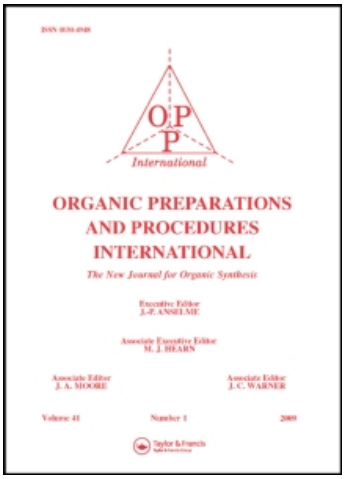


Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

REACTION OF 4-[BIS(ALKYLTHIO)METHYLENE]-2-PHENYL-2-OXAZOLIN-5-ONES WITH AMBIDENT NUCLEOPHILES

Jalpana Roy[a]; N. S. Rawat[a]
[a] Department of Applied Chemistry, Indian School of Mines, Dhanbad, INDIA

To cite this Article Roy, Jalpana and Rawat, N. S.(1991) 'REACTION OF 4-[BIS(ALKYLTHIO)METHYLENE]-2-PHENYL-2-OXAZOLIN-5-ONES WITH AMBIDENT NUCLEOPHILES', Organic Preparations and Procedures International, 23: 4, 450 — 455
To link to this Article: DOI: 10.1080/00304949109458236
URL: http://dx.doi.org/10.1080/00304949109458236

REFERENCES

1. P. E. Cassidy, Ed. "Thermally Stable Polymers, Synthesis and Properties", Marcel Dekker, New York, N.Y., 1980, pp. 154-158.

2. R. Wolf, M. Okada and C. S. Marvel, J. Poly. Sci. Part A-1, 6, 1503 (1968).

3. R. Jones and H. A. Shonle, J. Am. Chem. Soc., 67, 1034 (1945).

4. L. F. Fieser and E. L. Martin, ibid., 57, 1844 (1935).

5. S. J. Backlund and R. E. Olsen, U. S. Patent 4,337,196 (1982); C. A. 96, 199308s (1982).

6. P. N. Rylander, "Catalytic Hydrogenation over Platinum Metals", Academic Press, New York, N.Y., 1967, p. 405.

7. A. Marxer, Helv. Chim. Acta, 39, 335 (1956).

******

REACTION OF 4-[bis(ALKYLTHIO)METHYLENE]-2-PHENYL-2-OXAZOLIN-5-ONES WITH AMBIDENT NUCLEOPHILES

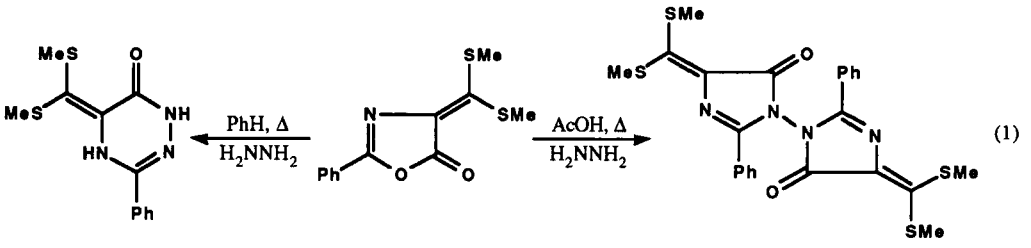
Submitted by (03/07/90) Jalpana Roy* and N. S. Rawat

Department of Applied Chemistry
Indian School of Mines
Dhanbad-826004, INDIA

Aminolysis of 4-[bis(methylthio)methylene]-2-phenyl-2-oxazolin-5-one (**1a**) with primary amines to give N-substituted-2-benzamido-3-[bis(methylthio)]acrylamides or N,N-disubstituted benzamidomalondiamides has been reported earlier.[1] In order to exploit the bielectrophilic property of compounds of type **1**, the reaction of **1a** with several binucleophiles such as hydrazine, phenylhydrazine, *o*-phenylenediamine and *o*-aminothiophenol was investigated under both neutral and acidic conditions.

