

H. A. Zaher* and R. Mohammady

Chemistry Department, Faculty of Education, Ain Shams University,
Cairo, Roxy, A. R. Egypt

Yehia A. Ibrahim

Chemistry Department, Faculty of Science, Cairo University,
Giza, A. R. Egypt

Received March 31, 1983

The action of phenylmagnesium bromide on 6-*p*-chlorostyryl-3-thioxo-1,2,4-triazin-5-one (**1**) was studied whereby a mixture of seven products was obtained. These were separated and characterised, and a reasonable mechanism for their formation is presented and discussed.

J. Heterocyclic Chem., **21**, 905 (1984).

It has been shown [1-4] that organomagnesium halides as nucleophilic reagents, attack the 1,2,4-triazine nucleus at the 5-position, illustrating the strong electrophilicity of this position.

In the present work, the title compound **1** is now subjected to the action of phenylmagnesium bromide. The results obtained prove by every means that the heterocyclic ring in case of thioxotriazine is very sensitive to Grignard reagents, where it is attacked at different sites giving rise to a mixture of products which can be rationalized in the following Scheme 1.

The mechanistic proposal for such fragmentation pathway seems to be controversial. No information in the literature is extant concerning this matter, but there is no doubt that the triazine ring is ruptured at different sites under the influence of the Grignard reagent. It is obvious, according to the diversity of products, that there are different nucleophiles (Grignard solutions contain variable species: RMgX , MgX_2 , R_2Mg and sometime MgXOH due to traces of moisture) and different electrophilic sites of attack which are possible on the triazine molecule. The evolution of ammonia during the decomposition of the Grig-

