50:50) solutions with a low pressure mercury vapor lamp (254 nm, 16 watts). From methanol solution, two main benzylic products were detected by gc analysis, bibenzyl and 2-phenylethanol, these two products being expected to result from the homolytic cleavage of the benzyl -C-N bond [2], with traces of benzylmethyl ether and other unidentified products. When the photolysis was done in water-methanol solutions, besides of bibenzyl and 2-phenylethanol, benzylmethyl ether and benzyl alcohol appeared in substantial amount, thus indicating that a heterolytic mechanism is favoured by the polarity of the medium. The amount of AT, detected by hplc, was found to be very weak from methanol solutions, and it also increased significantly with the polarity of the solvent. In more concentrated solution and by using a more powerful lamp, AT was not detected. This last observation may be explained by the degradation of AT in the presence of radicals [11], giving urea, cyanamide and carbon dioxide. Thus, the *N*-arylmethyl AT derivatives **2-5** behave similarly on photolysis as other arylmethyl derivatives previously studied [2], and particularly as *N*-arylmethyl heterocyclic or aliphatic derivtives [1,3], giving products resulting both from homolytic or heterolytic cleavage (Scheme IV). Generation of radicals would then induce partial or total AT decomposition.

In conclusion, the four kinds of *N*-arylmethyl derivatives of AT **2-5** may be easily prepared by combination of different methods: directly from AT by arylmethylation of the ring nitrogen atoms (compounds **3-5**), by condensation of 3-chloro-1,2,4-triazole **(6)** with arylmethylamines (compounds **2**), or by cyclization methods (compounds **3-4**). The photolysis of the *N*-arylmethyl derivatives of AT induces the elimination of the arylmethyl substituents with production of AT which may be further decomposed at a rate depending on the conditions of photolysis. Thus *N*-arylmethyl derivatives of AT absorbing the natural light through appropriate arylmethyl groups, may be considered as potential photoactivatable herbicides.

EXPERIMENTAL

Melting points were determined on a Büchi apparatus and are uncorrected. The ^{1}H nmr spectra were recorded on a Varian EM 360 instrument in various solvents using tetramethylsilane as an internal standard. Mass spectra were obtained from a Varian MAT 112 spectrometer equipped with an electron impact ionization source (ei-ms). Elemental analysis were performed by the Service de Microanalyses du CNRS, Vernaison France. The uv spectra were recorded on a Kontron Uvikon 860 spectometer, and ir spectra on a Beckman Acculab II apparatus, from nujol suspensions. The gc analyses were carried out in an OV1 capillary column (25 m x 0.22 mm ID), with nitrogen as carrier gas, on a Carlo Erba GC 6100 Vega apparatus equipped with a flame ionization detector and a split-splitless injector working in split mode. Hplc analysis were run on Lichrosorb RP 18 (10 μm) columns (25 cm x 4.1 mm ID), using eluents containing variable proportions of water and methanol, 2% acetic acid and sodium heptanesulfonate (0.005 *M*). The chromatograph was from Waters (M 6000A pump, U6K injector and M 440 uv detector working at 254 nm) and the chromatograms were recorded on a Shimadzu CR3A integrator. A Kontron 432 multiwavelength uv detector set at 235 nm was used for the analyses of photolysis products.

3-Benzylamino-1,2,4-triazole (**2a**).

3-Chloro-1,2,4-triazole (**6**) (1.035 g, 10 mmoles) and benzylamine (2.5 g, 23.4 mmoles) were heated at 180° for 20 hours. After cooling to room temperature, the mixture was diluted with diethyl ether (50 ml). The precipitate which was then obtained was filtered and recrystallized from benzene to give 0.75 g (44%) of **2a**, white powder, mp 164°, lit [5] 164-165°; ^{1}H nmr, see Table II.

4-Chlorobenzylhydrazine (**7**).

