CCA-184 541.61:547.873.07:547.573

Syntheses and Structure of Some 5-Substituted 2,3-Dihydro-1,2,4-triazine-3-thiones

M. Tišler

Department of Chemistry, Faculty of Science, University of Ljubljana, Ljubljana, Yugoslavia

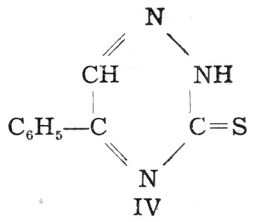
Received April 18, 1960

The synthesis of some 5-substituted and 2,5-disubstituted 2,3-dihydro-1,2,4-triazine-3-thiones from arylglyoxals and the corresponding thiosemicarbazides is described. Prepared were also different *S*-substituted 5-aryl-3-mercapto-1,2,4-triazines and some reactions of these compounds are described. Comparison of the ultraviolet and infrared spectra of some of these compounds revealed that the first mentioned class of compounds exists in the thione form.

Interest for different derivatives of 1,2,4-triazine was exhibited recently in the works of Metze[1,2,3,4,5,6,7,8] and others[9,10,11,12]. It is known that particularly 3-, 5- or 6-substituted derivatives exhibit an intensive effect on central nervous system[13] and some were tested for their anti-TBC activity[14]. 5-Substituted 2,3-dihydro-1,2,4-triazine-3-thiones are in literature usually formulated as derivatives of 3-mercapto-1,2,4-triazine and they were not fully investigated. Most of them are 5,6-disubstituted compounds, prepared from thiosemicarbazide and 1,2-diketones[15,16,17] or diethyl oxomalonate[18]. Of the few 5-substituted compounds known[18,19,20] the 5-phenyl one (IV) was one of the first, prepared by the following reaction sequence:

$$C_6H_5—CO—Cl + CH_2N_2 \longrightarrow \underset{\text{I}}{C_6H_5CO—CHN_2} \longrightarrow \underset{\text{II}}{C_6H_5COCH_2N=N—CN}$$

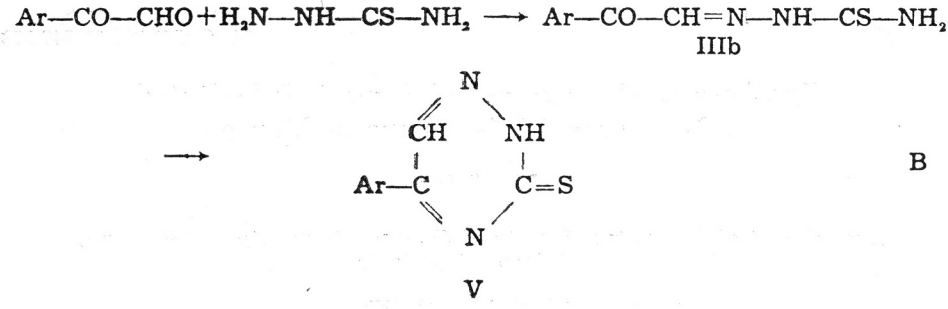
$$\longrightarrow \underset{\text{IIIa}}{C_6H_5CO—CH_2—N=N—CS—NH_2} \longrightarrow$$



A

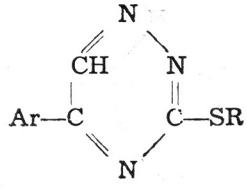
In continuation of our work on substituted 1,2,4-triazines[21], we were interested in the synthesis of 5-substituted 2,3-dihydro-1,2,4-triazine-3-thiones and in the possible tautomerism associated with such compounds. Besides the already mentioned synthesis a much simpler route leading to these compounds

is the reaction of different arylglyoxals with thiosemicarbazide. The intermediate monothiosemicarbazones can be readily cyclized to the corresponding triazines:

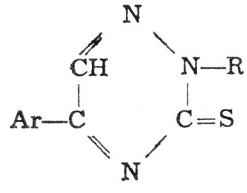


The compounds IIIa and IIIb from the reaction sequences A and B are tautomers. The decision which of them is actually present could not be reached by means of chemical examination of this compound. However, the structure can be deduced from the preceding compound, *e. g.* II, which is on the basis of its IR spectrum, where a typical NH-absorption band is revealed, correctly represented as $C_6H_5CO—CH=N—NH—CN$. Thus the structure IIIb seems to be more adequate than the corresponding IIIa.

