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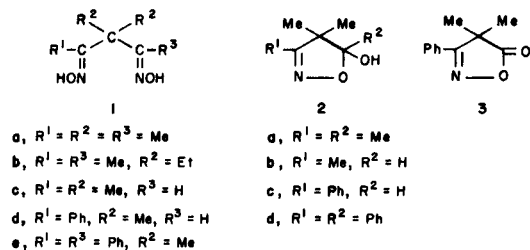
Oxidation of 1,3-dioximes **1** with lead tetraacetate gives di-*N*-oxides of pyrazolines **4** or pyrazoles **5** or *N*-oxides of oxadiazines **7** as the main reaction products. The reaction mechanism is discussed.

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Mono-oximes are known to undergo easily oxidation with a variety of oxidizing agents to a variety of products [1,2] whereas 1,2-dioximes undergo oxidation [1,2,3] to yield furoxan derivatives. As far as 1,3-dioximes are concerned the only oxidations reported are the phenyliodine-(III)bis trifluoroacetate and the sodium hypobromide oxidation of some 1,3-dioximes with an active methylene group leading to the formation of 4-oxo-2*H*-pyrazole-1,2-dioxides and 3,5-disubstituted isoxazoles [4] and the 4,4-dibromo-2*H*-pyrazole-1,2-dioxides [5], respectively.

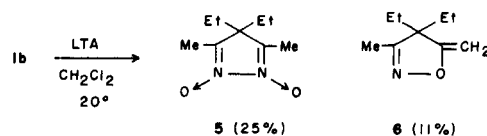
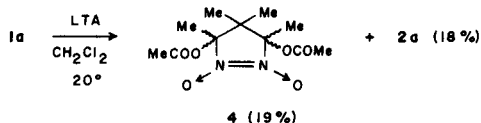
In the course of our interest in lead tetraacetate oxidations and in order to study the changes in the reaction sequence by dialkylating the active methylene group, we prepared and oxidized with lead tetraacetate some 1,3-dioximes **1a-e** dialkylated in the active methylene group.

The dioximes **1c-e** are known compounds and the first two, **1c** and **1d**, were prepared as mixtures with the corresponding 5-hydroxy-2-isoxazolines **2b** and **2c**, respectively. In the case of the dioxime **1d** the 3-phenyl-4,4-dimethyl-5-oxo-2-isoxazoline **3** was also isolated [6].

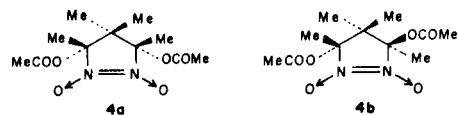


The products obtained by the lead tetraacetate oxidation of the 1,3-dioximes **1** vary and greatly depend on the type of the substituents  $\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$ .

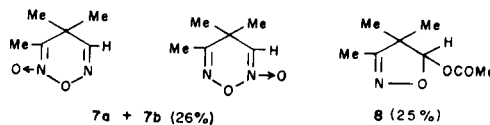
Oxidation of the dioximes **1a** and **1b** with alkyl substituents gives di-*N*-oxides of pyrazolines or pyrazoles and substituted isoxazoles as the main reaction products as shown below:



The di-*N*-oxide **4** was isolated as a mixture of two possible diastereomers, **4a** and **4b**, as indicated by the nmr spectrum (see Experimental). An analogous example is reported in the literature [7] for the 3,4-dibromo- and the 3-chloro-4-bromo-3,5,5-trimethylpyrazoline di-*N*-oxides.

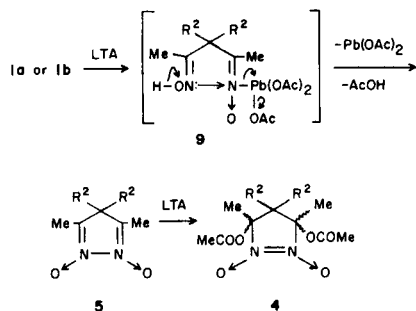


However, oxidation of the dioxime **1c** with  $\text{R}^3 = \text{H}$  gives instead of the expected pyrazole derivative a mixture of two isomeric compounds for which the structure of the two *N*-oxides, **7a** and **7b**, could be proposed on account of the nmr spectrum (see Experimental). The acetoxy pyrazoline **8** was also isolated.



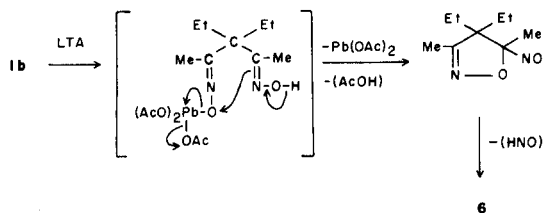
Finally, oxidation of the dioximes **1d** and **1e** with phenyl substituents follows a different pathway. So, from the oxidation of the dioxime **1d** with one phenyl substituent the isoxazoline **3** was isolated in 73% yield whereas the diphenyl substituted dioxime **1e** decomposes to the 5-hydroxypyrazoline **2d** and the 2,2-dimethyl-1,3-diphenyl-1,3-propanedione.