4-Chlorobenzyl chloride (6 g, 37 mmoles) in 30 ml of ethanol was added dropwise to a solution of hydrazine hydrate (18.5 g, 0.37 mole) in 40 ml of ethanol. The mixture was kept at room temperature for 24 hours. Ethanol and the excess of hydrazine were evaporated under reduced pressure. The residue was taken with 50 ml of a 50% solution of sodium hydroxide in water. The aqueous solution was extracted with diethyl ether (3 x 40 ml). The ether extracts were dried over magnesium sulfate. Evaporation of the solvent left 4.9 g (83%) of a colorless liquid which was characterized through its hydrochloride. To 0.3 ml of crude **7** dissolved in 5 ml of diethyl ether and cooled in ice-water, was added 1 ml of a 10 *M* hydrogen chloride solution in water. A precipitate was immediately obtained. Recrystallization from ethanol gave the hydrochloride of **7**, white crystals, mp 166°; ^{1}H nmr (DMSO-d_6): δ 7.53 (m, 4H, H phenyl), 4.16 (s, 2H, CH_2).

Anal. Calcd. for $C_7H_{10}Cl_2N_2$: C, 43.54; H, 5.22; Cl, 36.72; N, 14.51. Found: C, 43.46; H, 5.22; Cl, 36.97; N, 14.34.

3-Amino-1-(4-chlorobenzyl)-1,2,4-triazole (**3b**).

Freshly prepared 4-chlorobenzylhydrazine (**7**) (4 g, 25 mmoles) was added to a solution of *S*-methylisothiourea sulfate (3.56 g, 12 mmoles) in water-ethanol (20:80). The solution was heated to reflux for 6 hours. After cooling to room temperature, the solution was concentrated under reduced pressure to half-volume, giving a precipitate of 1-(4-chlorobenzylamino)guanidinium sulfate (**9**), 2.7 g (43%), white powder; ^{1}H nmr (DMSO-d_6): δ 7.50 (m, 4H, H phenyl), 3.83 (s, 2H, CH_2). This compound **9** did not react with benzaldehyde. It was used without further purification. Compound **9** (1.088 g, 4.4 mmoles) was dissolved in 10 ml of formic acid. To the solution was added dropwise, while stirring, 3.50 ml of acetic anhydride. Stirring at room temperature was maintained for 4 hours. The excess of volatile reagents was evaporated under reduced pressure. The residue crystallized on cooling to 0°. The solid was triturated with ether and filtered giving 1.0 g (89%) of 1-[*N*-(4-chlorobenzyl)-*N*-formylamino]guanidinium sulfate (**11**), white powder; ^{1}H nmr (DMSO-d_6): δ 8.20 (s, 1H, H formyl), 7.33 (m, 4H, H phenyl), 4.50 (s, 2H, CH_2); ir: 1665 cm^{-1}, (CO); ei-ms: m/z 226, 228 (M^+), 101 (M^+-Cl-C_6H_4-CH_2), 59 [H_2N-C(=NH)NH_2^+], 43 (spectrum of the neutral molecule, FW 226.5). The crude compound **11** (0.80 g, 3 mmoles) was dissolved in 15 ml of ethanol and the solution was heated to reflux for 4 hours. The solvent was evaporated under reduced pressure, and the residue was dissolved in water (20 ml). The solution was neutralized at *p*H 7 by addition of a saturated solution of sodium hydrogenocarbonate in water. A precipitate was obtained by cooling in ice-water. It was filtered and recrystallized in ethanol, giving 0.50 g (82%) of **3b**, white powder, mp 146°; ^{1}H nmr see Table II; ei-ms: m/z 208, 210 (M^+), 125, 127 (Cl-C_6H_4-CH_2^+), 89.

Anal. Calcd. for $C_9H_9ClN_4$: C, 51.80; H, 4.34; Cl, 16.99; N, 26.85. Found: C, 51.68; H, 4.10; Cl, 16.89; N, 26.76.

General Procedure for the Synthesis of the 2-Amino-1-arylmethylguanidinium Iodides **13**.

An arylmethylamine (50 mmoles) and *S*-methylisothiosemicarbazide hydroiodide (**12**) (11.65 g, 50 mmoles) were mixed together in 60 ml of absolute ethanol. The mixture was heated to reflux for 6 hours. The solution was then evaporated to half-volume, and 40 ml of diethyl ether were added. The solution was cooled in ice-water and the obtained precipitate was filtered and recrystallized from ethanol, giving the products **13**.

2-Amino-1-benzylguanidinium iodide (**13a**).

This compound was obtained as a white powder, 7.44 g (51%), mp 111°; ^{1}H nmr (DMSO-d_6): δ 7.36 (s, 5H, H phenyl), 4.46 (s, 2H, CH_2).