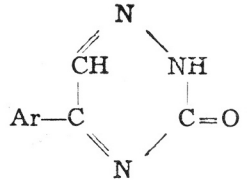
5-Substituted 2,3-dihydro-1,2,4-triazine-3-thiones form readily disulphides in neutral ethanolic solution with aqueous iodine and these are readily reduced back to the parent compounds with a solution of potassium metabisulphite or with sodium sulphide. They react with an ethereal solution of diazomethane giving rise to the corresponding *S*-methyl ethers (VI, R = CH_3—). The iodine--azide reaction[22], typical for compounds with the C=S or C—SH groups was positive when the compounds contained a free sulphur group, whereas the *S*-substituted compounds did not react. The sulphur atom is firmly bound and the 5-phenyl (IV) or 5-phenyl-*S*-methyl compound (VI, Ar = C_6H_5-, R = CH_3-) could not be desulphurized with Raney-nickel or with boiling 20% aqueous monochloroacetic acid, the reaction which does easily proceed with the 4-substituted compounds[21]. Here, instead of the desulphurization process, *S*-carboxymethyl compounds were formed (VI, R = —CH_2COOH).



VI



VII



VIII

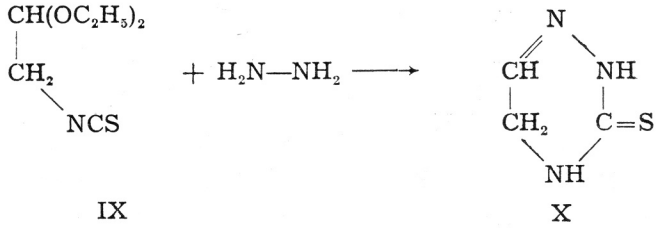
The 5,6-disubstituted derivatives were demonstrated to split with 25% nitric acid in the diketones from which they were prepared[23], but with 33% hydrogen peroxide in 10% sodium hydroxide solution they were desulphurized by prolonged heating[23,24]. We have found that compound IV was rapidly de-

sulphurized with hydrogen peroxide in *conc.* ammonia solution and the obtained compound (VIII, Ar = C_6H_5-) was identical with the synthetic one, prepared from phenylglyoxal monosemicarbazone[25]. No splitting of the molecule was observed. The oxo-compound can be transformed back into the thione by refluxing it with a suspension of phosphorous pentasulphide in toluene.

The *N*-methyl- (VII, Ar = C_6H_5-, R = CH_3-) and *N*-phenyl-compound (VII, Ar = R = C_6H_5-) were prepared from the correspoding 2-substituted thiosemicarbazides. The last mentioned compound was obtained directly without the isolation of the intermediate thiosemicarbazone only when phenylglyoxal was used in large excess. Using molal amounts of components a bis-thiosemicarbazone was isolated as the only product.

The attempt to prepare a 5,6-dimethyl compound proved to be unsuccessful, the experience which was encountered already in the case of the oxo--analogue[26].

The parent compound, 1,2,4-triazine, remains still unknown[20] and it was hoped to prepare it from 2,3,4,5-tetrahydro-1,2,4-triazine-3-thione (X) by simultaneous dehydrogenation and desulphurization. The last mentioned compound was prepared from acetalylisothiocyanate (IX)[27] which was condensed with hydrazine hydrate and after acidification the expected product (X) was obtained.



IX X

All further efforts to prepare the parent 1,2,4-triazine or to obtain the known 3-mercapto-1,2,4-triazine[17] were not successful.

