

**SOME REACTIONS OF 4-AMINO(HYDRAZINO)-3-MERCAPTO-
5-ARYL-1,2,4-TRIAZOLE**

BY

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ABSTRACT

In this work we are dealing with the preparation of several new compounds containing the triazole ring fused with some heterocyclic moiety.

INTRODUCTION

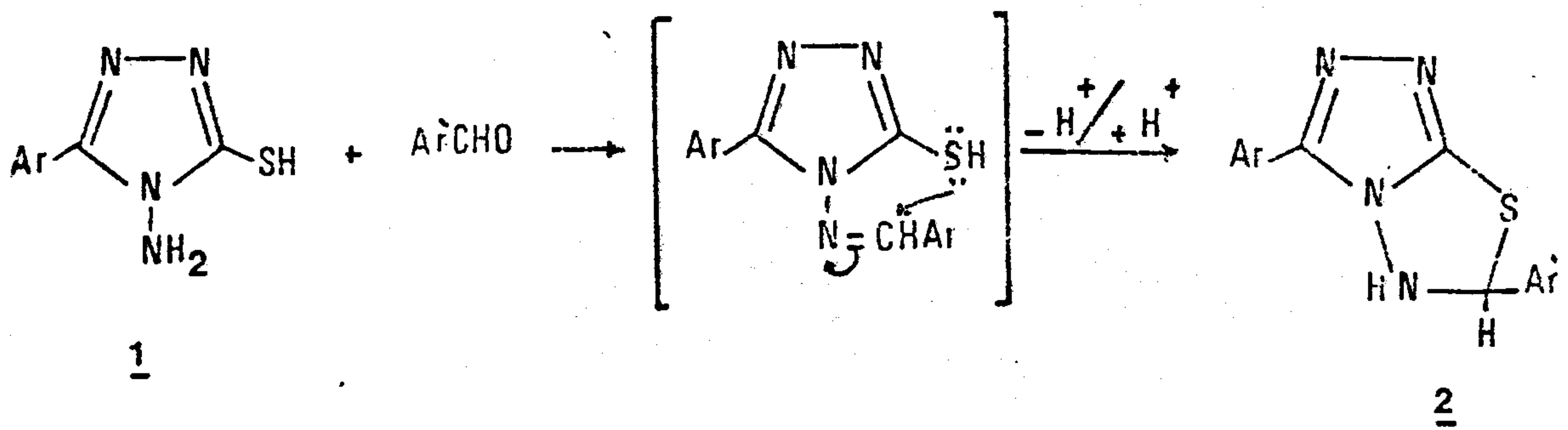
The triazole nucleus has aroused great interest in recent years due to a wide variety of biological activities [1,3 - 5].

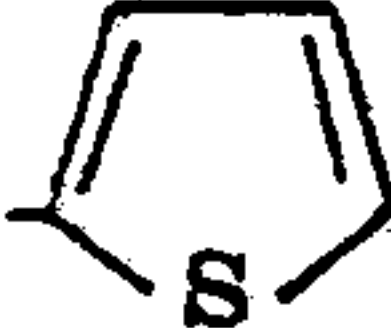
RESULTS AND DISCUSSIONS

Firstly, 4-amino-3-mercapto-5-phenyl-1,2,4-triazole [6] 1 condenses with benzaldehyde and / or 2-thiophenolaldehyde in absolute ethanol giving 3,4-dihydro-3,6-diphenyl-1,2,4-triazole [3,4-b] 1, 3,4-thiadiazole 2a, and 3,4-dihydro-6-phenyl-3(2'-thieno)-1,2,4-triazolo [3,4-b] -1,3,4-thiadiazole 2b , respectively.