2-Amino-1-(4-chlorobenzyl)guanidinium Iodide (**13b**).

This compound was obtained as a white powder, 8.98 g (55%), mp 126°; ^{1}H nmr (DMSO-d_6): δ 7.38 (m, 4H, H phenyl), 4.40 (s, 2H, CH_2).

2-Amino-1-(3,5-dimethoxybenzyl)guanidinium Iodide (**13c**).

This compound was obtained as a white powder, 8.55 g (50%), mp 184°; ^{1}H nmr (DMSO-d_6): δ 6.5 (m, 3H, H phenyl), 4.33 (s, 2H, CH_2), 3.76 (s, 6H, 2 CH_3).

2-Amino-1-(1-naphtylmethyl)guanidinium Iodide (**13d**).

This compound was obtained as a white powder, 8.70 g (51%), mp 148°; ^{1}H nmr (DMSO-d_6): δ 7.80 (m, 7H, H naphtyl), 4.70 (s, 2H, CH_2).

General Method of Preparation of 3-Amino-4-arylmethyl-1,2,4-triazoles **4** by Cyclization of the 2-Amino-1-arylmethylguanidinium Iodides **13**.

A compound **13** (5 mmoles) was added to a mixture of 10 ml of formic acid and 15 ml of DMF. The solution was heated to reflux for 5 hours. DMF and excess of formic acid were eliminated to dryness by evaporation under reduced pressure. The viscous residue was dissolved in water-methanol (50:50) (50 ml) and the solution was neutralized to *p*H 7 by addition of a saturated solution of sodium hydrogenocarbonate. Concentration of the solution by evaporation under reduced pressure allowed the product **4** to precipitate. It was recrystallized in ethanol.

3-Amino-4-benzyl-1,2,4-triazole (**4a**).

This compound was obtained as a white powder, 435 mg (50%), mp 210°, lit [6g] 213-215°; ^{1}H nmr, see Table II.

Anal. Calcd. for $C_9H_{10}N_4$: C, 62.05; H, 5.78; N, 32.16. Found: C, 61.80; H, 5.80; N, 32.02.

3-Amino-4-(4-chlorobenzyl)-1,2,4-triazole (**4b**).

This compound was obtained as a white powder, 542 mg (52%), mp 179°; ^{1}H nmr, see Table II.

Anal. Calcd. for $C_9H_9ClN_4$: C, 51.80; H, 4.34; Cl, 16.99; N, 26.85. Found: C, 51.99; H, 4.32; Cl, 16.71; N, 26.81.

3-Amino-4-(3,5-dimethoxybenzyl)-1,2,4-triazole (**4c**).

This compound was obtained as a white powder, 560 mg (50%), mp 185°; ^{1}H nmr, see Table II.

Anal. Calcd. for $C_{11}H_{14}N_4O_2$: C, 56.39; H, 6.02; N, 23.91. Found: C, 56.00; H, 5.99; N, 23.62.

3-Amino-4-(1-naphtylmethyl)-1,2,4-triazole (**4d**).

This compound was obtained as a white powder, 636 mg (57%), mp 225°; ^{1}H nmr, see Table II.

Anal. Calcd. for $C_{13}H_{12}N_4$: C, 69.62; H, 5.39; N, 24.98. Found: C, 69.27; H, 5.30; N, 24.59.

General Method of Preparation of 3-Amino-4-arylmethyl-1,2,4-triazole **4** by Alkylation of 3-Amino-1,2,4-triazole (**1**) in the Absence of Base.

To freshly distilled DMF (40 ml) were added 3-amino-1,2,4-triazole (**1**) (3.0 g, 36 mmoles) and 36 mmoles of the arylmethyl bromide or 4-chlorobenzyl chloride. The solution was heated at 50° for 4 hours with the bromides or for 20 hours with 4-chlorobenzyl chloride. DMF was then evaporated to dryness under reduced pressure. The residue was dissolved in a water-methanol mixture (50:50) (100 ml), and the solution was neutralized to *p*H 7 with a saturated solution of sodium hydrogenocarbonate in water. The solvents were evaporated under reduced pressure. The residue was then triturated with boiling chloroform (40 ml). The hot solution was filtered and on cooling the filtrate gave a precipitate which was recrystallized from ethanol, giving pure compounds **4**, with similar properties (mp, ^{1}H nmr) as compounds prepared by the cyclization method above. Each compound was obtained in the following yield: **4a**, 2.19 g (35%); **4b**, 2.33 g (31%); **4c**, 2.42 g (30%); **4d**, 2.81 g (35%).