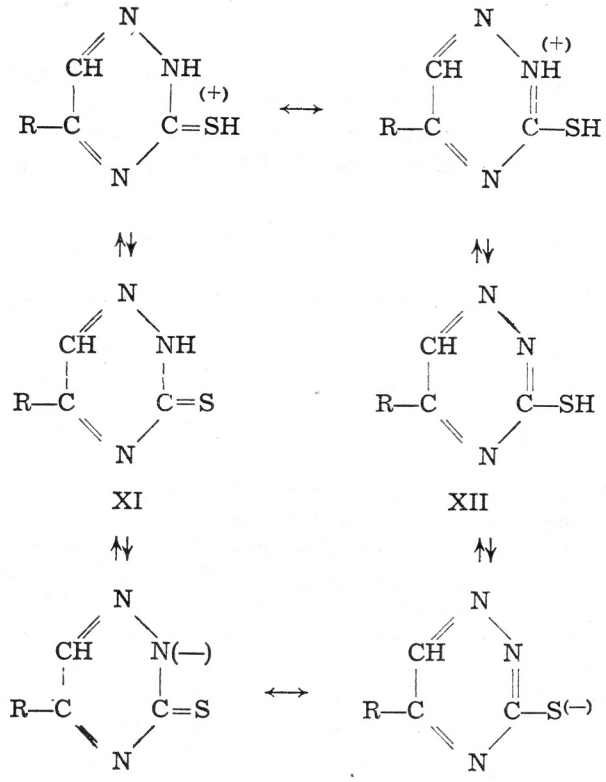
The reactivity of 5-substituted 2,3-dihydro-1,2,4-triazine-3-thiones towards oxidation when disulphides are formed or the reaction with diazomethane account for the presence of a thiol form. One can assume that both forms (XI) and (XII) are interconvertible through an intermediate cation or anion.

It is therefore evident that only on the basis of chemical evidence no decision for any structure can be reached. The thiol form was attributed so far on the basis of acidity of these compounds and their behaviour in chemical reactions, mainly oxidation. The weak acidity of these compounds is consistent with both forms and the oxidation can be explained through the above mentioned transitional forms.

In order to establish unequivocally the presence or absence of the thiol form, the ultraviolet and infrared spectra were recorded and correlated.

The thiol-thione tautomerism is of particular interest because there are many natural or synthetic heterocyclic compounds which are of biological interest (ergothioneine, thiourea derivatives, thiouracils, *etc.*) and where such groups are involved in the oxidation processes. Recently, also a quantitative approach to this problem was made in the case of simple mercapto-pyridines and related compounds[28,29].

We have obtained much of the information about the possible formulation from the ultraviolet absorption spectra. So far we know, there are no recorded UV absorption spectra of the 5-substituted 2,3-dihydro-1,2,4-triazine-3-thiones, except those of some 5,6-disubstituted compounds[18,30]. Spectroscopic investigation of the thiol-thione tautomerism was extensively studied in the case of different 2-mercaptobenzothiazoles[31,32,33]. The presence of the thione form in an alcoholic solution became evident by comparison of the spectra of the *N*-methyl derivative, which differed but little from the unmethylated compound, and that of the *S*-methyl derivative where the absorption at a lower wavelenght and a great reduction of intensity were observed. In alkaline solution, however, the thiol form was favoured since the spectra of the *S*-methyl and *S*-sodium derivatives were very similar.



We found an analogous situation in the case of our compounds. The ultraviolet absorption spectra have revealed the presence of the thione form and not the thiol form, contrary the customary formulation of the whole class of compounds. First of all, replacement of hydrogen at the ring-nitrogen (position 2) of the heterocycle for methyl group does not change much the position of the main absorption maximum. The 5-phenyl compound (IV) has the main maximum at 300 mμ (ε = 33.290), whereas its *N*-methyl derivative (VII, Ar = = C_6H_5-, R = CH_3-) absorbs at 297,5 mμ (ε = 36.590). Substitution of the hydro-

gen in the postulated thiol form of the same compound for the methyl group (*e. g.* the *S*-methyl derivative, VI, Ar = C_6H_5-, R = CH_3-) results in a hypsochromic shift in absorption, formation of an additional absorption maximum at 262 mμ and lowering of the absorption intensities. A hypsochromic shift is also observed when the spectrum of IV was recorded in 0.1 *N* sodium hydroxide solution (λ_{max} 285-6 mμ, ε = 27.580) indicating conclusively the presence of the thione form (Fig. 1.). This finding is supported also on the basis of IR data, where in the case of the 5-phenyl compound (IV) typical NH-absorption can be found and this is only possible when the thione form is present (XI, R = C_6H_5-).

