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One-Step Conversion of Mesoionic Olate to Thiolate by Lawesson's Reagent

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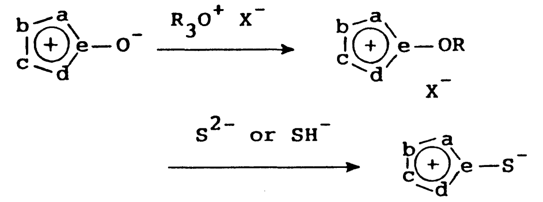
(Received March 29, 1988)

Synopsis. Treatment of mesoionic olates with Lawesson's reagent provides a convenient one-step conversion to mesoionic thiolates.

Mesoionic compounds, expressed by the general formula **1**, where a—f are suitably substituted carbons or heteroatoms, are an interesting family of heterocycles because of their unique structure, reaction behavior, and pharmaceutical activity.[1] Most of mesoions bear oxygen, sulfur, nitrogen, and carbon as the exocyclic group (f), and are called meso-ionic olate, thiolate, aminide, and methylide, respectively; and their interconversion is important from a synthetic standpoint. Mesoionic olates were hitherto converted to the corresponding thiolates via following two steps: alkylation with a trialkyloxonium salt and then replacement of the resulting alkylthio group by sulfide or hydrogensulfide anion (Eq. 1).[2]

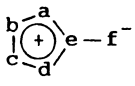


(1)

Lawesson's reagent (**2**), 2,4-bis(*p*-methoxyphenyl)-1,3-dithiadiphosphetane-2,4-disulfide, is known as an excellent reagent for the conversion of various types of carbonyl group to the corresponding thiocarbonyl group.[3] However, the reaction of **2** with mesoionic olates has not to our knowledge been reported so far. Here, we describe the reaction of **2** with several mesoionic olates which provides a convenient method for the one-pot conversion of mesoionic olates to thiolates.

A mixture of 1,3-diphenyltetrazolium-5-olate (**3**) and Lawesson's reagent (**2**) in toluene was heated at reflux for 18 h. Purification by column chromatography gave 93% yield of the thiolate **4**, identical with the authentic sample prepared according to the literature method.[2a] Table 1 summarizes the results for other mesoionic olates. 3-Phenyl-1,2,3-thiadiazolium- (**5**) and 3-phenyl-1,2,3,4-thiatriazolium-5-olates (**7**) were converted to the corresponding thiolates **6** and **8** in high yields, whereas 3-*p*-methoxyphenyl-1,2,3-thiadiazolium-4-thiolate (**10**) was obtained in only 16%. The yields of the thiolates **4**, **6**, **8**, and **10** are much higher than or at least equivalent to those obtained by the existing method (Eq. 1).[2]

Treatment of 3-phenyl-1,2,3-oxadiazolium-5-olate (3-phenylsydnone) (**11**) with **2** gave 1,4-diphenyl-1,4-dihydro-1,2,4,5-tetrazine (**12**) quantitatively, and the expected thiolate **13** could not be obtained at all. The tetrazine **12** has been obtained from the reaction of **11** with P_4S_{10} in a low yield.[4] The thiolate **13** prepared by an independent method[2b] also gave **12** in 88% yield upon the treatment with **2**, suggesting the intermedi-



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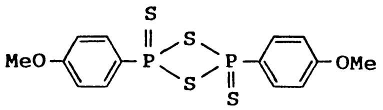

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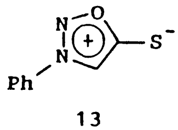

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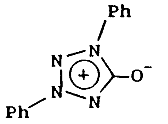
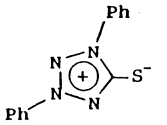
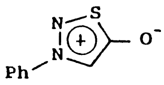
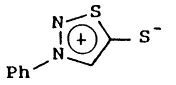
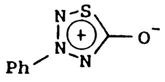
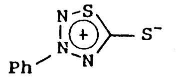
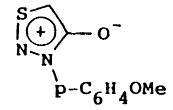
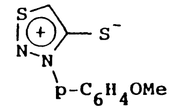
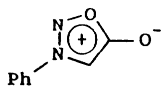
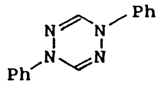
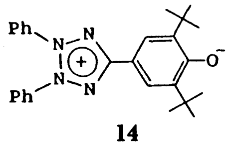
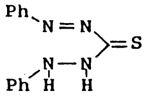
Table 1. Reaction of Mesoionic Olates with Lawesson's Reagent

Run	Olate	Product	Yield/%[a]
1	 **3**	 **4**	93 (59)[b]
2	 **5**	 **6**	98 (63)[c]
3	 **7**	 **8**	93 (25)[d]
4	 **9**	 **10**	16 (19)[e]
5	 **11**	 **12**	100
6	 **14**	 **15**	100

a) Numbers in parentheses refer to the reported yields of the existing two-step conversion (Eq. 1). b) Ref. 2a. c) Ref. 2b. d) Ref. 2c. e) Ref. 2d.

acy of **13** in the reaction of the olate **11** and **2**. Interestingly, the sulfur analog **5** of sydnone gave a high yield of the thiolate **6**. The reaction of a quinonoid mesoionic olate **14**[5] with **2** resulted in the cleavage of the pivotal carbon-carbon bond giving diphenylthiocarbazone (dithizone) **15** in a quantitative yield. Unfortunately, mesoionic olates of type B[1] such as 2,3-diphenyltetrazolium-5-olate and 3,5-diphenyl-1,2-dithiolium-4-olate gave complex mixtures of products on the treatment with **2**.

In summary, the thionation of mesoionic olates of type A by Lawesson's reagent (**2**) provides a convenient route to the corresponding mesoionic thiolates.

