Arylazoisoxazolinthiones:
Preparation and Reactions of 4-Arylazo-3-methyl-2-isoxazolin-5-thiones

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Alkylation, Grignard’s Reaction, Arylazoisoxazolinimines, Arylazoisoxazolinhydrzones, Ring Cleavage

The aryazo derivatives (2) of 3-methyl-2-isoxazolin-5-thione were prepared. Alkylation of 2 with alkyl halides results in the formation of the S-alkyl derivatives (5). The S-acetate esters undergo thermal isomerisation to the corresponding 1,3,5-triazole derivatives (6).

The thiones 2 condense with hydrazines and primary amines to afford the corresponding 5-hydrzones and 5-imines (8) and (10), respectively. Treatment of 2 with hydrazine hydrate and phenylhydrazine in boiling alcohol effects cleavage with the formation of 9.

Four potentially tautomeric structures (1–4) (X = O) are possible for 4-arylazo-3-methyl-2-isoxazolin-5-ones, which have been extensively studied owing to their biological evaluation.

Recently, the arylyhydrazono structure (1) was favoured on the basis of spectral data. But, little attention has been paid for the arylyazoisoxazolin-thione analogues.

The present investigation deals with the synthesis and chemical behaviour of 4-arylazo-3-methyl-2-isoxazolin-5-thiones (1–4, X = S) towards a variety of nucleophilic and alkyllating reagents to gain an insight into the structure of azo compounds.

The 4-arylazo-3-methyl-2-isoxazolin-5-thiones were prepared by refluxing 4-arylaylhydrazono-3-methyl-5-isoxazolinone (1a–e)5,4 and phosphorus pentasulphide in toluene. The infrared spectra of the thione derivatives reveal the absence of characteristic N–H or S–H absorption, thus excluding structures 1, 3 and 4 and favouring the azo structure (2) (X = S) by exhibiting absorption characteristic for azo7 and thiocarbonyl groups. This assignment is in contrast with the favoured hydrazone structure4 for the original oxygen analogue (1) (X = O). The UV spectra of compounds 2 (X = S) show a noticeable red shift compared with the spectra of the arylhydrazinoisoxazolones (1).

Subjecting the 4-arylazo-3-methyl-2-isoxazolin-5-thiones (2a–e) to the action of different alkylating agents such as, chloroacetamide, phenacyl bromide and ethyl bromoacetate afforded the corresponding coloured S-alkylated aryazo derivatives (5a–i). The IR spectra of the S-alkylated derivatives exhibit an absorption around 1600 cm⁻¹ characteristic forazo group. Subjecting compound 5a to mild treatment with ethanolic hydrochloric acid effected alkylmercaptop elimination to afford the original 4-phenylhydrazono-3-methyl-2-isoxazolin-5-one (1a).

Refuxing the deeply coloured 4-arylazoisoxazol-5-thioacetate esters (5g–i) in benzene yielded the products 6a–e. The 1,2,3-triazole structure assigned for compound 6 is inferred from the fact that they are colourless and their IR spectra exhibit two carbonyl absorption bands at \(\nu_C=O\) 1725 (–COOEt).

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and at $\nu_\text{C=O} 1690$ (–CO–S–) and the UV spectrum for 6a exhibits absorption at $\lambda_{\text{max}}$ 280 nm. These findings are in accord with structure 6, which would be expected to arise by a transformation analogous to the known thermal isomerisation of 4-phenylazo-3-methyl-5-phenylisoxazole to 5-benzoyl-4-methyl-2-phenyl-1,2,3-triazole.

Treatment of the thiones 2a–e with phenylmagnesium bromide effected 1,2-addition on the thiocarbonyl group followed by hydrogen sulphide elimination to yield the corresponding coloured 4-arylazo-3-methyl-5-phenylisoxazoles (7a–e). The structure of 7 was established by spectral and analytical data, basides 7a is identical with an authentic sample.