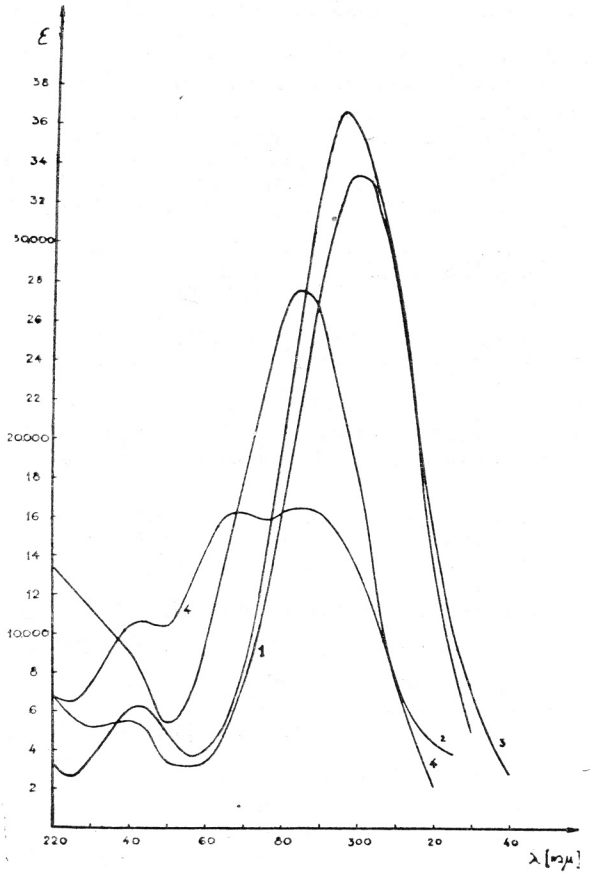


Fig. 1. Ultraviolet absorption spectra of: 1 — 5-Phenyl-2,3-dihydro-1,2,4-triazine-3-thione (in ethanol), 2 — the same compound in 0.1 *N* sodium hydroxide, 3 — 2-Methyl-5-phenyl-2,3-dihydro--1,2,4-triazine-3-thione (in ethanol), 4 — 3-methylthio-5-phenyl-1,2,4-triazine (in ethanol)

The UV spectra of the *S*-carboxymethyl compound (VI, Ar = C_6H_5-, R = = —CH_2COOH) and its methyl ester (VI, Ar = C_6H_5-, R = —CH_2COOCH_3) resemble very close that of the *S*-methyl compound, indicating that the reaction with monochloroacetic acid proceeds with an attack on the sulphur atom.

On the basis of all these spectroscopic data we can conclude that the thiol form is imperceptible with 5-substituted 2,3-dihydro-1,2,4-triazine-3-thiones, either with solid compounds or when dissolved in neutral solvents.

The examination of the IR spectrum of the desulphurized compound (VIII, R = C_6H_5-) revealed the presence of a carbonyl group (absorption band at 1650 cm^{-1}) and the absence of OH-absorption bands. Thus, instead as a hydroxy-derivative[25], the substance should be more correctly represented as 5-phenyl--2,3-dihydro-1,2,4-triazine-3-one.

EXPERIMENTAL

All melting-points were determined with Kofler's heating microscope. If not otherwise stated the yields were good, allways over 70%.

I) *Condensation of arylglyoxals with thiosemicarbazides*

Phenylglyoxal-monothiosemicarbazone (IIIb, Ar = C_6H_5-)

Into a solution of 1.52 g. phenylglyoxal hydrate in 25 ml. of hot water a solution of 0.91 g. thiosemicarbazide in 50 ml. of hot water, acidified with few drops of glacial acetic acid, was added. Soon a yellow precipitate was formed, which was after cooling collected with filtration and recrystallized from ethanol and water (1:1). The product melted at 170—71°C (lit.[19] gives m. p. 170°). Yield: 1.80 g., (88%).