It is noteworthy that the aminolysis of **1** with binucleophiles proceeded through the cleavage of 1,5-bond[1] instead of 1,2-bond cleavage in 2-oxazolin-5-one as reported by Hanumanthu *et al.*[2] As

shown in Eq. 1, heating **1a** with equimolar portion of hydrazine hydrate in benzene yielded **2**, while in boiling glacial acid containing catalytic amount of fused sodium acetate, a sulfur-containing bright yellow crystalline compound **3** (15%) was obtained by separation *via* column chromatography

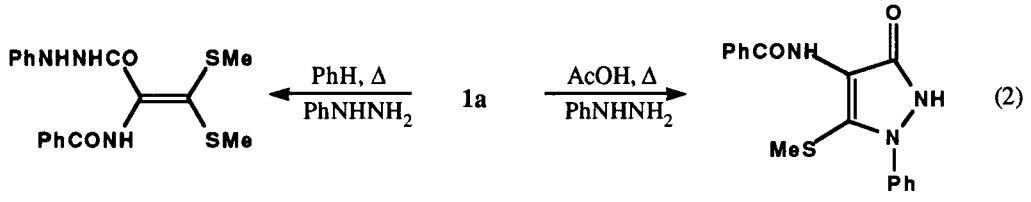


(1)

2 **1a** **3**

(silica gel/benzene). Its IR spectrum showed no absorption bands at 3450-3100 cm^{-1} (for NH_2 or NH group). Its mass (m/e 526) spectra and the nmr suggest that hydrazine condensed with two molecules of **1a** to yield **3**.

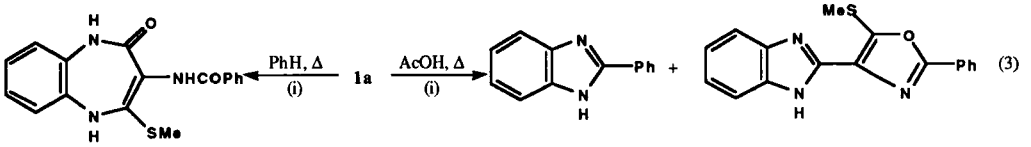
Heating of **1a** with equimolar amount of phenylhydrazine in benzene yielded **4** (m/e 373), while in glacial acetic acid **5** was formed in 79% yield (Eq. 2).



(2)

4 **5**

When **1a** was heated under reflux with a two-fold excess of *o*-phenylenediamine in benzene, a white crystalline sulfur containing compound **6** was obtained [mass spectrum M^+ (m/e 325)], while in glacial acetic acid at reflux, 2-phenylbenzimidazole (**7**, 15% and **8**, 51%) were obtained (Eq. 3).