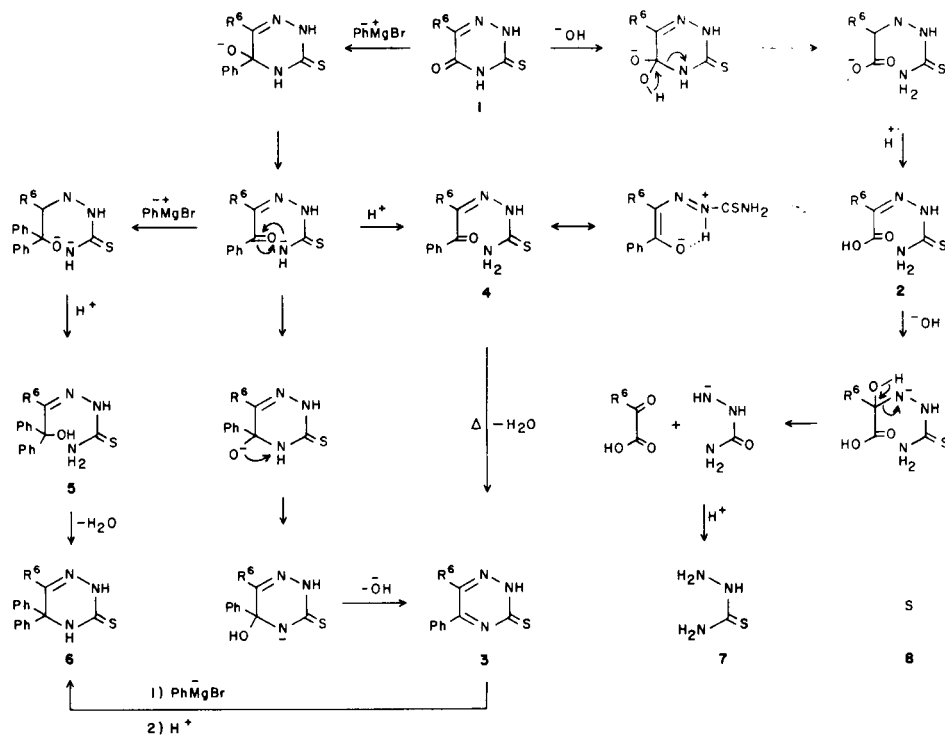


Table
Physical Data of Grignard Products

Products	Mp °C	Formula (Molecular weight)	Analysis % [a]		
			N	S	Cl
2	194	C ₁₁ H ₁₀ ClN ₃ O ₂ S (283.73)	14.81	11.30	12.50
	(Ethanol)		14.80	11.28	12.42
3	150	C ₁₇ H ₁₂ ClN ₃ S (325.81)	12.90	9.84	10.88
	(Ethanol)		12.67	9.58	10.63
4	130	C ₁₇ H ₁₄ ClN ₃ OS (343.83)	12.22	9.31	10.33
	(Benzene)		12.10	9.18	10.18
5	189	C ₂₃ H ₂₀ ClN ₃ OS (421.94)	9.96	7.59	8.42
	(Ethanol)		9.79	7.48	8.23
6	215	C ₂₃ H ₁₈ ClN ₃ S (403.18)	10.40	7.94	8.78
	(Carbon tetra- chloride)		10.36	7.90	8.73
7 [b]	183 [d]	CH ₅ N ₂ S (91.13)	46.11	35.18	
	(Ethanol)		46.09	35.23	
8 [b]	122	S (32.06)			
	(Benzene)				

[a] All compounds gave satisfactory C and H analysis. [b] Identical with pure specimen.

nard complex (with dilute hydrochloric acid) and its detection in the aqueous layer (Nessler's solution) is an important feature that loss of nitrogen is a dominant process in this case [5]. Also, the presence of thiosemicarbazone products, offers a new and unique proof for our earlier results in the same field.

It is logical that the first step of the reaction may be the addition of a nucleophile (Ph⁻, OH⁻) at the more reactive 5-position, thus leading to the formation of the thiosemicarbazones **2**, **4** and the 5,6-disubstituted-1,2,4-triazine-3-thione **3**. The formation of 6-*p*-chlorostyryl-5,5-diphenyl-1,2,4-triazine-3-thione **6** may be attributed to the attack of the nucleophile (Ph⁻) at the 5-position of **3**, a reaction which illustrates the formal analogy between the action organomagnesium halide and reducing agents where the 4,5-dihydro derivatives are always obtained. The isolation of thiosemicarbazide **7** may be explained through the nucleophilic attack (OH⁻) at the imino double bonds of **2-5**, resulting in the hydrolysis of these bonds, thus indicating that the imino double bonds in 1,2,4-triazines are reactive similar to that of a hydrazone. This result is supported by our findings in recent work [5] where benzil was isolated from the reaction mixture of phenylmagnesium bromide with 3-chloro-5,6-diphenyl-1,2,4-triazine. The presence of elemental sulfur **8** among the reaction products is a fact, which means that desulfurization occurs, but an explanation of such a process remains controversial.

The structures assigned for the products **2-8** are supported by the following facts:

- 1) All compounds gave correct elemental analysis.
- 2) The ir spectrum of α -ketoacid thiosemicarbazone **2**

reveals a very broad band with a series of minor peaks over the range 3400-2800 cm⁻¹. Product **2** was also found identical with an authentic sample [6].

3) The ir spectrum of product **4** reveals a broad NH band at 3350-3000 cm⁻¹ assignable to a hydrogen bonded OH or NH group. The lack of a carbonyl absorption in such a case can be explained by a conjugated chelation between the carbonyl and the NH group and by α,β -unsaturation. This agrees with the findings of Sadler [7], that in α -diketone monothiosemicarbazones, strong intramolecular NH...O=C bonds predominate. Furthermore thermolysis of **6** produces the 6-*p*-chlorostyryl-5-phenyl-1,2,4-triazine-3-thione (**3**). The ir spectrum of **3** shows a band at 3120 cm⁻¹ (NH) and no SH band can be observed.