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Some reactions of 4-amino (hydrazino)

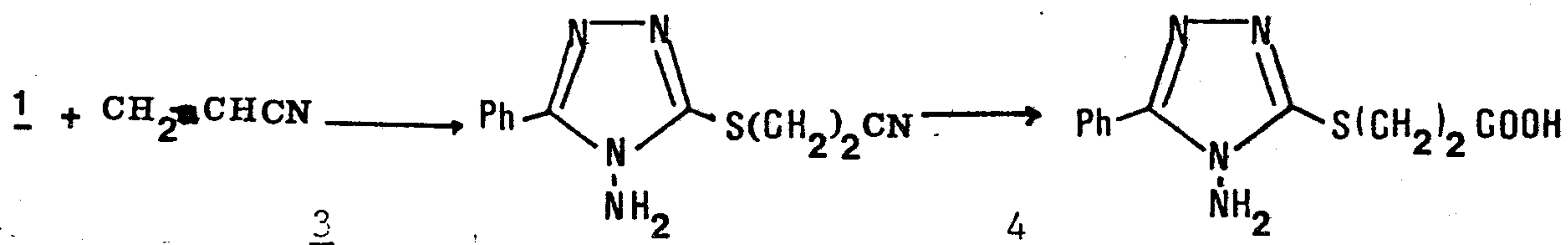
a, Ar = C₆H₅

	Ar	Ar'
a	C ₆ H ₅	C ₆ H ₅
b	C ₆ H ₅	

On treatment of 1a with acrylonitrile in methanolic solution of triethylamine, it affords 4-amino-5-phenyl-3-cyanoethylthio-1,2,4-triazole, 3 which on hydrolysis with HCL yielded 4-amino-5-phenyl-1,2,4-triazolo-3-yl-thiopropionic acid 4.

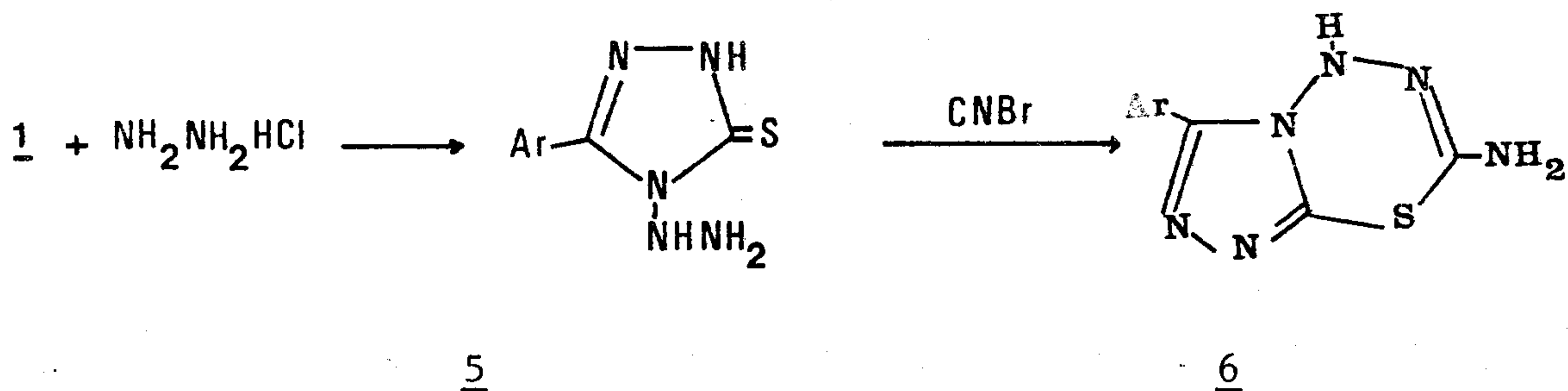
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4-Hydrazino-5-aryl-1,2,4-triazole-3-thione 5 could be obtained by the reaction of compound 1 with hydrazine hydrochloride in boiling ethylene glycol [2].

The reaction of 5a with cyanogen bromide in aqueous ethanol afforded 3-amino-7-phenyl-1H-1,2,4-triazolo[3,4-b]1,3,4,5 thiatiazine, 6a.