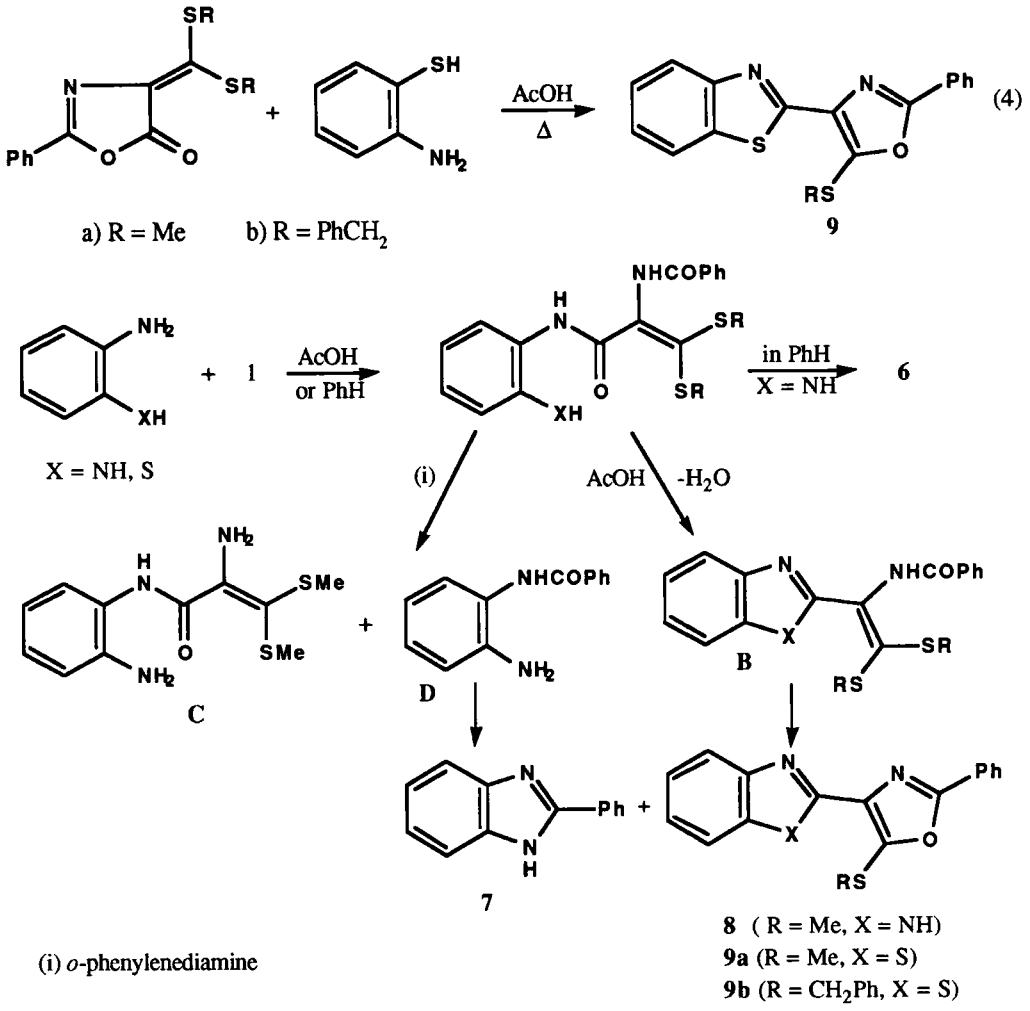


(3)

6 **7** **8**

Although **1a** did not react with *o*-aminothiophenol in benzene, rapid cleavage of 1,5-bond in glacial acetic acid afforded **9** in 68% yield (Eq. 4). An initial nucleophilic attack by the amino group on the C-5 of **1a** with concomitant cyclization to give intermediate **B**[3-5] and elimination of CH_3SH from the same intermediate leads to **8** and **9**. Transbenzoylation of *o*-phenylenediamine by intermediate **A** gives the N-benzoyl-*o*-phenylenediamine (**D**), which cyclized to **7**. The same pathway was followed in the reaction between 4-[bis(benzylthio) methylene]-2-phenyl-2-oxazolin-5-one (**1b**) and *o*-aminothiophenol as shown by the formation of **9b** in good yield. Under neutral conditions, the

aminolysis was rapid and quite selective, the ketone thioacetal moiety remaining unaffected with all the binucleophiles except *o*-phenylenediamine. The present investigation thus established that **1a** and **1b** are amenable to selective aminolysis.



Scheme 1

EXPERIMENTAL SECTION

Melting points are uncorrected. IR spectra were recorded in Nujol on a Pye Unicam PU 9512, PMR spectra were determined on R-32 spectrophotometer with TMS as an internal standard and mass spectra were obtained on Jeol JMS-D 300 instruments. The required 4-bis[(methylthio)methylene]-2-phenyl-2-oxazolin-5-one(**1a**) and 4-bis[(benzylthio)methylene]-2-phenyl-2-oxazolin-5-one (**1b**) were prepared according to the method described earlier.[6,7]

5-[bis(Methylthio)]methylene-6-oxo-3-phenyl-1,2,5,6-tetrahydro-1,2,4-triazine (**2**).- A mixture of **1a**

(0.265 g 0.001 mole), 80% hydrazine hydrate (0.04 ml, 0.001 mole) and benzene (5 ml) was refluxed for 30 min. The solvent was completely removed under reduced pressure. The residue thus obtained was recrystallized from benzene.

