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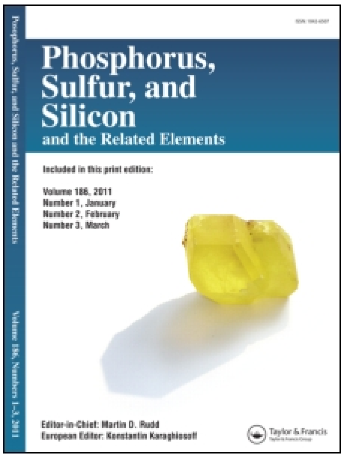

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Novel Photochemical Synthesis of Spiro-1,2,6,8,9 Pentaza-4-thia(4,4)nonane via Rearrangement of Aliphatic Arylazo Compounds

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Novel Photochemical Synthesis of Spiro-1,2,6,8,9 Pentaza-4-thia(4,4)nonane via Rearrangement of Aliphatic Arylazo Compounds

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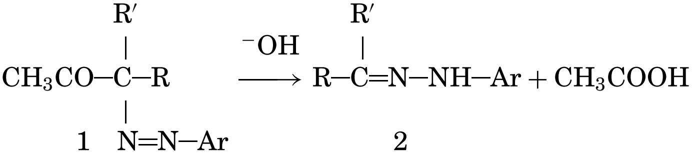
Irradiation of N-phenyl-2-phenylazo-3-oxo-3-[(4-phenyl-5-aryl)-1,2,4-triazol-3-yl)-thio]butanamides $\mathbf{4_{a-c}}$ *gave the corresponding title spiro compounds* $\mathbf{5_{a-c}}$ *as end products via tandem rearrangement and cyclization of* $\mathbf{4_{a-c}}$ *in their excited states.*

Keywords Photochemical; rearrangement; spiro heterocycles

INTRODUCTION

Several 3-thioxo-4H-1,2,4-triazoles, which were reported to be active against gram-positive organisms,[1] have also been shown to exhibit marked antifalammatory activity against corrageenin-induced oedema in albino rats and are nontoxic.[2] Also, aliphatic arylazo compounds of type **1** are known to undergo thermal-base catalyzed cleavage of the acetyl group to give the respective hydrazones **2**, a reaction which is known as Japp- Klingemann reaction (Eq. 1).[3]



$$\underset{1}{CH_3CO\text{—}\overset{\overset{\displaystyle R'}{|}}{\underset{\underset{\displaystyle N{=}N\text{—}Ar}{|}}{C}}\text{—}R} \xrightarrow{^{-}OH} \underset{2}{R\text{—}\overset{\overset{\displaystyle R'}{|}}{C}{=}N\text{—}NH\text{—}Ar} + CH_3COOH \qquad (1)$$

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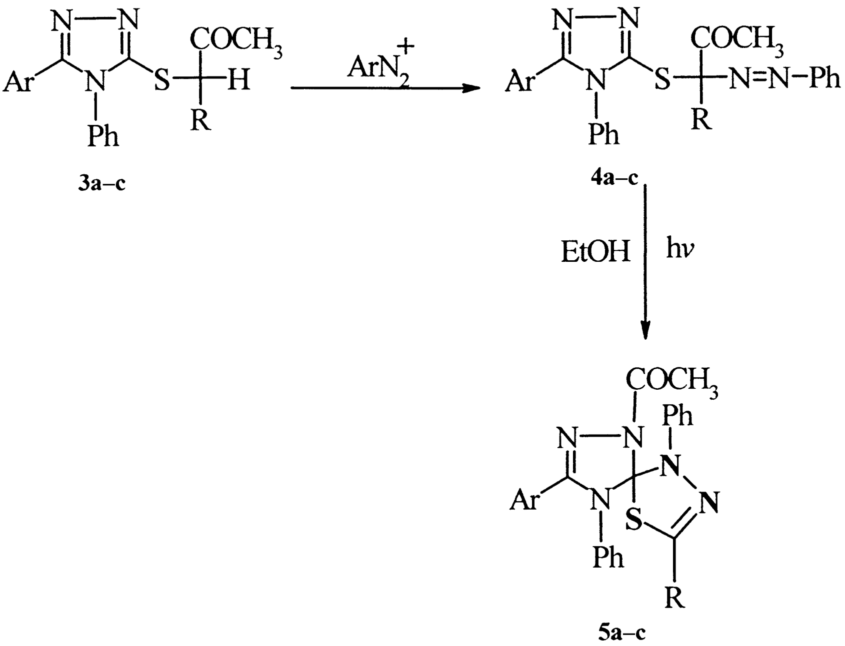


SCHEME 1

In conjunction with our interest in photolysis of azo compounds,[4] we wish to report the results of our study of photolysis of N-phenyl 2-phenylazo-3-oxo-2-[(4-phenyl-5-aryl-1,2,4-3-triazol-3-yl)thio] butanamide derivatives $\mathbf{4_{a-c}}$ [5,6] (Scheme 1).