The behaviour of the isoxazolinone ring towards the action of hydrazines has been intensively investigated, to afford either cyclic or acyclic products depending on the nucleophile or on the temperature conditions. Thus, phenylhydrazine reacts with 4-arylhydrazono-3-methyl-2-isoxazolin-5-ones (1) at room temperature to yield the arylhydrazones of acetoacetic hydrazides. On the other hand, hydrazine hydrate or phenylhydrazine reacts with 1 in boiling alcohol to give the 4-arylhydrazones of 3-methyl-2-pyrazolin-5-ones. Now, treatment of the thiones 2a–e with molar ratio of phenylhydrazine or hydrazine hydrate at room temperature affords the deeply coloured 4-arylazo-3-methyl-2-isoxazolin-5-hydrazones (8a–f) or its tautomer. The structure assigned for 8 was established based on analytical and IR spectra revealing C=N and N–H absorptions. Boiling 8a–e in alcohol effected ring cleavage yielding 9a–e.

Compounds 9a–e are obtained directly from 2a–e by the action of phenylhydrazine in boiling ethanol. The IR spectra of 9a–e show absorption at $\nu_{\text{N–H}}$ 3320 cm$^{-1}$, $\nu_\text{C–O}$ 1660 cm$^{-1}$ (amide I) and $\nu_{\text{N–N}}$ 1600 cm$^{-1}$. Further evidence for 9a–e is their cyclisation to the corresponding 4-arylazo-3-methyl-1-phenyl-2-pyrazolin-5-ones by the action of acetic acid.

Refluxing 2a–e with alcoholic solution of aniline or benzylamine causes hydrogen sulphide evolution and the formation of the 4-arylhydrazono-3-methyl-2-isoxazolin-5-imines (10a–f). The structure of 10 was assigned on the basis of spectral and analytical date baside refluxing 10a with ethanolic hydrochloric acid afforded the corresponding 4-phenylhydrazono-3-methyl-5-isoxazolone (1a).

The simplicity, good yield, and straight forward products isolation of the investigated reactions provide a method for preparation of compounds 8–10.

**Experimental**

Melting points are uncorrected. IR spectra were obtained as a KBr disc with a Pye-Unicam SP 1100 spectrophotometer. Ultraviolet and visible measurements were made with a Pye-Unicam SP 8000 spectrophotometer.

4-Arylazo-3-methyl-2-isoxazolin-5-thiones (2a–e)

2a–e were prepared by refluxing each of 1a–e (10 g) and phosphorus pentasulphide (11 g) in 100 ml of benzene for 1 h. The mixture was filtered and cooled to give 2a–e, in a yield that varies (50–70%). 2a–e were all crystallized as deep red crystals from ethanol (Table I). The IR spectrum of 2a as a typical example for 2a–e show absorption at $\nu_{\text{C=S}}$ 1620 cm$^{-1}$, $\nu_{\text{N–N}}$ 1590 cm$^{-1}$ and $\nu_{\text{C–N}}$ 1325 cm$^{-1}$. UV absorption spectrum in dioxan exhibits absorption at $\lambda_{\text{max}}$ 410 nm ($e$ 11.471).

4-Arylazo-5-alkylthio-3-methylisoxazoles (5a–l)

**General procedure:** Each of 2a–e (1.0 g) was dissolved in 20 ml of ethanolic potassium hydroxide (10%) and the solution was refluxed for 20 min, then to the solution was added chloroacetic acid, phenacylbromide or ethyl bromoacetate in molar quantities. The reaction mixture was refluxed for 20 min and left to cool. The separated crystals were filtered off, washed with water several times and crystallized from ethanol. 5a–l are all yellow coloured and listed in Table I.

IR spectrum of 5a as an example of the S-acetamide derivatives 5a–e show absorption at $\nu_{\text{NH}}$ 3360 and 3190 cm$^{-1}$, $\nu_{\text{C–O}}$ 1670 cm$^{-1}$ (amide I stretching), $\nu_{\text{C–S}}$ 1620 cm$^{-1}$ and at $\nu_{\text{C–N}}$ 1590 cm$^{-1}$.

IR spectrum of 5d as an example of the S-phenacyl derivatives 5d–f show absorption at $\nu_{\text{C–O}}$ 1725 cm$^{-1}$, $\nu_{\text{C–N}}$ 1620 cm$^{-1}$, $\nu_{\text{S–N}}$ 1600 cm$^{-1}$. 
Table I. Analytical data for 2a-c and 5a-i.