Anal. 3.892 mg. subst.: 0.692 ml. N_2 (19°, 743 mm.)
$C_9H_9ON_3S$ (207.25) calc'd.: N 20.28%
found: N 20.32%

The product was found identical with compound prepared by the procedure of Wolff and Lindenhayn[19] from ω-cyano-azoacetophenone and hydrogen sulphide.

p-*Chlorophenylglyoxal-monothiosemicarbazone* (IIIb, Ar = p-Cl-C_6H_4-)

was prepared as above and recrystallized from ethanol and water (1:1). The compound had no sharp m. p. and melted in an interval from 170° to 195° with decomposition. Yield: 56%.

Anal: 3.425 mg. subst.: 0.516 ml. N_2 (17°, 739 mm.)
$C_9H_8ON_3SCl$ (241.70) calc'd.: N 17.39%
found: N 17.24%

p-*Bromophenylglyoxal-monothiosemicarbazone* (IIIb, Ar = p-Br-C_6H_4-)

M. p. 189—190° (from ethanol). Prepared as above with 72% yield.

Anal. 3.729 mg. subst.: 0.490 ml. N_2 (24°, 736 mm.)
$C_9H_8ON_3SBr$ (286.16) calc'd.: N 14.69%
found : N 14.62%

Phenylglyoxal-mono-2-methylthiosemicarbazone

A solution of 1.52 g. of phenylglyoxal hydrate in 10 ml. of boiling water was added to 1.05 g. of 2-methylthiosemicarbazide[34], dissolved in 10 ml. of hot water and acidified with two drops of glacial acetic acid. A red oil soon separated and after cooling the product solidified. After recrystallization from ethanol the pale yellow needles melted at 162—163°. Yield: 1.65 g., (75%).

Anal. 3.487 mg. subst.: 0.583 ml. N_2 (19°, 742 mm)
$C_{10}H_{11}ONS$ (221.27) calc'd.: N 19.00%
found : N 19.08%

Phenylglyoxal-bis-(2-phenylthiosemicarbazone)

0.1 g. of 2-phenylthiosemicarbazide and 0.09 g. of phenylglyoxal hydrate were refluxed with (10 ml.) of ethanol for 5 min. After cooling the solution was diluted

with the same volume of water, the precipitate collected and recrystallized from ethanol and water (1:1). Yield: 0.115 g. (89%). M. p. 204°.

Anal. 3.579 mg. subst.: 0.618 ml. N_2 (20°, 747 mm)
$C_{22}H_{20}N_6S_2$ (432.56) calc'd.: N 19.44%
found : N 19.77%

II) *Syntheses and reactions of 1,2,4-triazine derivatives*

5-Phenyl-2,3-dihydro-1,2,4-triazine-3-thione (IV)

When phenylglyoxal-monothiosemicarbazone (1 g.) was refluxed for 10 min. with a 10% aqueous solution of potassium carbonate and after cooling the solution acidified with hydrochloric acid (1:1) a red precipitate was obtained which crystallized from ethanol or ethanol and water (1:1) in red needles with m. p. 197—198° (lit.[19] gives m. p. 200°). Light absorption: in ethanol: $\lambda_{max.}$ 240 mμ (ε = 5.520) and $\lambda_{max.}$ 300 mμ (ε = 33.290); in 0.1 *N* sodium hydroxide: $\lambda_{max.}$ 285—6 mμ (ε = 27.580).

Anal. 2.575 mg. subst.: 0.512 ml. N_2 (22°, 735 mm)
$C_9H_7N_3S$ (189.23) calc'd.: N 22.21%
found : N 22.25%

By the same procedure the following three 1,2,4-triazine derivatives were prepared and in all cases the yields were fairly good.

5-(p-Chlorophenyl)-2,3-dihydro-1,2,4-triazine-3-thione (V, Ar = p-Cl-C_6H_4-)

M. p. 208—210° (from ethanol).

Anal. 3.463 mg. subst.: 0.565 ml. N_2 (18°, 740 mm)
$C_9H_6N_3SCl$ (223.68) calc'd.: N 18.78%
found : N 18.63%

5-(p-Bromophenyl)-2,3-dihydro-1,2,4-triazine-3-thione (V, Ar = p-Br-C_6H_4-)

M. p. 202—203° (from ethanol).

Anal. 3.832 mg. subst.: 0.539 ml. N_2 (23°, 736 mm)
$C_9H_6N_3SBr$ (268.14) calc'd.: N 15.67%
found : N 15.70%

2-Methyl-5-phenyl-2,3-dihydro-1,2,4-triazine-3-thione (VII, Ar = C_6H_5-, R = CH_3-)

M. p. 194° (from ethanol). Light absorption (in ethanol): $\lambda_{max.}$ 243 mμ (ε = 6.260) and $\lambda_{max.}$ 297.5 mμ (ε = 36.590).