5

Ar

a

C_6H_5

b

4-OCH₃ C₆H₄

c

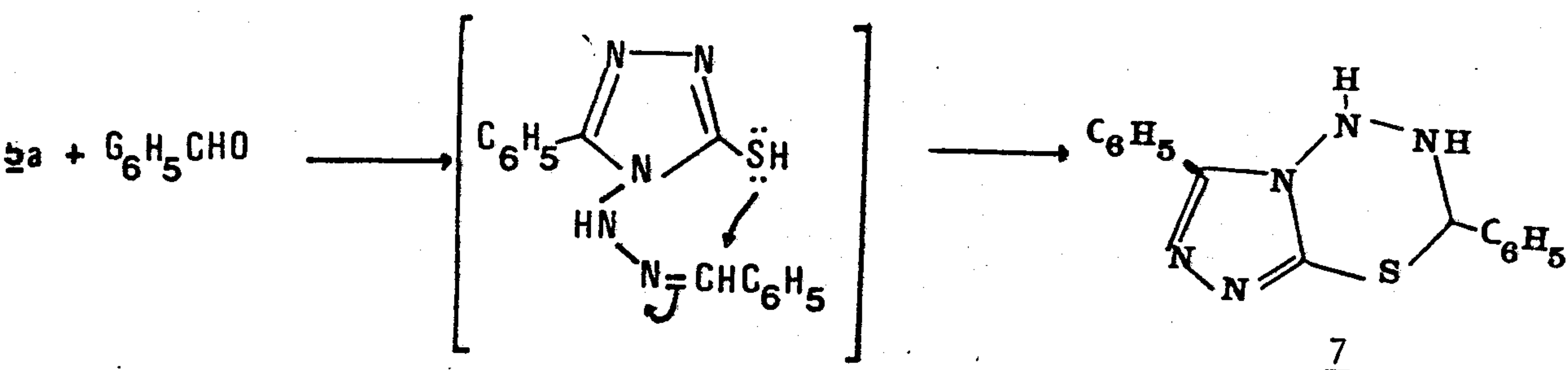
4-ClC₆H₄

Treatment of 5a with benzaldehyde in boiling absolute

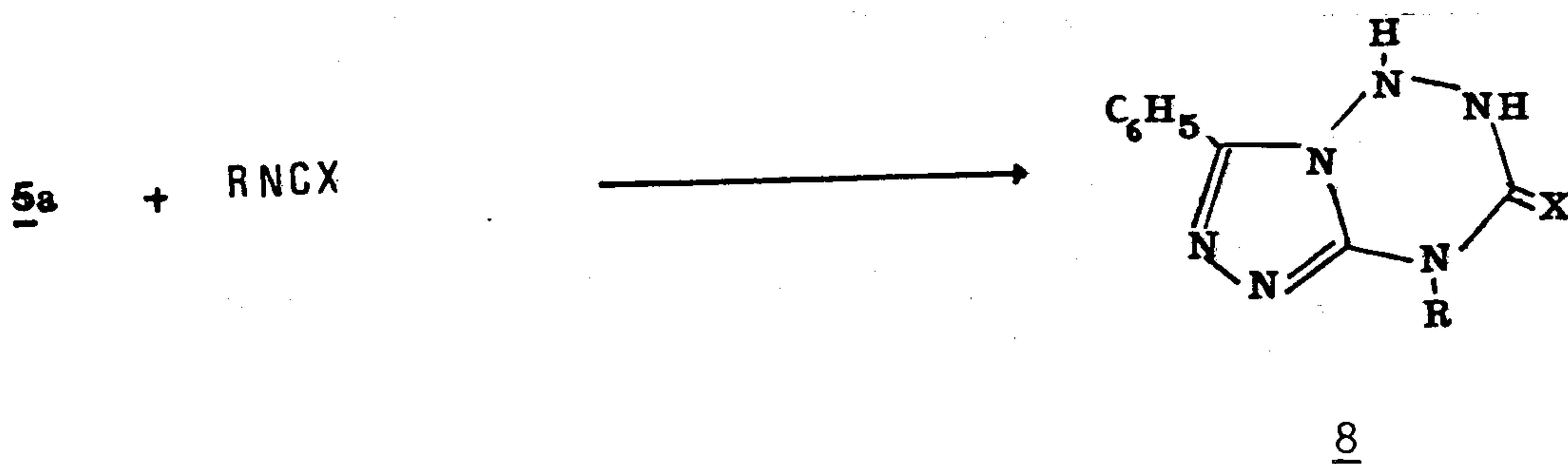
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Some reactions of 4-amino (hydrazino)

