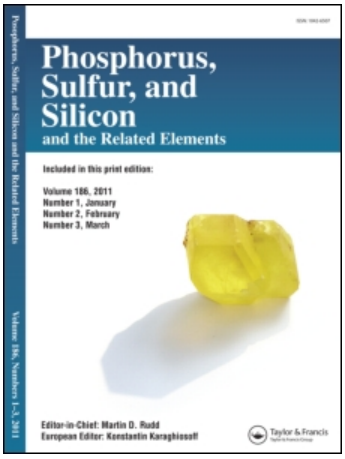


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

ADDUCTS FROM 2, 3-DIARYL-5-PHENYLMETHYLENE-4-OXO-1, 3-THIAZOLIDINE-1-OXIDES

Mohamed T. Omar[a]; Aly M. Youssef[a]; Fatma A. Sherif[a]
[a] Chemistry Department, Faculty of Science, Ain Shams University, Cairo, Egypt

To cite this Article Omar, Mohamed T. , Youssef, Aly M. and Sherif, Fatma A.(1990) 'ADDUCTS FROM 2, 3-DIARYL-5-PHENYLMETHYLENE-4-OXO-1, 3-THIAZOLIDINE-1-OXIDES', Phosphorus, Sulfur, and Silicon and the Related Elements, 53: 1, 267 — 270
To link to this Article: DOI: 10.1080/10426509008038035
URL: http://dx.doi.org/10.1080/10426509008038035

Phosphorus, Sulfur, and Silicon, 1990, Vol. 53, pp. 267–270
Reprints available directly from the publisher
Photocopying permitted by license only Printed in the United Kingdom

ADDUCTS FROM 2,3-DIARYL-5-PHENYLMETHYLENE-4-OXO-1,3-THIAZOLIDINE-1-OXIDES

MOHAMED T. OMAR*, ALY M. YOUSSEF and FATMA A. SHERIF
Chemistry Department, Faculty of Science, Ain Shams University, Abbassia, Cairo, Egypt

(Received January 9, 1990; in final form January 26, 1990)

5-Phenylmethylene-2,3-diaryl-4-oxo-1,3-thiazolidine-1-oxides **2** which synthesised via peracetic acid oxidation of the respective 1,3-thiazolidines **1** reacted with benzylamine and Grignard reagents to afford the respective 5-α-substituted benzyl-2,3-diaryl-4-oxo-1,3-thiazolidine-1-oxides **3** and **4**. Structures of **3** and **4** were based on analytical and spectral evidence.

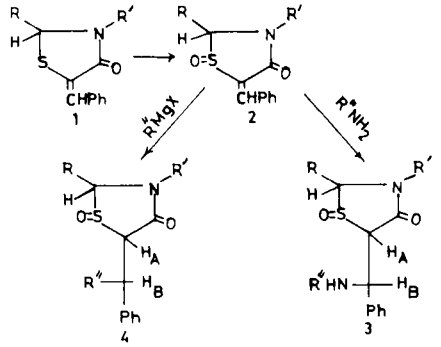
Key words: 4-Oxo-1,3-thiazolidine-1-oxides; 5-(α-substituted benzyl)-4-oxo-1,3-thiazolidine-1-oxides; benzylamine; Grignard reagents.

INTRODUCTION

Our continuing interest in the chemistry of 4-thiazolidinones[1] especially in the synthesis of thiazolidine-oxides[2] and the expanding use of these oxides as agrochemicals[3–6] prompted us to synthesise some new thiazolidine-l-oxides bearing substituents at the 5-position and appear highly promising for biological activity studies. Our intention is to synthesise these 5-substituted derivatives via nucleophilic addition at the β-carbon atom of an α,β-unsaturated sulfoxide system using its latent ability for such a reaction. Thus, a series of 5-phenylmethylene-2,3-diaryl-4-oxo-1,3-thiazolidine-1-oxides **2** has been prepared and experimented with benzylamine and Grignard reagents.