<table>
<thead>
<tr>
<th>Compound</th>
<th>m.p.  [°C]</th>
<th>Yield [%]</th>
<th>Formula (mol. wt.)</th>
<th>Analysis</th>
<th>Caled</th>
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</tr>
<tr>
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<td>(290.25)</td>
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<td>17.92 13.72</td>
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<td>(310.7)</td>
<td>63.87 4.29</td>
<td>12.18 9.18</td>
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<td>70</td>
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<td>11.00 8.00</td>
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<td>(371.8)</td>
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<td>10.79 8.52</td>
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<td>11.00 8.00</td>
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<td>(305.3)</td>
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<td>5h</td>
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<td>50</td>
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<td>(339.8)</td>
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</table>

IR spectrum of 5g as an example of the S-acetate esters (5g–i) show absorption at νc=O 1715 cm⁻¹, νC=N 1625 cm⁻¹.

4-Thioxycarbonyl-2-aryl-5-methyl-1,2,3-triazoles (6a–c)

They were obtained as colourless crystals by refluxing compounds 5g–i in benzene for 3 h, then evaporated to dryness, the solid obtained was crystallized from petrol ether. 6a–c are listed in Table II.

The IR spectrum of 6a as a typical example for 6a–c shows absorption at νc=O 1735 cm⁻¹ (ester C=O), νC=O 1680 cm⁻¹ (thiocarbonyl) and νC=N 1630 cm⁻¹. The UV spectrum shows absorption at λmax 305 nm (ε 17,000).

Action of ethanolic hydrochloric acid on 5a

A suspension of 5a (1.0 g) in a mixture of ethyl alcohol (10 ml) and hydrochloric acid (10 ml) was refluxed for 2 h and allowed to cool, then diluted with water and the solid product was crystallized from ethanol, m.p. 190 °C (yield 60%), proved to be identical (m.p. and mixed m.p.) with 4-phenyl-hydrazono-3-methyl-2-isoxazolin-5-one.

Action of phenylmagnesium bromide on 4-arylazo-3-methyl-2-isoxazolin-5-thiones (2a–c)

General procedure: To a Grignard solution (prepared from 1.0 g magnesium and 9.0 g bromo-benzene in 100 ml dry ether), a suspension of each of 2a–e (2.0 g) in dry ether (100 ml) was added. The reaction mixture was refluxed for 2 h, left to cool then decomposed with saturated ammonium chloride solution. The ethereal layer was separated, dried (Na₂SO₄) and allowed to evaporate slowly. The oily residue was triturated with cold acetic acid and the resulting solid was crystallized from acetic acid.

The 4-arylazo-5-phenyl-3-methylisoxazoles (7a–c) (Table II) are yellow to orange in colour. 7a is identical m.p. and mixed m.p. with an authentic sample.

4-Arylazo-3-methyl-2-isoxazolin-5-hydrazones (8a–f)

General procedure: To each of 2a–c (1.0 g), phenylhydrazine (1.0 ml) or hydrazine hydrate (1.0 ml) was added, and the mixture was left at room temperature till the odour of hydrogen-sulphide was no more detected. The reaction mixture was treated with acetone and the solid formed was filtered off and crystallized from acetone.

4-Arylazo-3-methylisoxazolin-5-phenylhydrazones (8a–c) listed in Table II are orange-red crystals. The IR spectrum of 8a as a typical example of the phenylhydrazones (8a–e) show absorption at νC=H 3390 cm⁻¹, νC=N 1620 cm⁻¹ and νN=N 1580 cm⁻¹. The UV spectrum for 8a show absorption at λmax 280 and 440 nm.
### Table II. Analytical data for 6a-c, 7a-c, and 8a-f.