Anal. 3.325 mg. subst.: 0.618 ml. N_2 (22°, 739 mm)
$C_{10}H_9N_3S$ (203.26) calc'd.: N 20,68%
found : N 20.91%

2,5-Diphenyl-2,3-dihydro-1,2,4-triazine-3-thione (VII, Ar = R = C_6H_5-)

0.2 g. of 2-phenylthiosemicarbazide were added to a boiling solution of 0.3 g. phenylglyoxal hydrate (77% excess) in 10 ml. ethanol, the mixture heated 1—2 min. to boiling and then left aside. The cooled solution was diluted with twice its volume of water and the milky solution was left overnight for crystallization. The crystals were purified by recrystalization from ethanol and melted at 192°. Light absorption (in ethanol): $\lambda_{max.}$ 244 mμ (ε = 7.930) and $\lambda_{max.}$ 305—306 mμ (ε = 29.940).

Anal. 4.367 mg. subst.: 0.608 ml. N_2 (21°, 740 mm)
$C_{15}H_{11}N_3S$ (265.32) calc'd.: N 15.84%
found : N 15.74%

Bis-(5-phenyl-1,2,4-triazine)-3-disulphide

When an ethanolic solution of (IV) was titrated with an aqueous solution of iodine an almost theoretical quantity was consumed and after dilution with water

the collected precipitate was recrystallized from ethanol. M. p. 189° (lit.[19] gives m. p. 183°) undepressed with a specimen, obtained by the nitric acid oxidation procedure[19]. Light absorption (in ethanol): λ_{max}. 243 mμ (ε = 24.510) and λ_{max}. 288 mμ (ε = 24.850).

Anal. 2.371 mg. subst.: 0.473 ml. N_2 (21°, 733 mm)
$C_{18}H_{12}N_6S_2$ (376.45) calc'd.: N 22.33%
found : N 22.34%

The disulphide can be reduced back to the parent compound using one of the following procedure:

a) *With potassium metabisulphite.* 0.1 g. of the disulphide were refluxed with 0.5 g. of potassium metabisulphite in 10 ml. of 0.1 *N* potassium hydroxide for 5 min. and the clear solution was thereafter acidified with hydrochloric acid (1:1) and again heated to boiling to expel sulphur dioxide. The obtained yellow-orange needles, which separated on cooling, were recrystallized from ethanol and melted at 197—198°, undepressed with an authentic specimen of IV.

b) *With sodium sulphide.* 0.1 g. of the disulphide, 0.5 ml. of ethanol and 1.0 g. of sodium sulphide ($Na_2S \cdot 9\,H_2O$) in 5 ml. of water were heated to boiling until a clear solution resulted. After acidification the obtained orange precipitate was crystallized from ethanol and melted at 197—198°, undepressed with an authentic specimen of IV.

3-Methylthio-5-phenyl-1,2,4-triazine (VI, *Ar* = C_6H_5-, R = CH_3-)

The 5-phenyl-compound (IV) reacted rapidly with an ethereal solution of diazomethane giving rise to the *S*-methyl compound. After purification from ethanol and water (2:1) it formed orange-yellow needles with m. p. 94°. Light absorption (in ethanol): λ_{max}. 244 mμ (ε = 10.640), 269 mμ (ε = 16.260) and 286 mμ (ε = 16.450).

Anal. 3.426 mg. subst.: 0.640 ml. N_2 (24°, 735 mm)
$C_{10}H_9N_3S$ (203.26) calc'd.: N 20.68%
found : N 20.76%

3-Methylthio-5-(p-chlorophenyl)-1,2,4-triazine (VI, Ar = *p*-Cl-C_6H_4-, R = CH_3-)

Prepared as above. After recrystallization from ethanol it formed yellow microcrystals with m. p. 163°.