Experimental

Melting points were determined with a hot-stage apparatus and are uncorrected. Infrared spectra were recorded on a JASCO IRA-1 spectrophotometer. Mass spectra were recorded on a Hitachi M-52 instrument at 20 eV. ^{1}H and ^{13}C NMR spectra were recorded on a Hitachi R-24A spectrometer (60 MHz) and on a Varian XL-200 spectrometer (50 MHz), respectively, with Me_4Si as an internal standard.

Reaction of Mesoionic Olates with Lawesson's Reagent (2). Run 1. 1,3-Diphenyltetrazolium-5-olate (**3**) (103 mg, 0.43 mmol) and **2** (118 mg, 0.29 mmol) in toluene (5 cm^3) were heated at reflux for 18 h. The reaction mixture was cooled and adsorbed on a silica-gel column and eluted with dichloromethane. A yellow band was collected and the solvent was evaporated leaving yellow crystals of thiolate **4** (102 mg, 93%). Mp 151 °C (CH_2Cl_2) (lit,[2a] mp 155 °C); IR (KBr): 1494, 1374, 1302, 1266, 1190, 774, 764, 692, 686 cm^{-1}; MS *m/z* 254 (M$^+$).

Run 2. 3-Phenyl-1,2,3-thiadiazolium-5-olate (**5**) (100 mg, 0.56 mmol) and **2** (159 mg, 0.39 mmol) in toluene (6 cm^3) were warmed to 100 °C during the period of 30 min. The mixture was cooled and column chromatographed on silica gel (CH_2Cl_2) to give red crystals of thiolate **6** (107 mg, 98%). Mp 165 °C (CH_2Cl_2) (lit,[2b] mp 170—171 °C); IR (KBr): 1430, 1252, 1198, 1030, 898, 760 cm^{-1}; MS *m/z* 194 (M$^+$).

Run 3. 3-Phenyl-1,2,3,4-thiatriazolium-5-olate (**7**) (176 mg, 1.1 mmol) and **2** (300 mg, 0.74 mmol) in toluene (11 cm^3) were heated at reflux for 50 min. The mixture was cooled and column chromatographed on silica gel to give orange needles of thiolate **8** (178 mg, 93%). Mp 125 °C (CH_2Cl_2) (lit,[2c] mp 128 °C); IR (KBr): 1270, 1226, 1056, 922, 762, 660 cm^{-1}; MS *m/z* 195 (M$^+$).

Run 4. 3-*p*-Methoxyphenyl-1,2,3-thiadiazolium-4-olate (**9**) (121 mg, 0.58 mmol) and **2** (163 mg, 0.40 mmol) in toluene (6 cm^3) were heated at reflux for 16 h. Column chromatography on silica gel (ethyl acetate) gave red needles of thiolate **10** (20 mg, 16%). Mp 189 °C (MeOH) (lit,[2d] mp 193—194 °C); IR (KBr): 1512, 1394, 1306, 1254, 1176, 1152, 1078, 1022, 988, 834 cm^{-1}; MS *m/z* 224 (M$^+$).

Run 5. 3-Phenylsydnone (**11**) (110 mg, 0.68 mmol) and **2** (191 mg, 0.47 mmol) in toluene (6 cm^3) were refluxed for 3.5 h. The solvent was evaporated under reduced pressure and the residue was column chromatographed on silica gel (benzene) to give pale yellow plates of dihydrotetrazine (**12**) (80 mg, 100 %). Mp 191 °C (acetone) (lit,[4] mp 189—189.5 °C); IR (KBr): 1600, 1494, 1318, 1156, 906, 892, 754, 750, 700 cm^{-1}; MS: *m/z* 236 (M$^+$); ^{1}H NMR ($CDCl_3$): δ=6.90 (s, 2H, =CH-), 7.30 (m, 10H, Ph); ^{13}C NMR ($CDCl_3$): δ=115.3, 123.8, 129.4, 139.5, 142.3.

Run 6. 2,6-Di-*t*-butyl-4-(2,3-diphenyl-5-tetrazolio)phenolate (**14**)[5] (13 mg, 0.032 mmol) and **2** (9 mg, 0.022 mmol) in toluene (2 cm^3) were slowly heated to reflux during the period of 20 min. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (benzene) to furnish dithizone **15** (8 mg, 100%). The melting point and spectral data were identical with those of a commercially obtained sample.

Reaction of 3-Phenyl-1,2,3-oxadiazolium-5-olate (13) with 2. A mixture of **13** (110 mg, 0.62 mmol) and **2** (177 mg, 0.44 mmol) in toluene (6 cm^3) was refluxed for 3.5 h. Column chromatography on silica gel (dichloromethane) gave dihydrotetrazine (**12**) (64 mg, 88%). The physical data were identical with those of the product of Run 5.

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2) a) R. N. Hanley, W. D. Ollis, and C. A. Ramsden, *J. Chem. Soc., Perkin Trans. 1*, **1979**, 741; b) K. Masuda, J. Adachi, and K. Nomura, *ibid.*, **1979**, 956; c) R. N. Hanley, W. D. Ollis, and C. A. Ramsden, *ibid.*, **1979**, 732; d) J. Adachi, H. Takahata, K. Nomura, and K. Masuda, *Chem. Pharm. Bull.*, **31**, 1746 (1983).

3) For a review, see: M. P. Cava and M. I. Levinson, *Tetrahedron*, **41**, 5061 (1985).

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5) S. Araki, N. Aoyama, and Y. Butsugan, unpublished work; see also: *idem, Tetrahedron Lett.*, **28**, 4289 (1987).