Method of Arylmethylation of 3-Amino-1,2,4-triazole (**1**) in the Presence of Sodium Methoxide in Methanol (Method A).

Sodium (0.82 g, 36 mmoles) was added in small pieces to 40 ml of anhydrous methanol. After dissolution, 3-amino-1,2,4-triazole (**1**) (3g, 36 mmoles) and 4-chlorobenzyl chloride (5.8 g, 36 mmoles)

were added, and the solution was heated to reflux for 6 hours. The solution was evaporated to dryness and the solid residue was triturated with boiling chloroform (60 ml). The hot suspension was filtered and the filtrate was evaporated to dryness. Recrystallization of the solid residue gave 2.33 g (31%) of **3b**. The mother liquors were then evaporated to dryness and the residue was triturated in acetone. A small amount of **4b** remained undissolved (600 mg, 8%). [These samples of **3b** and **4b** exhibited the same properties (mp and ^{1}H nmr) as samples prepared by the above methods]. Acetone was evaporated from the solution obtained, and the residue was recrystallized from benzene, giving **5b**, 2.03 g (27%).

3-Amino-2-(4-chlorobenzyl)-1,2,4-triazole (**5b**).

This compound was obtained by method A as a white powder, mp 170°; ^{1}H nmr, see Table II.

Anal. Calcd. for $C_9H_9ClN_4$: C, 51.80; H, 4.34; Cl, 16.99; N, 26.85. Found: C, 51.68; H, 4.10; Cl, 16.89; N, 26.76.

Method of Arylmethylation of 3-Amino-1,2,4-triazole (**1**) in the Presence of Sodium Methoxide in DMF (Method B).

To a solution of sodium methoxide obtained by addition of 0.82 g (36 mmoles) of sodium in 40 ml of methanol, was added 3-amino-1,2,4-triazole (**1**) (3.0 g, 36 mmoles). The solution was evaporated to dryness, and the residue was taken in dry DMF (40 ml). Benzyl bromide or 4-chlorobenzyl chloride (36 mmoles) were then added, and the solution was stirred at room temperature for 3 hours. DMF was evaporated under reduced pressure, and the residue obtained was treated in a similar manner as in method A. The isomers **3** and **5** were the only products isolated: **3a**, 2.07 g (33%); **5a**, 2.19 g (35%); **3b**, 2.33 g (31%) and **5b**, 2.25 g (30%). The isolated samples of **3b** and **5b** exhibited similar properties (mp and ^{1}H nmr) as samples obained by method A or by the cyclization method.

3-Amino-1-benzyl-1,2,4-triazole (**3a**).

This compound was obtained by method B as a white powder, mp 132°, lit [7] 133-134°; ^{1}H nmr, see Table II.

3-Amino-2-benzyl-1,2,4-triazole (**5a**).

This compound was obtained by method B as a white powder, mp 128°; ^{1}H nmr, see Table II.

Anal. Calcd. for $C_9H_{10}N_4$: C, 62.05; H, 5.78; N, 32.16. Found: C, 61.77; H, 5.72; N, 32.02.

Method of Arylmethylation of 3-Amino-1,2,4-triazole (**1**) by Phase Transfer Catalysis (Method C).

3-Amino-1,2,4-triazole (**1**) (3.0 g, 36 mmoles) was added to a mixture of water (30 ml), sodium hydroxide (2.85 g, 72 mmoles) and benzyltriethylammonium chloride (4 g, 18 mmoles). A solution of 4-chlorobenzyl chloride (5.8 g, 0.036 mole) in benzene (60 ml) was then added, and the mixture was heated to reflux under vigorous stirring for 48 hours. After cooling and decantation, the organic layer was washed with water (20 ml). Benzene was evaporated under reduced pressure and the solid residue was treated as in methods A and B giving **3b**, 2.70 g (36%) and **5b**, 2.48 g (33%), which were the only isomers isolated. Their properties (mp and ^{1}H nmr) were found identical to the properties of similar samples obtained by the above methods.