1,1-bis[4(Methylthio)methylene]5-oxo-2-phenyl-4,5-dihydroimidazole (**3**).- A mixture of **1a** (0.265 g, 0.001 mole), 80% hydrazine hydrate (0.04 ml, 0.001 mole) and acetic acid (5 ml) was refluxed for 3 hrs in the presence of fused sodium acetate. The reaction mixture was then concentrated over a

TABLE 1. Reaction of **1a** with Ambident Nucleophiles

Cmpd	Yield (%)	mp. (°C)	IR (Nujol) (cm^{-1})	^1H NMR ($CDCl_3$) δ (ppm)	Mass M^+
2	65	203-204	3220, 1650 1608, 710	3.18 (s, 6H, CH_3, 7.1-8.0 (m, 5H, Ar-H), 9.25 (bs, 1H, NH, D_2O exchangeable). 10.0 (bs, 1H, NH, D_2O exchangeable) ($DMSOD_6$)	279
3	15	196-197	1700, 1600	2.5 (s, 6H, CH_3), 2.7 (s, 6H, CH_3) 7.1-7.8 (m, 10H, Ar-H)	526
4	79	144-145	3255, 1650, 1550, 710	2.2 (d, 6H, CH_3), 6.6-7.9 (m, 10H, Ar-H), 8.4 (d, 2H, NH-NH, D_2O exchangeable), 8.7 (s, 1H, NHCO, D_2O exchangeable)	373
5	69	168-169	3305, 1665, 1645	2.2 (s, 3H, CH_3), 7.5 (m, 11H, Ar-H & NH), 8.2 (s, 1H, NH, D_2O exchangeable)	325
6	76	182-184	3300, 2900	2.3 (s, 6H, CH_3), 3.5 (bh, 1H, NH, D_2O exchangeable), 6.4-7.9 (m, 9H, Ar-H & NH), 8.4 (bs, 1H, NH, D_2O) exchangeable	325
7	15	288[8]	3380, 1590	-	194
8	15	228	3180, 1700	2.2 (s, 3H, CH_3), 7.2 (m, 7H, Ar-H), 7.4-7.7 (m, 2H, Ar-H), $CDCl_3$ & TFA)	308
9a	68	162-163	1565, 1540	2.6 (s, 3H, CH_3), 7.3 (m, 5H, Ar-H), 7.9 (m, 4H, Ar-H)	325
9b	72	170-172	1565, 920	4.2 (s, 2H, CH_2), 7.3 (m, 10H, Ar-H), 7.9 (m, 4H, Ar-H)	401

steam bath. The oily residue so obtained solidified to a yellow solid when triturated with aqueous ethanol. Finally a yellow crystalline product **3** was separated by column chromatography (silica gel/benzene).

N-Anilino-2-benzamido-3-[bis(methylthio)]acrylamide (**4**).- Prepared according to the procedure used for compound **2**. The product was recrystallized from benzene-hexane.

4-Benzamido-5-methylthio-3-oxo-2-phenylpyrazole (**5**).- Prepared by the procedure used for compound **3**. The product was recrystallized from aq. ethanol.

Conversion of **4** into **5**.- A mixture of 100 mg of **4**, 2 ml of gl. acetic acid and catalytic amount of fused sodium acetate was heated to reflux for 3 hrs. Work up gave a product identical (mixture mp) with **5** obtained earlier.

6-Benzamido-7-methylthio-5-oxo-1,4-benzodiazephine (**6**).- Prepared by using the procedure used for compound **2**. The product was recrystallized from benzene-ethanol.

4-(2-benzimidazolyl)-5-methylthio-2-phenyl-1,3-oxazole (**8**).- *o*-Phenylenediamine and **1a**, in a 2:1 molar ratio, was converted to **8** by the same procedure as described for **3**. Fractional crystallization of the crude product from chloroform yielded **7**; crystalline product **8** was separated from the filtrate.