ethanol gives one product which is proved to be 3,7-di-phenyl-1,2,4-triazolo[3,4-b]-4,5,6-trihydro-1,3,4,5 thia-triazine, 7 .



The reaction of 5a with phenylisocyanate and/or (Ethyl or phenyl)-isothiocyanate in boiling benzene gives 1,2-dihydro-4-phenyl or (ethyl)-7-phenyl-1,2,4-triazolo-[4,3,c]asate-triazin-3-4H-one, 8 .

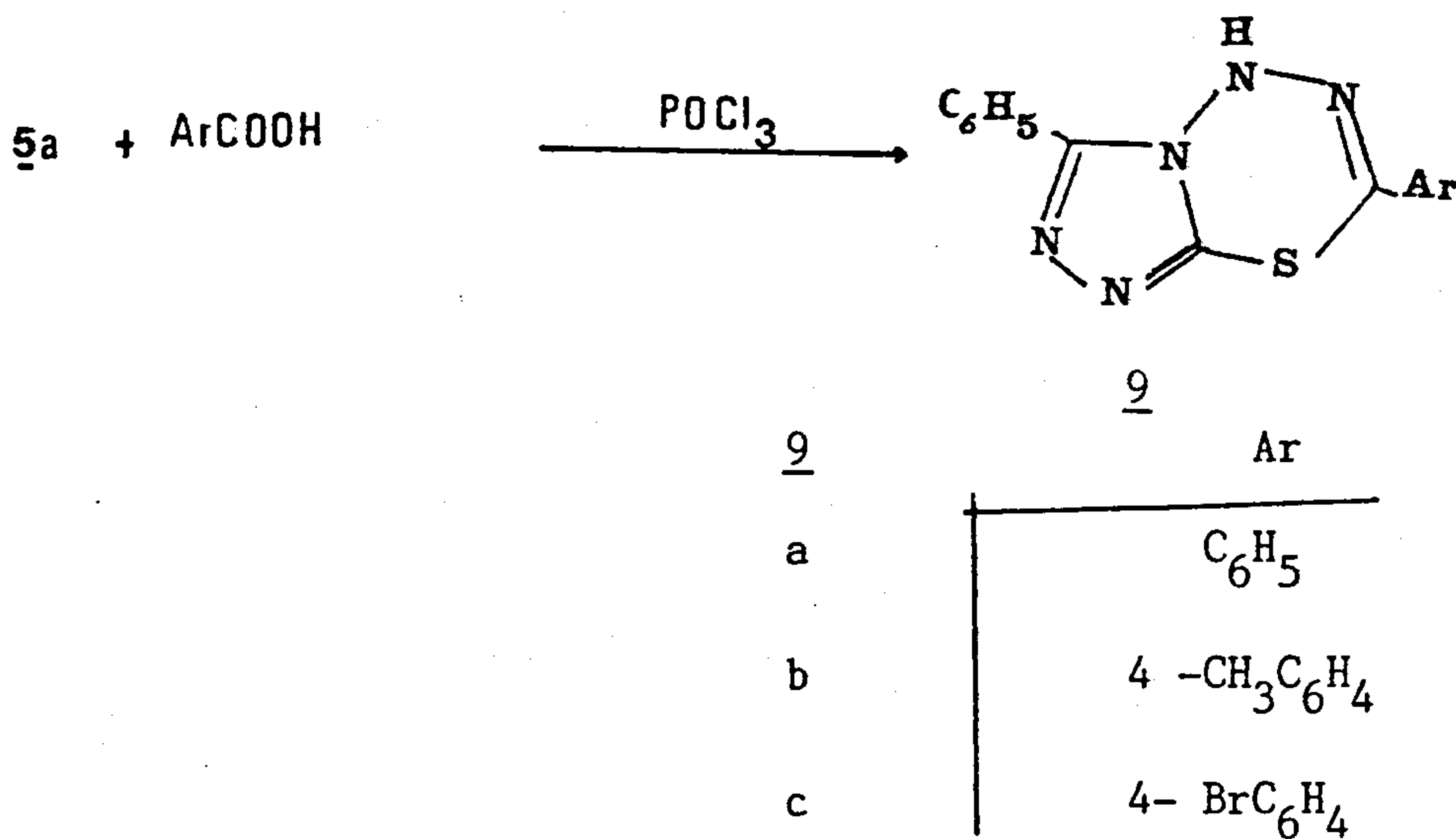


<u>8</u>	R	X
a	C_6H_5	O
b	C_6H_5	S
c	C_2H_5	S

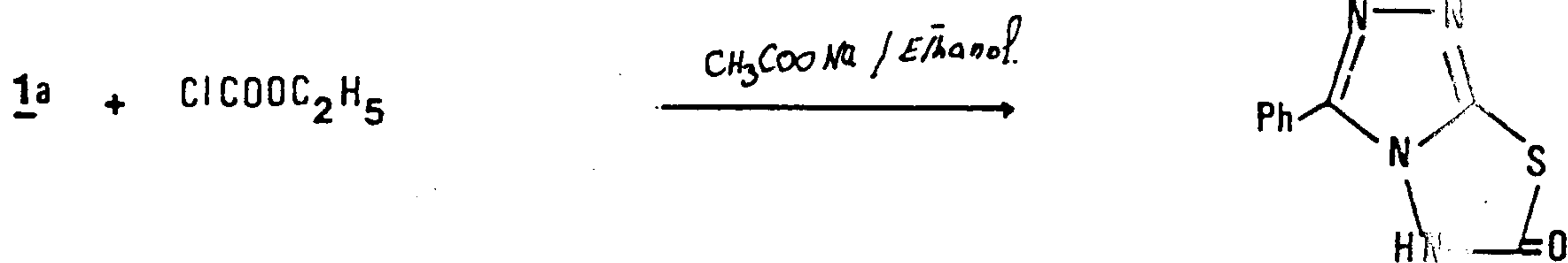
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Refluxing of 5a with some aromatic acids in the presence of phosphorus oxychloride affords 7-phenyl-3-substituted-1H-1,2,4-triazolo [3,4-b]- 1,3,4,5-thiatriazines, 9 .



The reactions of compound 1a with ethylchloroformate in boiling ethanol gives 6-Phenyl-3-oxo-1,2,4-triazole-[3,4-b]-4-hydro-1,3,4- thiadiazole 10 in a good yield.



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EXPERIMENTAL:

The melting points were taken on a Gallenklamp Apparatus, and are uncorrected. The I.R. spectra were determined using I.R. 10 fully automatic double beam Infra-Red Spectrophotometer Carl Zeiss Jene, a PYE UNICAM SP200G and SP 100 spectrophotometers (using KBr). ^1H n.m.r. spectra were recorded using Varian-T90-MHZ. DMSO was used as a solvent and TMS as an internal standard.

Reaction of compound 1 with aromatic aldehydes. Formation of 2.

A mixture of compound 1 (0.01 mole) and aromatic aldehydes (benzaldehyde and 2-thiophenoaldehyde)(0.01 mole) was refluxed in 30 ml absolute ethanol for 5 hours. After cooling, the resulting soild was filtered off and re-crystallised.

Reaction of compound 1 with acrylonitrile. Formation of 3.