RESULTS AND DISCUSSION

The starting materials $\mathbf{4_{a-c}}$ were prepared by reaction of benzenediazonium chloride with N-phenyl–2-[(4-phenyl-5-Aryl-1,2,4-triazol-3-yl)thio]-3-oxobutanamide $\mathbf{3_{a-c}}$ as previously described.[5,6]

Irradiation of 150 mL solution of each of $\mathbf{4_{a-c}}$ in absolute ethanol using a high-pressure mercury lamp (Philips HPK 125 W lamp) equipped in Pyrex vessel, $\lambda > 313$ nm was carried out for 20–24 h. Such a treatment gave, in each case, a single product that proved to be the respective spiro-1,2,6,8,9–pentaza-4-thia(4,4)nonane derivative $\mathbf{5_{a-c}}$, as fine colorless crystalline solid (Scheme 1).

The structures of the products $\mathbf{5_{a-c}}$ were established on the basis of their analytical and spectral data (MS, IR, and ^{1}H NMR, see Experimental section). Further evidence in support of structure **5** for the isolated products was evidenced by comparison

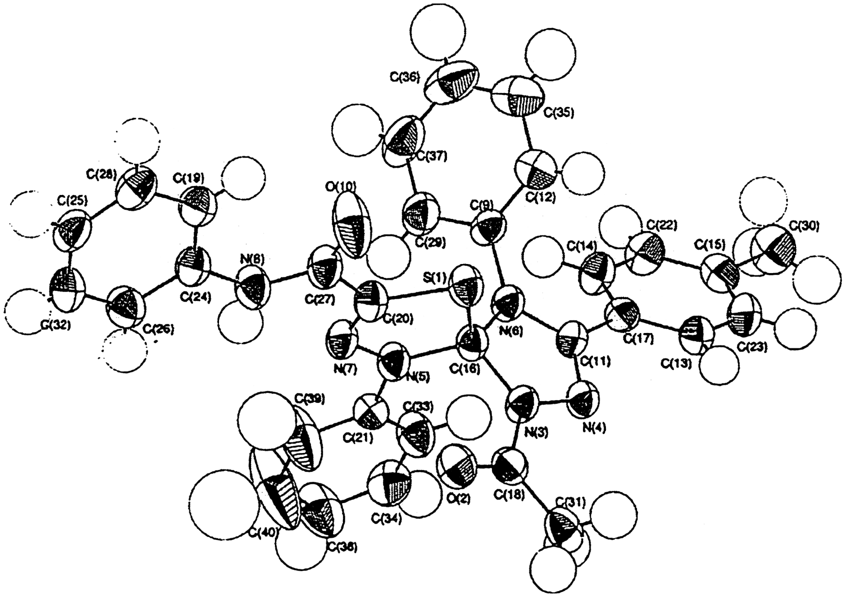
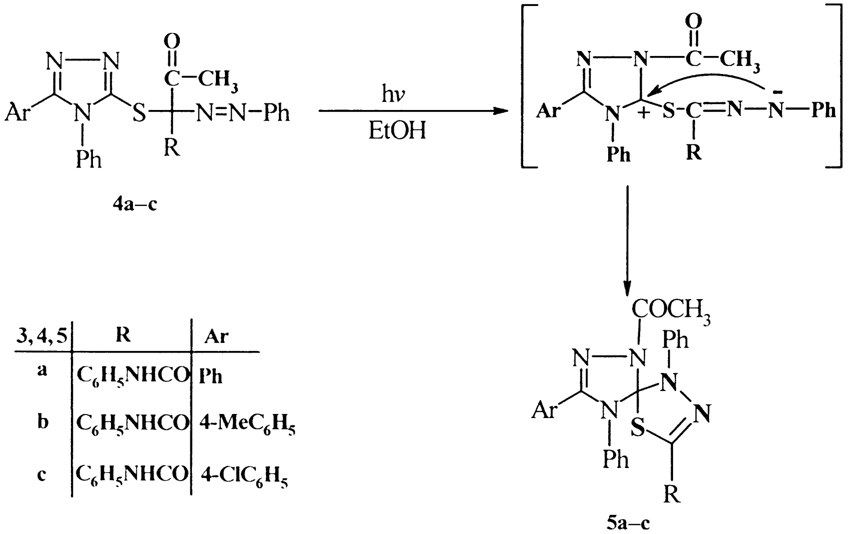


FIGURE 1 Molecular structure of product 5_b in the crystal; the crystallographic numbering does not represents the systematic numbering.