4-(2-benzthiazolyl)-5-methylthio/benzylthio-2-phenyl-1,3-oxazoles (**9a** and **9b**). General Procedure.- *o*-Aminothiophenol and **1**, in a 1:1 molar ratio was converted to **9** following the procedure used for compound **8**. Recrystallization from ethanol yielded pure **9**.

TABLE 2. Elemental Analysis Data

Cmpd.	C		H		N	
	Calcd.	Found	Calcd.	Found	Calcd.	Found
2	51.61	51.90	4.65	4.78	15.05	15.31
4	57.90	58.21	5.09	5.34	11.26	11.01
5	62.76	62.68	4.61	4.88	12.92	13.21
6	62.76	63.09	4.61	4.31	12.92	12.60
7	80.41	80.11	5.15	5.27	14.43	14.54
8	66.23	66.41	4.22	3.96	13.63	13.88
9a	62.76	63.06	3.69	4.00	8.61	8.54
9b	68.82	69.12	3.99	3.79	6.98	6.70

Acknowledgements.- One of the authors (J. R.) is grateful to the UGC, New Delhi for the award of a Research Associateship and to Dr. A. K. Mukerjee, BHU, Va ranasi, for fruitful suggestions. Thanks are due to RSIC, Lucknow, for providing NMR and mass spectra facilities and also to Mr. M. M. Konar, ISM, Dhanbad, for recording IR spectra.

REFERENCES

1. R. Ashare, J. Roy and A. K. Mukerjee, Heterocycles, **24**, 1325, (1986).

2. N. J. Prameela Subhashini and P. Hanumanthu, Indian J. Chem., **26B**, 32 (1987).

3. A. F. A. Harb, A. M. Zayed, E. I. Maghraby and S. A. Metwally, Heterocycles, **24**, 1873 (1986).

4. A. R. Katritzky, J. Sakizadeh, S. M. Hellmann, L. R. Krepski, S. V. Pathre and J. K. Rasmussen, Synth. Commun., **18**, 651 (1988).

5. A. M. Tikadari and A. K. Mukerje, Indian J. Chem., **26B**, 73 (1987).

6. P. K. Tripathy, J. Roy and A. K. Mukerjee, ibid., **25B**, 1275 (1986).

7. J. Roy, ibid., **30B**, 433 (1991).

8. "Dictionary of Organic Compounds", Oxford University Press, New York, NY, Vol. 4, 2671 (1978).

****

A RAPID PREPARATION OF 2,2'-DIMERCAPTOBIPHENYL

Submitted by (03/18/91)

Sergio Cossu,[†] Giovanna Delogu,*[††] Davide Fabbri,[††] and Paola Maglioli[†]

[†] *Dipartimento di Chimica, Universita' di Sassari via Vienna 2, I-07100 Sassari, ITALY*

[††] *Istituto CNR per l'Applicazione delle Tecniche Chimiche Avanzate ai Problemi Agrobiologici via Vienna 2, I-07100 Sassari, ITALY*

The several methods of preparation of 2,2'-dimercaptobiphenyl (**1**) reported in the literature,[1] reflect its widespread utilization as a substrate for redox[2] and thermodynamic[3] studies, as a ligand and as an atropisomeric chiral reagent.[4] Dithiol **1** is available *via* the Ullman coupling of appropriate precursors,[1b,d] Newman-Kwart rearrangement of thioesters,[5] lithium reduction of dibenzothiophene,[6] and other routes.[7] We now report the experimental details for its preparation from the dianion **3**, which was generated directly *via* *n*-butyllithium (*n*-BuLi)-N,N,N',N'-tetramethylethylenediamine (TMEDA) deprotonation of biphenyl by a known procedure.[8]

Biphenyl was treated under various conditions; the best results were obtained when *n*-BuLi was treated with TMEDA at 25° before the addition of biphenyl. Metallation of biphenyl with 1:1 *n*-BuLi-TMEDA at -15° for *ca* 15 hrs provided optimum conversion to its dianion.[9] Treatment of the dilithio intermediate **3** with 1.1 eq. of elemental sulfur at -35° gave the disulfide **2** in higher yield