Anal. 3.790 mg. subst.: 0.605 ml. N_2 (24°, 734 mm)
$C_{10}H_8N_3SCl$ (237,71) calc'd.: N 17.68%
found : N 17.69%

3-Carboxymethylthio-5-phenyl-1,2,4-triazine (VI, Ar = C_6H_5-, R = CH_2-COOH)

0.5 g. of (IV) were refluxed with 10 ml. of 20% aqueous monochloroacetic acid for one hour. After cooling colourless crystals separated and they were recrystallized from ethanol. M. p. 193°. Yield: 0.6 g. (92%). Light absorption: in ethanol: λ_{max}. 266 mμ (ε = 14.690) and 283 mμ (ε = 14.150); in 0.1 *N* sodium hydroxyde: λ_{max}. 268 mμ (ε = 14.950).

Anal. 3.898 mg. subst.: 0.603 ml. N_2 (21°, 728 mm)
$C_{11}H_9O_2N_3S$ (247.27) calc'd.: N 17.00%
found : N 17.20%

The acid, after treatment with an ethereal solution of diazomethane, afforded the methyl ester (VI, Ar = C_6H_5-, R = — CH_2COOCH_3). This ester was purified from ethanol and water (3:1) and the yellow plates melted at 91°. Light absorption (in ethanol): λ_{max}. 244 mμ (ε = 12.860), 262 mμ (ε = 13.690) and 283 mμ (ε = 13.380).

Anal. 4.215 mg. subst.: 0.597 ml. N_2 (21°, 738 mm.)
$C_{12}H_{11}O_2N_3S$ (261.29) calc'd.: N 16.09%
found : N 16.97%

5-Phenyl-2,3-dihydro-1,2,4-triazine-3-one (VIII, Ar = C_6H_5-)

0.2 g. of compound (IV) were dissolved in 2 ml. of *conc.* ammonia solution, 2 ml. of water added and then 0.5 ml. of 55% hydrogen peroxide were added dropwise. After gentle heating a yellow precipitate was formed which turned green after acidification with hydrochloric acid. The obtained precipitate was filtered, washed with water and for purification dissolved in 0.1 *N* sodium hydroxide, filtered and slowly precipitated with acid. The compound was recrystallized from water and had m. p. 234°, undepressed with an authentic sample of 5-phenyl-2,3-dihydro-1,2,4-triazine-3-one[25]. This oxo-compound can be transformed back to the thiono-compound using the following procedure: 0.5 g. of the oxo-compound were suspended in 15 ml. of boiling toluene and 0.15 g., of commercial phosphorous pentasulphide added. The mixture was refluxed one hour, filtered hot and after cooling an orange precipitate was obtained which was purified from ethanol and melted at 198°, m. p. undepressed with an authentic specimen of IV.
The attempted desulphurization of IV with Raney-nickel in boiling absolute ethanol proved to be unsuccessful as after many hours of refluxing the unchanged compound was recovered. The same happened also with 3-methylthio-5-phenyl-1,2,4--triazine.

2,3,4,5-tetrahydro-1,2,4-triazine-3-thione (X)

5.5 g. of acetalylisothiocyanate (IX)[27], dissolved in 5 ml. of ethanol were added to a solution of 1.5 g., of 100% hydrazine hydrate in 5 ml. ethanol. The solution was refluxed for 5 min., left to cool to room temperature and then 5 ml. of diluted sulphuric acid (1:2) were added. The acid solution was again heated to boiling so that the formed precipitate completely dissolved. After refluxing for 15 min. and cooling, colourless needles separated from the solution and they were recrystallized from water. M. p. 200—202°, with decomposition. Yield: 1.6 g. (44%).

Anal. 2.526 mg. subst.: 0.823 ml. N_2 (21°, 736 mm)
$C_3H_5N_3C$ (115.15) calc'd.: N 36.51%
found : N 36.63%

Acknowledgment. Thanks are due to Prof. D. Hadži for measurements and help in the interpretation of the infrared spectra.