A mixture of 1 (0.01 mole), acrylonitrile (0.01 mole) and triethylamine (5 ml) was refluxed in (20 ml) methanol for 3 hours. The reaction mixture was cooled, poured into ice. The resulting soild was filtered off and recrystallised.

Hydrolysis of compound 3. Formation of 4.

A mixture of compound 3 (1 gm) and conc. HCl (5 ml) was refluxed for 6 hours. The reaction mixture was cooled, neutralized with 5% NaOH. The resulting soild was filtered off, and recrystallised.

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Reaction of 5a with cyanogen bromide. Formation of 6.

A mixture of 5a (0.01 mole) and cyanogen bromide (0.01 mole) was refluxed in ethanol (30 ml) for 3 hrs. The reaction mixture was evaporated to one-fourth its original volume, and diluted with saturated aqueous sodium acetate. The residual solid was filtered and recrystallised.

Reaction of compound 5a with benzaldehyde. Formation of 7.

A mixture of 5 (0.01 mole) and benzaldehyde (0.01 mole) was refluxed in absolute ethanol (50 ml) for 7 hours. After cooling, the solid was filtered off.

Reaction of compound 5 with isocyanate and isothiocyanate.

Formation of 8.

A mixture of 5 (0.01 mole) and phenylisocyanate (0.03 mol) and/or (ethyl or phenyl) isocyanate was refluxed in benzene (50 ml). After cooling, the solid formed was filtered off, and recrystallised.

Reaction of compound 5 with aromatic acids. Formation of 9.

A mixture of 5 (0.005 mole), aromatic acids (0.01 mole) and phosphorus oxychloride (10 ml) was refluxed for one hour. After distillation of phosphorus oxychloride under reduced pressure, the residue was titrated with dilute NaOH solution. The solid formed was filtered off and recrystallised.

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Reaction of compound 1 with ethylchloroformate . Formation of 10.

A mixture of compound 1 (0.01 mole), ethylchloroformate (0.01 mole) and fused sodiumacetate (0.01 mole) was refluxed in absolute alcohol (30 ml) for 6 hours. After cooling, pour into ice. The resulting solid was filtered off and recrystallised.

Experimental and Spectral data are grouped in table 1.

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 Table 1. Experimental and Analytical data of compounds 2 - 10.