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<tr>
<th>Compound</th>
<th>m.p. [°C]</th>
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<th>Formula (mol. wt.)</th>
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<tr>
<td>6a</td>
<td>52</td>
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<td>C14H15N3O3S (305.3)</td>
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<td>13.77 10.40</td>
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<td>13.59 10.31</td>
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<td>6b</td>
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<td>C14H17N3O3S (319.3)</td>
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<td>13.16 10.02</td>
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<td>56.39 5.31</td>
<td>12.88 9.79</td>
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<tr>
<td>6c</td>
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<td>12.11 9.26</td>
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<td>57.03 5.57</td>
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4-Arylazo-3-methylisoxazolin-5-hydrazones (8d-f) listed in Table II are yellow-orange crystals. The IR spectrum of 8d as a typical example of 8 d-f shows absorption at $>$NH 3430 cm$^{-1}$ and 3300 cm$^{-1}$, and VN=N 1585 cm$^{-1}$. The UV spectrum of 8d exhibits absorption at $\lambda_{max}$ 420 nm.

**Action of phenylhydrazine on 2a-c in boiling ethanol to afford 9a-c**

To a solution of 2 a-c (1.0 g) in ethanol (100 ml) was added 1.0 ml phenylhydrazine, the solution was refluxed for 2 h or till the odour of hydrogen sulphide ceased. The reaction mixture was left to cool, and the solid crystals so obtained were filtered off and crystallized from ethanol.

The oximes of a-arylhydrazono-acetoacetic phenylhydrazide (9a-c) listed in Table III are all yellow coloured crystals. The IR spectrum of 9a show absorption at $\nu_{NH}$ 3320 cm$^{-1}$, $\nu_{C=O}$ 1660 cm$^{-1}$, $\nu_{C=N}$ 1630 cm$^{-1}$, and at $\nu_{N=N}$ 1590 cm$^{-1}$. The UV spectrum show absorption at $\lambda_{max}$ 430 nm.

**Conversion of 8a-c to 9a-c**

A solution of each of 8 a-c (1.0 g) in 20 ml ethanol was refluxed for 2 h, the reaction mixture was left to cool, whereby yellow crystals were separated filtered off and crystallized from ethanol. The product so obtained proved to be identical with 9a-c by m.p. and mixed m.p.

**Cyclisation of 9a to 4-phenylazo-1-phenyl-3-methyl-5-pyrazolone**

A suspension of 9a (1.0 g) in 20 ml acetic acid was refluxed for 3 h, left to cool, the solid crystals were filtered off and then recrystallized from acetic acid, m.p. 156 °C (yield 45%), proved to be identical (m.p. and mixed m.p.) with an authentic sample.

4-Arylazo-3-methyl-2-isoxazolin-5-imines (10a-f)

Each of 2 a-c (1.0 g), aniline (1.0 ml) or benzylamine (1.0 ml) and ethyl alcohol (20 ml) were refluxed on a water bath for 2 h or till the odour of hydrogen sulphide ceased. The reaction mixture was cooled, the separated crystals were filtered off and crystallized from ethyl alcohol.

The 4-arylazo-3-methyl-2-isoxazolin-5-phenyl-imines (10a-c) listed in Table III are yellow coloured crystals.

The 4-arylazo-3-methyl-2-isoxazolin-5-benzyl-imines (10d-f) listed in Table III are pale yellow coloured crystals. The IR spectra of the imines 10a-f exhibit strong absorption around 1640 cm$^{-1}$ and 1590 cm$^{-1}$ for C=N and N=N absorptions. Their UV absorption spectra revealed absorption around $\lambda_{max}$ 420 nm.

**Action of ethanolic hydrochloric acid on 10a**

A suspension of 10a (1.0 g) in a mixture of ethyl-alcohol (10 ml) and hydrochloric acid (10 ml) was refluxed for 2 h and allowed to cool, then diluted...
with water and the solid was filtered off and crystal-
lized from ethanol to give 1a, m.p. 190 °C (yield 55%), proved to be identical with an authentic sample.5

Table III. Analytical data for 9a–c and 10a–f.

<table>
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<th>Compound</th>
<th>m.p.</th>
<th>Yield</th>
<th>Formula (mol. wt.)</th>
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<th>H</th>
<th>N</th>
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<td>213</td>
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<td>C₁₅H₁₇N₅O₂ (311.3)</td>
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