4) The structure of **5** is supported by its ir spectrum where a band appears at 3340 cm⁻¹ (OH) while no C=O band is detected. Further evidence for the proposed structure is that when an ethanolic solution of **5** containing hydrochloric acid is heated under reflux, cyclodehydration takes place affording a compound which is identical with **6**. The ir spectrum of **6** shows no OH band but exhibits a band at 3140 cm⁻¹ (NH).

EXPERIMENTAL

All melting points are uncorrected. The ir spectra (potassium bromide) were recorded with IR-4 instrument. Compound **1** was prepared after the procedure described by Slouka [6].

Action of Phenylmagnesium Bromide on **1**.

To a suspension of **1** (25 g) in dry benzene (200 ml) was added an ethereal solution of phenylmagnesium bromide (prepared from 20 g of magnesium and 120 ml of freshly distilled bromobenzene in 200 ml of dry ether). The reaction mixture was heated under reflux for 5 hours, left overnight at room temperature and then decomposed with a cold hydrochloric acid solution. The organic layer was dried over anhydrous sodium sulfate and evaporated on a steam bath. The semisolid remained was treated in the following manner: 1) On trituration with ethanol, a solid precipitated. This was collected proved to be sulfur, yield *ca* 4%. 2) The ethanolic solution from the above treatment was evaporated and the oil remaining was trituated with methanol, whereby a solid precipitated. This was collected and recrystallized into pale yellow crystals of **7** (yield 10%). 3) The solution from the above step was evaporated and the oil remaining was trituated with petroleum ether (40-60), whereby two fractions were separated by decantation, an oily fraction (A) and an ethereal fraction (B).

(a) The oily fraction A solidified on trituration with ethyl acetate, the solid obtained was recrystallized to give **3** as yellow crystals, in about 12% yield. The mother liquor from **3**, on dilution with water, precipitated a solid which was recrystallized to yield **4** as yellow crystals, in about 5% yield.

(b) The ethereal layer B was evaporated and the oil obtained was trituated with ethyl acetate whereby a solid was precipitated, this was collected and recrystallized into yellow crystals of **2** yield *ca* 8%.

The ethyl acetate filtrate from the last step was evaporated and the oil obtained was trituated with methanol to give a solid which was collected and recrystallized into **6**, yield *ca* 5%.

The methanolic filtrate was evaporated and the remaining oil was dissolved in ethyl acetate and kept overnight at room temperature whereby

a solid was precipitated, which was collected and recrystallized into yellowish crystals of **5**, yield *ca* 8%.

Action of Heat on **4**.

Compound **4** (0.2 g) was heated at 160° for ½ hour, cooled and recrystallized from ethanol into crystals of **3** (mixed mp showed no depression).

Action of Hydrochloric Acid on Ethanolic Solution of **5**.

Compound **5** (0.4 g) was dissolved in ethanol (40 ml) and concentrated hydrochloric acid (3 ml) was added. The reaction mixture was heated under reflux for 3 hours and concentrated to 10 ml and left to cool in the refrigerator overnight whereby crystals of **6** separated out.

REFERENCES AND NOTES

- [1] A. Mustafa, A. K. Mansour and H. A. Zaher, *Ann. Chem.*, **733**, 177 (1970).
- [2] A. Mustafa, A. K. Mansour and H. A. Zaher, *J. Prakt. Chem.*, **313**, 699 (1971).
- [3] A. K. Mansour and Y. A. Ibrahim, *ibid.*, **314**, 896 (1972).
- [4] A. K. Mansour and Y. A. Ibrahim, *Indian J. Chem.*, **12**, 301 (1974).
- [5] H. A. Zaher, Y. A. Ibrahim, O. Sherif and R. Mohammady, *J. Fac. Educ. Ain Shams Univ.*, **5**, 333 (1982).
- [6] J. Slouka and K. Nalepa, *Acta Univ. Palacki. Olomuc. Fac. Rerum. Nat.*, **30**, 373 (1979).
- [7] P. W. Sadler, *J. Chem. Soc.*, 957 (1961).