Comp.	M.P. °C	Solvent	Yield %	Formula (Mol. Wt.)	Analyses %	I.R. $\mu\text{m. cm}^{-1}$	$^1\text{H n.m.r.}$ δ ppm
					C H N S		
2a	155	Ac	70	$\text{C}_{15}\text{H}_{12}\text{N}_4\text{S}$ (280.1)	Calcd. 59.9 4.2 20.0 11.4 Found 59.7 4.0 20.5 11.5	3100(NH), 1590(C=N)	s/1(CH)3.5; m/10(2 C_6H_5) 7.5, s/1(NH)9.9 exchangeable
2b	178	Ac	50	$\text{C}_{13}\text{H}_{10}\text{N}_4\text{S}_2$ (286.4)	Calcd. 54.5 3.5 19.6 22.3 Found 54.8 3.6 19.4 22.0	3100(NH), 1590(C=N).	
2	135	B	70	$\text{C}_{11}\text{H}_{11}\text{N}_5\text{S}$ (245.3)	Calcd. 53.9 4.5 28.6 13.1 Found 53.9 4.8 27.8 13.6	2260(C=N)	t/2(CH_2)3.0, t/2(S- CH_2). 4.3, s/2(NH_2)6.0.
6a	245	B	80	$\text{C}_9\text{H}_8\text{N}_6\text{S}$ (232.3)	Calcd. 46.5 3.5 36.2 13.8 Found 46.6 4.0 36.3 14.5	3350(NH_2), 1570(C=N), 3140(NH).	s/2(NH_2)3.4, m/5(aromatic) 7.6, s/1(NH)8.0.
7	130	B	70	$\text{C}_{15}\text{H}_{13}\text{N}_5\text{S}$ (295.4)	Calcd. 60.9 4.4 23.7 10.8 Found 60.4 4.4 23.8 10.5	3120(NH), 1580(C=N).	s/1(CH)3.4, m/5(C_6H_5)7.9, s/1(NH)9.8.
9a	150	B	60	$\text{C}_{15}\text{H}_{12}\text{N}_6\text{O}$ (292.3)	Calcd. 61.6 4.1 28.8 Found 61.6 4.0 28.9	3330(NH), 1720(C=O), 1610(C=N).	
9b	215	B	50	$\text{C}_{15}\text{H}_{12}\text{N}_6\text{S}$ (308.4)	Calcd. 58.4 3.9 27.3 10.3 Found 58.0 3.6 27.4 10.1	3210(NH), 1640(C=N). 1330(C=S)	
8c	200	B	55	$\text{C}_{11}\text{H}_{12}\text{N}_6\text{S}$ (260.3)	Calcd. 50.8 4.5 32.3 12.3 Found 51.1 4.0 31.8 12.0	3310(NH), 1640(C=N), 1320(C=S).	s/1(NH)5.8, m/5(C_6H_5)7.6, s/1(NH)13.9.
9a	205	B	70	$\text{C}_{15}\text{H}_{11}\text{N}_5\text{S}$ (293.4)	Calcd. 61.4 3.8 23.8 10.9 Found 61.4 3.7 23.5 10.8	3390(NH), 1610(C=N).	
9b	148	B	75	$\text{C}_{16}\text{H}_{13}\text{N}_5\text{S}$ (307.4)	Calcd. 62.4 4.2 22.8 10.4 Found 62.0 4.6 22.5 11.5	3390(NH), 1610(C=N), 690(C-S-C).	s/3(CH_2)2.3, m/5(C_6H_5)7.3 s/1(NH)7.9, m/4(C_6H_4)8.2.
9c	245	B	70	$\text{C}_{15}\text{H}_{10}\text{BrN}_5\text{S}$ (372.4)	Calcd. 48.4 2.7 18.8 8.6 Found 48.3 3.2 19.0 8.5	3250(NH), 1590(C=N).	
10	125	B	70	$\text{C}_9\text{H}_6\text{N}_4\text{OS}$ (218.3)	Calcd. 49.5 2.8 25.7 14.7 Found 49.3 3.1 25.3 14.5	3150(NH), 1770(C=O).	m/5(C_6H_5)7.5, s/1(NH)8.6 NH proton exchangeable with D_2O .

E: ethyl alcohol
 Ac: Acetic acid

بعض تفاعلات ٤- أمينو (هيدرازينو) -٣- مركبتو -٥- أرايل -١, ٢, ٤- ترايازول
 أحمد البربرى ، محمد البرعى ، محمود فهمى ، حامد النجار
 قسم الكيمياء - كلية العلوم - جامعة طنطا

يتناول البحث تكاثف ٤- أمينو -٣- مركبتو -٥- فينيل -١, ٢, ٤ ،
 ٤ - ترايازول مع الألكدهيدات الأروماتيه معطيا نواتج حلقيه .

ويتفاعل مع الأكريلونيتريل فى وسط قاعدى معطيا ناتج ويتحلله تم
 الحصول على الحامض المقابل .

وتتفاعل ٤- هيدرازينو -٥- آريل -١, ٢, ٤ ، ٤- ترايازول -٣-
 شيون مع السيانوجين بروميد والاحماض الأروماتيه معطيا نواتج حلقيه
 (ثيا - ترايازين)

ويتفاعل مع أيزوسيانات الفينيل فى وجود البنزين معطيا ناتج حلقى
 - أساتترازين ويتفاعل مع كلوروفورمات الايثيل معطيا (ثيا - دايازول) .
 وقد تم اثبات تراكيب المواد المختلفه بواسطة التحليل الدقيق وطيف الرنين
 المغناطيسى .