Photolyses of the *N*-Benzyl Derivatives of 3-Amino-1,2,4-triazole **2a-5a**.

Irradiations in Diluted Solution.

Irradiations were carried out with a low pressure mercury vapor lamp (254 nm, 16 watts). The compounds **2a-5a** were dissolved (10^{-3} *M*) in methanol or methanol-water (50:50) mixtures. The samples were contained in quartz tubes surrounding the lamp in a carrousel photoreactor [12] and were cooled by running water. After 24 hours of irradiation, the reaction mixture was analyzed by hplc (225 nm detection) and gc. From methanol solutions, bibenzyl and 2-phenylethanol were the main products with traces of other products including benzylmethyl ether and 3-amino-1,2,4-triazole (**1**). From methanol-water solutions, the two first products were also detected, but benzylmethyl ether, benzyl alcohol and 3-amino-1,2,4-triazole (**1**) appeared in equivalent relative amount. Assignment of the peaks in the chromatograms were obtained by comparison of the retention times with those observed from authentic pure samples of the products.

Irradiation in Concentrated Solution.

Compound **3b** (800 mg, 3.8 mmoles), was dissolved in 400 ml of methanol. The solution was photolyzed for 2 hours with a medium pressure mercury vapor lamp (450 watts) in a quartz reactor. The analysis (hplc, gc) of the photoproducts showed the formation of the same products as in the photolysis in diluted solution, except 3-amino-1,2,4-trizole (**1**) which was not detected, with new unidentified secondary products.

Acknowledgement.

We thank ANVAR Pays de Loire for their financial assistance (Aide à l'Innovation A 84 07 085 R 0610), and Rhône-Poulenc Agrochimie (Centre de Recherches, Lyon, France) for their collaboration.

REFERENCES AND NOTES

[1] N. Mohsinaly and R. Mornet, *J. Agric. Food Chem.*, **39**, 2022 (1991).

[2] S. J. Cristol and T. H. Bindel, in Organic Photochemistry, Vol **6**, A. Padwa, ed, Dekker, New York, 1983, pp 327-415.

[3] A. Er-Rhaimini, N. Mohsinaly and R. Mornet, *Tetrahedron Letters*, **31**, 5757 (1990).

[4] French Patent 1,523,729 (1968); *Chem. Abstr.*, **71**, 124443g (1969).

[5] M. Pesson and G. Polmanss, *Compt. Rend. Acad. Sci.*, **247**, 787 (1958).

[6a] J. Augstein, S. M. Green, A. R. Katritzky and A. M. Monro, *J. Med. Chem.*, **8**, 395 (1965); [b] J. E. Robertson, J. H. Biel and F. DiPierro, *J. Med. Chem.*, **6**, 381 (1963); [c] E. G. Podrebarac, W. H. Nyberg, F. A. French and C. C. Cheng, *J. Med. Chem.*, **6**, 283 (1963); [d] J. H. Short, U. Biermacher, D. A. Dunnigan and T. D. Leth, *J. Med. Chem.*, **6**, 275 (1963); [e] C. Cipens and V. Grinsteins, *Zh. Obshch. Khim.*, **32**, 3811 (1962); [f] A. H. Greer and G. B. L. Smith, *J. Am. Chem. Soc.*, **72**, 874 (1950); [g] G. J. Durant, G. M. Smith, R. G. W. Spickett and S. H. B. Wright, *J. Med. Chem.*, **9**, 22 (1966).

[7] M. Iizuka, N. Igari and S. Maeda, German Patent 1,925,475 (1973); *Chem. Abstr.*, **73**, 36546d (1973).

[8] C. F. Kroger, G. Schocknecht and H. Beyer, *Chem. Ber.*, **97**, 396 (1964).

[9] G. W. Kirsten and G. B. L. Smith, *J. Am. Chem. Soc.*, **58**, 800 (1936).

[10] J. L. Barascut, R. M. Claramunt and J. Elguero, *Bull. Soc. Chim. France*, 1849 (1973).

[11] J. R. Plimmer, P. C. Kearney, D. D. Kaufman and F. S. Guardia, *J. Agric. Food Chem.*, **15**, 996 (1967).

[12] S. L. Murov, Handbook of Photochemistry, Dekker, New York, 1973, pp 132-133.