As far as the reaction mechanism is concerned for the formation of the di-*N*-oxides **4** and **5** a formation of a bond between one nitrogen and lead is proposed as the first reaction step. Cleavage of the N-Pb bond and attack of the lone electron pair of the second nitrogen leads to the formation of pyrazole di-*N*-oxides which by further acetoxylation give the pyrazoline di-*N*-oxides.



From the intermediate **9** the oxadiazine **7** can be obtained by cleavage of the N-Pb bond and formation of a new bond between this nitrogen and the oxygen of the second oxime group.

For the formation of the substituted isoxazolines formation of a bond between lead and one of the oxygens is accepted for the first step of the reaction sequence. Cleavage of the O-Pb bond leads to the formation of the intermediate nitroso-compound from which the various products can be obtained. A typical example is shown in the following Scheme for the formation of the oxadiazole **6**.



The di-*N*-oxides **4** and **5**, the *N*-oxide **7** and the isoxazolines **6** and **8** are new compounds and their spectral and experimental data are given in the Experimental.

## EXPERIMENTAL

All melting points are uncorrected and they are obtained with a Kofler hot stage apparatus. The ir spectra were obtained with a Perkin-Elmer Model 297, whereas nmr spectra reported in  $\delta$  units with a Varian Associates CFT-20 spectrometer with TMS as internal reference. The mass spectra were obtained with a Hitachi-Perkin-Elmer Model RMU-6L spectrometer with ionization energy of 70 eV. Analysis were performed with a Perkin-Elmer Model 240 CHN Analyser.

Preparation of 1,3-Dioximes.

The dioximes **1** were prepared according to known procedures [8-11].

### 3,3-Dimethyl-2,4-pentanedione Dioxime (**1a**).

This compound was prepared in 41% yield, mp 185-187° (lit [8] mp 183-186°, lit [9] mp 188°).

### 3,3-Diethyl-2,4-pentanedione Dioxime (**1b**).

This compound was prepared in 51% yield, mp 255-258° (lit [9] mp 259-260° dec).

### $\alpha$ -Acetylisobutyraldehyde Dioxime (**1c**).

The dioxime **1c** was prepared by a modification of the method given in ref [10]. To a solution of 2.07 g of hydroxylamine hydrochloride in 4 ml of water neutralised with 2.08 g potassium carbonate 1.14 g  $\alpha$ -acetylisobutyraldehyde [12] was added and the reaction mixture was heated on a water bath for 3 hours with stirring. The organic material was extracted with chloroform, dried and subjected after evaporation of the solvent to column chromatography on silica gel (petroleum ether-ethyl acetate 3:1) to give in elution order the 3,4,4-trimethyl-5-hydroxy-2-isoxazoline (**2b**), 0.19 g (10%), mp 46-48° (lit [13] mp 51°) and the dioxime of  $\alpha$ -acetylisobutyraldehyde **1c**, 0.87 g (60%), mp 106-108°; ir (nujol): 3300 (NOH), 1630 (C=N)  $\text{cm}^{-1}$ ; <sup>1</sup>H nmr (deuteriochloroform):  $\delta$  1.22 (s, 6H, 2  $\times$  Me), 1.88 (s, 3H, N=CMe), 4.94 (s, 1H, CH), 6.43 (br s, 2H, NOH, deuterium oxide-exchangeable); ms (70 eV, electron impact) m/e (relative intensity) 144 (M<sup>+</sup>, 14), 145 (M<sup>+</sup>+1, 70), 127 (67), 112 (64), 100 (68), 70 (93), 42 (100).

Anal. Calcd. for C<sub>6</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>: C, 49.98; H, 8.39; N, 19.43. Found: C, 50.12; H, 8.24; N, 19.65.

### $\alpha$ -Benzoylisobutyraldehyde Dioxime (**1d**).

The dioxime **1d** was prepared from  $\alpha$ -benzoylisobutyraldehyde [12] by the method described above for the preparation of dioxime **1c**. By column chromatography on silica gel (petroleum ether-ethyl acetate 5:1) the following products were separated in elution order:

### 3-Phenyl-4,4-dimethyl-5-oxo-2-isoxazoline (**3**).

This compound was obtained in 20% yield, mp 73-75° (lit [6] mp 70-71°); ir (nujol): 1790 (C=O)  $\text{cm}^{-1}$ ; <sup>1</sup>H nmr (carbon tetrachloride):  $\delta$  1.52 (s, 6H, 2  $\times$  Me), 7.18-7.82 (m, 5H, Ph); ms: (70 eV, electron impact) m/e (relative intensity) 189 (M<sup>+</sup>, 29), 144 (14), 131 (100), 116 (21), 115 (30), 104 (31), 103 (17), 77 (38).