of their mass spectra with those of 4_{a-c}. Intramolecular bond lengths and bond angles. Selected bond lengths [A°] and Bond Angles [°] limits use covalent radu + 0.020A° S(1)-C(16) 1.861(2); S(1)-C(20) 1.732(2); N (7)-C(20) 1.283 (2); N (5)-N (7) 1.363 (2); N (5)-c(16) 1.485 (2); N(3)-C(16) 1.443(2); N(4)-C(11)1.295; N(3)-C(18) 1.385(2); 0(2)-C(18) 1.212(2); C(18)-(31) 1.494(3)A°. C(16)-S(1)-C(20)89.77(9); S(1)-C(20)-N(7)117.8(14) N(5)-N(7)-C(20) 112.3 (2); N(7)-N(5)-C(16)117.42(14);S(1)-C(16)-N(5)102.58(11), S(1)-C(16)-N(6)112.36(13); C(16)-N(3)-C(18)123.85(14), N(3)-C(16)-N(5) 115.3 (2)[°].

For example, each of the compounds 5_{a-c} exhibited in its mass spectrum a characteristic peak at m/z corresponding to the 1-acetyl-3-aryl-4-phenyl-1,2,4-traizol-5-thiol fragment (for 5_a peak at 295 [33%]; 5_b at 310 [29%]; 5_c at 330 [25%]). A final proof for the assigned structure **5** was provided by X-ray crystal structure analysis of 5_b taken as a representative example of the series prepared (see Fig. 1).

To account for the formation of **5**, it is suggested, as depicted in Scheme 2, that the photochemically excited compound **4** undergoes in situ intramolecular acetyl transfer from carbon to nitrogen to give the 1,5-dipolar intermediate *A*, which in turn cyclizes to give the corresponding spiro derivative **5** as end product (Scheme 2).



4a–c

5a–c

3,4,5	R	Ar
a	C_6H_5NHCO	Ph
b	C_6H_5NHCO	4-MeC_6H_5
c	C_6H_5NHCO	4-ClC_6H_5

SCHEME 2

EXPERIMENTAL

All melting points were uncorrected. The IR spectra were recorded on a PU 9712 IR spectrophotometer. The mass spectra were run at 75 eV on Kratos Ms equipment. Analytical data were obtained from the Microanalatical unit at the National Research Centre, Giza, Egypt.

The crystallographic study of 5_b was undertaken to establish its three-dimensional structure. Geometries are tabulated below. All diagrams and calculations were performed using bruker nonius, Delft, and macScience.

Crystal date

C_{31} H_{26} N_6 O_2 S $M_w = 546.653$ Triclinic p- 1

a 10.4257(2) A^0
b 10.8299 (3) A^0
c 13.5891 (4) A^0
α 67.7432(12)^0
β 76.8841 (12)^0
δ 85.9554(14)^0
V 1382.77 (6) A^3
Z 2

D_x 1.313 Mgm^{-3} cell parameters from reflection 10048

Q = 2.91–27.485^0
$\mu = 0.16$
Fooo 572

Date collection

KappaCCD diffractomenter
ψ s and w scans with kaffisent
Absorption correction: meltiscan
(sortav; Blessing, 1995, 1997)
7432 measured reflections
361 parameters
10048 independent reflections
2782 reflection with I > 3 segma(I)
$R_{int} = 0.047$
$Q_{max} = 27.485^0$
h = o–13
k = −13–14
l = −16–17

Refinement

Refinement on F^2
R $\{F^2 > 3$ segma $F^2\} = 0.047$
WR $(F^2) = 0.095$
S = reflection
2782 reflection
361 paramenter
H-atom parameters constrained
$w = 1/\{s^2 (Fo^2) + 1.100\ Fo^2\}$

REACTION OF BEZENEDIAZONIUM CHLORIDE WITH 3_{a-c}[5, 6]

To a solution of the appropriate $\mathbf{3_{a-c}}$ (10 mmol) in ethanol (40 mL) sodium acetate trihydrate (3 g) was added and the mixture was cooled in an ice bath to 0–5°C while being stirred. Cold solution was added portionwise a cold solution of bezenediazonium chloride, prepared as usual by diazotizing aniline (10 m mol) in hydrochloric acid (6 mL, 6 M) with sodium nitrite (0.7 g, 10 m moL) in water (10 mL). After all the diazanium salt solution was added, the reaction mixture was stirred for 30 min and was cooled in an ice bath. The solid precipitate was filtered off, washed with water, air dried, and crystallized from the appropriate solvent to give the corresponding phenylazo derivative $\mathbf{4_{a-c}}$. The preparation of products $\mathbf{4_{a-c}}$ are listed in the following paragraphs.