REFERENCES

1. R. Metze, *Ber.* **87** (1954) 1540.
2. R. Metze, *Ber.* **88** (1955) 772.
3. R. Metze, *Ber.* **89** (1956) 2056.
4. R. Metze and P. Schreiber, *Ber.* **89** (1956) 2466.
5. R. Metze, and S. Meyer, *Ber.* **90** (1957) 481.
6. R. Metze and W. Kort, *Ber.* **91** (1958) 417.
7. R. Metze and G. Rolle, *Ber.* **91** (1958) 422.
8. R. Metze, *Ber.* **91** (1958) 1863.
9. R. Fusco and S. Rossi, *Rend. ist. lombardo sci. Pt. I. Classe sci. mat. e nat.*, **88** (1955) 173
10. S. Rossi, *Atti accad. nazl. Lincei, Rend. Classe sci. fis., mat. e nat.*, **14** (1953) 113.
11. F. Kröhnke and H. Leister, *Ber.* **91** (1958) 1479.
12. R. Rätz and H. Schroeder, *J. Org. Chem.* **23** (1958) 1931.
13. P. Mantegazza, R. Tommasini, R. Fusco, and S. Rossi, *Arch. intern. pharmacodynam.* **95** (1953) 123.
14. R. Fusco, P. Mantegazza, S. Rossi, and R. Tommasini, *Boll. soc. ital. biol. sper.* **27** (1951) 1730.
15. M. Gianturco, *Gazz. chim. ital.* **82** (1952) 595.
16. S. Rossi, *Gazz. chim. ital.* **83** (1953) 133.
17. *Belg. pat.* 503.980 (1951); *cf. C. A.* **50** (1956) 404.
18. M. Gianturco and A. Romeo, *Gazz. chim. ital.* **82** (1952) 429.
19. L. Wolff and H. Lindenhayn, *Ber.* **36** (1903) 4126.
20. J. G. Erickson, P. F. Wiley, and V. P. Wystrach, *The 1,2,3- and 1,2,4--triazines, tetrazines and pentazines*, New York 1956.

21. M. Tišler and Ž. Vrbaški, *J. Org. Chem.* **25** (1960) 770.
22. F. Feigl, *Spot Tests*, Vol. II., Organic Applications, Amsterdam 1954, p. **164.**
23. J. Klosa, *Arch. Pharm.* **288/60** (1955) 465.
24. M. Polonowski and M. Pesson, *Compt. rend.* **232** (1950) 1260.
25. L. Wolff, *Ann.* **325** (1902) 129.
26. O. Diels, *Ber.* **35** (1902) 347.
27. A. P. T. Easson and F. L. Pyman, *J. Chem. Soc.* **1932,** 1806.
28. A. Albert and G. B. Barlin, *J. Chem. Soc.* **1959,** 2384.
29. A. Albert, *Current Trends in Heterocyclic Chemistry,* London 1958, p. **51.**
30. M. Gianturco, *Gazz. chim. ital.* **82** (1952) 595.
31. R. A. Morton and A. L. Stubbs, *J. Chem. Soc.* **1939,** 1321.
32. C. Hasan and R. F. Hunter, *J. Chem. Soc.* **1936,** 1672.
33. H. P. Koch, *J. Chem. Soc.* **1949,** 401.
34 A. H. Greer and G. B. L. Smith, *J. Am. Chem Soc.* **72** (1950) 874.

IZVLEČEK

Sinteze in struktura nekaterih 5-substituiranih 2,3-dihidro-1,2,4-triazin-3-tionov

M. Tišler

Sintetizirani so bili nekateri 5-substituirani in 2,5-disubstituirani 2,3-dihidro--1,2,4-triazin-3-tioni iz arilglioksalov in odgovarjajočih tiosemikarbazidov ter različni *S*-substituirani 5-aril-3-merkapto-1,2,4-triazini ter opisane razne reakcije teh spojin. Na podlagi primerjave ultravijoličnih in infrardečih spektrov posameznih spojin je bilo ugotovljeno, da obstajajo prvo imenovane spojine predvsem v tionski obliki.

KEMIJSKI ODDELEK
NARAVOSLOVNE FAKULTETE
UNIVERZE V LJUBLJANI

Sprejeto 18. travnja 1960.