Anal. Calcd. for C<sub>11</sub>H<sub>11</sub>NO<sub>2</sub>: C, 69.82; H, 5.86; N, 7.40. Found: C, 70.08; H, 5.93; N, 7.30.

### 3-Phenyl-4,4-dimethyl-5-hydroxy-2-isoxazoline (**2c**).

This compound was obtained in 24% yield, mp 92-94° (lit [13] mp 88°).

### $\alpha$ -Benzoylisobutyraldehyde Dioxime (**1d**).

This compound was obtained in 24% yield, mp 130-131°; ir (nujol): 3310 (NOH), 1695 (C=N)  $\text{cm}^{-1}$ ; <sup>1</sup>H nmr (deuteriochloroform):  $\delta$  1.62 (s, 6H, 2  $\times$  Me), 7.20-7.77 (m, 6H, Ph and CH); ms (70 eV, electron impact) m/e (relative intensity) 205 (M<sup>+</sup>-1, 22), 188 (9), 173 (5), 159 (13), 145 (38), 131 (100), 115 (92), 103 (90), 77 (100).

Anal. Calcd. for C<sub>11</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>: C, 64.06; H, 6.84; N, 13.58. Found: C, 64.19; H, 6.98; N, 13.66.

### 2,2-Dimethyl-1,3-diphenyl-1,3-propanedione Dioxime (**1e**).

The dioxime **1e** was prepared by the method given in ref [11] in 67% yield, mp 130-132°; ir (nujol): 3460 and 3240 (NOH)  $\text{cm}^{-1}$ ; <sup>1</sup>H nmr (deuteriochloroform):  $\delta$  0.85 (s, 3H, Me), 1.52 (s, 3H, Me), 5.12 (br s, 2H, NOH, deuterium oxide exchangeable), 7.10-7.68 (m, 10H, 2  $\times$  Ph); ms (70 eV, electron impact) m/e (relative intensity) 282 (M<sup>+</sup>, <0.5), 267 (<0.5), 251 (9), 145 (100), 104 (100), 103 (95), 77 (94).

Anal. Calcd. for C<sub>17</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>: C, 72.32; H, 6.43; N, 9.92. Found: C, 72.18; H, 6.44; N, 9.74.

### Oxidation of 1,3-Dioximes **1** with Lead Tetraacetate.

A general procedure is described. To a solution of 0.01 mole of the 1,3-dioxime **1** in 40 ml methylene chloride a solution of 0.015 mole of lead tetracetate in 40 ml methylene chloride was added and the mixture was stirred at room temperature for 2 hours. The methylene chloride solution was treated with water and filtered. The organic layer was washed with sodium carbonate solution and water and then dried. The oil which was left behind was subjected to column chromatography on silica gel.

### Oxidation of 3,3-Dimethyl-2,4-pentanedione Dioxime (**1a**).

With petroleum ether-ethyl acetate 4:1 as eluent were isolated the

3,4,4,5-tetramethyl-5-hydroxy-2-pyrazoline (**2a**), 18% yield, mp 51-53° (lit [8] mp 52-54°) and the di-*N*-oxide of 3,5-diacetoxy-3,4,4,5-tetramethyl-1-pyrazoline (**4**), 19% yield, mp 123-125°; ir (nujol): 1745 (C=O) cm<sup>-1</sup>; <sup>1</sup>H nmr (deuteriochloroform): δ 1.28, 1.35 and 1.42 (three s, 6H, 2 × Me), 2.01 and 2.07 (two s, 6H, 2 × N=CMe), 2.15 (s, 6H, 2 × COOMe). This complicated nmr spectrum suggests the formation of two diastereomers. Peaks at 1.28, 1.42 and 2.01 (intensities nearly twice as great as the accompanying diastereomer) are due to one diastereomer and peaks at 1.35 and 2.07 may be interpreted to the other; ms: (70 eV, electron impact) m/e (relative intensity), 274 (M<sup>+</sup>, 2), 224 (19), 171 (31), 142 (30), 129 (100), 126 (52).

*Anal.* Calcd. for C<sub>11</sub>H<sub>18</sub>N<sub>2</sub>O<sub>6</sub>: C, 48.17; H, 6.62; N, 10.21. Found: C, 48.28; H, 6.83; N, 10.14.