N-Phenyl-2-phenylazo–3-oxo-3-[(4,5-diphenyl-1,2,4-triazol–3-yl)-thio] butanamide 4_a

3.72 g (70%); m.p 192–193°C (EtOH); ν (KBr), 3299 (NH), 1691, 1656(CO) cm^{-1}; δ ($CDCl_3$), 3.2(s, 3H, $\mathbf{CH_3}$), 7–7.6(m, 20H, **Ar—H**), 8.4(s, 1H, **NH**); m/z 532 (M^+); Anal. Found: C, 67.7; H, 4.50; N, 15.8; S, 6.0, $C_{30}H_{24}N_6O_2S$ requires C, 67.67; H, 4.54; N, 15.79; S, 6.02%.

2-Phenylazo-3-oxo-3-[(4-phenyl-5-p-tolyl-1,2,4-triazol-3-yl)thio] butanamide 4_b

3.71 g (68%); m.p 198°C (EtOH); ν (KBr), 3243(NH), 1691, 1645(CO) cm^{-1}; $\delta_{\mathbf{H}}$ ($CDCl_3$), 2.2(s, 3H, $\mathbf{CH_3}$), 2.3(s, 3H, $\mathbf{CH_3}$) 7–7.6(m, 19H,

Ar—H), 8.4(s, 1H, **NH**); m/z 546 (M^+); Anal. Found: C, 68.20; H, 4.8; N, 15.4; S, 5.9, $C_{31}H_{26}$ N_6O_2S requires C, 68.13; H, 4.76; N, 15.38; S, 5.86%.

2-Phenylazo-3-oxo-3[4-phenyl-5-(4-chlorophenyl)-1,2,4-triazol-3-yl-thio] butanamide 4_c

4.13 g (73%); m.p 200 (EtOH); ν cm-1 (KBr), 3374(NH), 1693, 1663(CO); δH ($CDCl_3$), 2.3(s, 3H, $\mathbf{CH_3}$), 7–7.6(m, 19H, **Ar—H**), 8.4(s, 1H, **NH**); m/z 566 (M^+); Anal. Found: C, 63.6; H, 4.1; N, 14.9; S, 5.7, $C_{30}H_{23}ClN_6O_2S$ requires C, 63.55; H, 4.06; N, 14.8; S, 5.65%.

Irradiation of $4_{a–c}$

General Method

A solution of **4** (1 mmol) in 150 mL of absolute ethanol was irradiated using a high pressure mercury lamp/Pyrex vessel, $\lambda > 313$ nm for 22–24 h. The reaction progress was followed up by TLC. The color of the reaction changed from yellow to colorless. The solvent was then evaporated at room temperature and the oil residue that was triturated with methanol and left for 3 h in a refrigerator. The product that was formed was collected by filtration and crystallized from ethanol to give **5**. In case of $\mathbf{4_b}$, the respective product $\mathbf{5_b}$ was separated out after removal of the solvent directly as colorless needles. The isolated products $\mathbf{5_{a-c}}$ are given below, together with their physical data.

1,6,7-Triphenyl-3-N-phenylaminocarbonyl-9-acetyl-spiro-1,2,6,8,9-pentaza-4-thia[4,4]nonane 5_a

0.419 g (78%); m.p. 179°C (EtOH); ν (KBr), 3402(NH), 3055(CH-Aromatic), 1681–1600(CO) cm^{-1}; ^{1}HNMR ($CDCl_3$) 2.03(s, 3H, $\mathbf{CH_3}$), 7.21–7.48(m, 15H, **Ar—H**), 8.45(s, 1H, **NH**); m/z 532(M^+, 18%), Anal. found: C, 67. 68; H, 4.54; N, 15. 80; S, 6.10, $C_{30}H_{24}N_6O_2S$ requires: C, 67.68; H, 4.54, N; 15. 79; S, 6.02%.

1,6-Diphenyl-7-(p-tolyl)-3-N-phenylcarbonyl-9-acetyl-spiro-1,2,6,8,9-pentaza-4-thia[4,4]Nonan 5_b (See Fig. 1)

0.43 g (80%); m.p. 185°C (EtOH); m/z 546 (M^+, 20%); Anal found: C, 68.13; H, 4.76; N, 15.38; S, 5.86, $C_{31}H_{26}N_6O_2S$ requires: C, 68.13; H, 4.76, N, 15.38; S, 5.86.

1,6-Diphenyl-7-(p-chlorophenyl)-3-N-phenyl-9-acetyl-spiro-1, 2, 6, 8, 9-pentaza-4-thia[4,4]nonane 5_c

0.42 g (75%); m.p. 178°C (EtOH); ν (KBr) 3320(NH), 3052(CH-Aromatic), 1679–1600(CO) cm^{-1}, m/z 566(M^+, 20%), 568($M^+ + 2$, 12%). Anal. Found C, 63.58; H, 4.2; N, 14.9; S, 5.17; $C_{30}H_{23}N_6$ SO_2Cl requires C, 63.55; H, 4.06; N, 14.83; S, 5.65.

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