#### Oxidation of 3,3-Diethyl-2,4-pentanedione Dioxime (**1b**).

With petroleum ether-ethyl acetate 10:1 as eluent the following two products were isolated:

#### 3-Methyl-4,4-diethyl-5-methyleneisoxazole (**6**).

This compound was obtained in 11% yield, liquid; ir (neat): 1680 (C=N) cm<sup>-1</sup>; <sup>1</sup>H nmr (deuteriochloroform): δ 0.75 (t, J = 7 Hz, 6H, 2 × Me), 1.50 (q, J = 7 Hz, 4H, 2 × CH<sub>2</sub>), 1.83 (s, 3H, N=CMe), 3.75 and 4.48 (two d, J = 2.5 Hz, 2H, C=CH<sub>2</sub>); ms: (70 eV, electron impact) m/e (relative intensity) 153 (M<sup>+</sup>, 59), 125 (97), 124 (64), 110 (95), 96 (100), 82 (79).

*Anal.* Calcd. for C<sub>9</sub>H<sub>15</sub>NO: C, 70.55; H, 9.37; N, 9.14. Found: C, 70.36; H, 9.69; N, 9.41.

#### Di-*N*-oxide of 3,5-Dimethyl-4,4-diethyl-4*H*-pyrazole (**5**).

This compound was obtained in 25% yield, mp 167-169°; ir (nujol): 1625 (C=N) cm<sup>-1</sup>; <sup>1</sup>H nmr (deuteriochloroform): δ 0.63 (t, J = 7 Hz, 6H, 2 × Me), 1.79 (q, J = 7 Hz, 4H, 2 × CH<sub>2</sub>), 2.10 (s, 6H, 2 × N=CMe); ms: (70 eV, electron impact) m/e (relative intensity) 184 (M<sup>+</sup>, 100), 154 (49), 127 (23), 112 (48), 97 (52).

*Anal.* Calcd. for C<sub>9</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>: C, 58.67; H, 8.75; N, 15.21. Found: C, 58.84; H, 8.88; N, 15.32.

#### Oxidation of α-Acetylisobutyraldehyde Dioxime (**1c**).

With petroleum ether-ethyl acetate 4:1 as eluent the following two products were isolated:

#### 3,4,4-Trimethyl-5-acetoxyisoxazole (**8**).

This compound was obtained in 25% yield, mp 56-58°; ir (nujol): 1740 (C=O) cm<sup>-1</sup>; <sup>1</sup>H nmr (carbon tetrachloride): δ 1.13 (s, 3H, Me), 1.19 (s, 3H, Me), 1.86 (s, 3H, N=CMe), 2.01 (s, 3H, COOMe), 6.07 (s, 1H, CH); ms: (70 eV, electron impact) m/e (relative intensity) 171 (M<sup>+</sup>, 4), 112 (61), 83 (89),

82 (46), 70 (100).

*Anal.* Calcd. for C<sub>8</sub>H<sub>13</sub>NO<sub>3</sub>: C, 56.12; H, 7.65; N, 8.18. Found: C, 56.33; H, 7.51; N, 8.01.

#### *N*-Oxide of 3,4,4-Trimethyl-1,2,6-oxadiazine (**7**).

This compound was obtained in 26% yield, mp 153-154°; <sup>1</sup>H nmr (deuteriochloroform): δ 1.23, 1.27, 1.33 (three s, 6H, 2 × Me), 1.91 and 1.93 (two s, 3H, N=CMe), 5.67 and 5.73 (two s, 1H, CH). This complicated nmr spectrum suggests the formation of two isomeric *N*-oxides; ms: (70 eV, electron impact) m/e (relative intensity) 142 (M<sup>+</sup>, <0.5), 126 (1), 112 (37), 99 (3), 85 (7), 84 (38), 82 (14), 70 (100), 69 (18), 55 (24).

*Anal.* Calcd. for C<sub>8</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub>: C, 50.69; H, 7.09; N, 19.71. Found: C, 50.79; H, 7.00; N, 19.58.

#### Oxidation of α-Benzoylisobutyraldehyde Dioxime (**1d**).

From the oxidation of the dioxime **1d** only one product was isolated, the 3-phenyl-4,4-dimethyl-5-oxo-2-isoxazoline (**3**), 73% yield, mp 73-75° (lit [6] mp 70-71°).

#### Oxidation of 2,2-Dimethyl-1,3-diphenyl-1,3-propanedione Dioxime (**1e**).

With petroleum ether-ethyl acetate 10:1 as eluent two compounds were isolated, the 2,2-dimethyl-1,3-diphenyl-1,3-propanedione in 17% yield and the 1,3-diphenyl-4,4-dimethyl-5-hydroxy-2-pyrazoline (**2d**), 53% yield, mp 169-171° (lit [9] mp 167°).

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