RESULTS AND DISCUSSION

Synthesis of 5-phenylmethylene-2,3-diaryl-4-oxo-1,3-thiazolidine-l-oxides **2** has been attempted via condensing the respective 2,3-diaryl-4-oxo-1,3-thiazolidine-1-oxides[2] with benzaldehyde using either the method of Lo *et al.*[7] or sodium ethoxide, but the results are not promising. Our trials are then shifted to another route in which 2,3-diaryl-4-oxo-1,3-thiazolidines are condensed at first with benzaldehyde using the method of Brown *et al.*[8] then treating the produced 5-phenylmethylene derivatives with peracetic acid. The use of peracetic acid for sulfoxidation is first reported by Findley *et al.*[9] then applied by other workers,[10] but, none of them used it to sulfoxidise an α,β-unsaturated system such as reported here. Thus, treating 2,3-diphenyl-, 2-phenyl-3-(4-methylphenyl)- and 2-(4-chlorophenyl)-3-phenyl- 4-oxo-1,3-thiazolidines with benzaldehyde in presence of sodium ethoxide gives the respective 5-phenylmethylene derivatives **Ia-c**.



1,2 a, $R = C_6H_5$; $R' = C_6H_5$
b, $R = C_6H_5$; $R' = 4\text{-}CH_3C_6H_4$
c, $R = 4\text{-}ClC_6H_4$; $R' = C_6H_5$

3,4 a, $R = C_6H_5$; $R' = C_6H_5$; $R'' = CH_2Ph$
b, $R = C_6H_5$; $R' = 4\text{-}CH_3C_6H_4$; $R'' = CH_2Ph$
c, $R = 4\text{-}ClC_6H_4$; $R' = C_6H_5$; $R'' = C_6H_5$

SCHEME I

The structure of **Ia** is based exclusively on comparison (m.p. and mixture m.p.) with an authentic sample.[8] The structure of **Ib-c** is deduced from analytical and infrared spectral data. The IR spectra (cm^{-1}) of **Ib,c** show bands at 1680–1685 (CO). Peracetic acid attacks the sulphur atom of **Ia-c** to afford the respective l-oxides **2a-c** whose structure is substantiated from analytical and spectral data. The IR spectra (cm^{-1}) of **Ia-c** exhibit absorptions at 1675–1680 (CO) and 1040–1045 SO) and their electronic spectra show two distinct highly intense maxima extending to 316 nm revealing a highly conjugated system. Their ^{1}H-NMR spectra (DMSO) show signals attributable to olefinic (s), aromatic (m) and heteroring methine (s) protons with the proper integration ratios (cf. exp.). The structure of **2a** gets a further support from MS spectrometry as it shows a molecular ion at 259 and a fragmentation pattern consistent with the proposed structure (cf. exp.). Benzylamine attacks the β-carbon atom of the exocyclic double bond of **2a-b** to afford the respective 2,3-diaryl-5-α-phenylmethylamino-benzyl-4-oxo-1,3-thiazolidine-1-oxides **3a-b**, respectively. The structures of **3** are confirmed by elemental analysis and spectral data. The IR spectra (cm^{-1}) show peaks at 3220 (NH); 1685 (CO) and 1050 (SO). The ^{1}H-NMR spectrum of **3a** (DMSO) revealed signals assignable to an AB system which is consistent with addition at the exocyclic double bond (cf. exp.).

Grignard reagents such as benzylmagnesium chloride add to the exocyclic double bond of **2a-b** to produce the respective 5-α-phenylmethyl-benzyl-derivatives **4a-b**. Similar treatment of **2c** with phenylmagnesium bromide affords 2-(4-chlorophenyl)-3-phenyl-5-diphenylmethyl-4-oxo-1,3-thiazolidine-1-oxide **4c**. The IR spectra (cm^{-1}) exhibited absorptions at 1685–1700 (CO) and 1050–1055 (SO). The electronic spectra of **4a-c** show absorptions at 238–244 nm (ϵ 8350–12000) and inflexions at 260 nm (ϵ 5000–7000), similar to those of the

parent unsubstituted counterparts,[2] which is consistent with an addition at the exocyclic double bond. The ^{1}H-NMR spectrum of **4a** (DMSO) does not show the olefinic singlet and exhibit an AB pattern (cf. exp.).

EXPERIMENTAL

All melting points are uncorrected. Infrared spectra were recorded on a Unicam SP 1200 spectrophotometer as KBr discs. Electronic spectra were taken on a Perkin–Elmer Lambda 3B apparatus using ethanol as a solvent. The ^{1}H-NMR spectra were recorded on a Varian EM-390-90 MHz instrument using TMS as an internal reference. Mass spectra were recorded on a Kratos MS 300 mass spectrometer operating at 70 eV. Elemental analysis were carried out at the Microanalytical Center, Cairo University, Egypt.

2,3-Diaryl-5-phenylmethylene-4-oxo-1,3-thiazolidines **1a-c.** To a mixture of **1a, b** or **c** (5.0 mmoles) and benzaldehyde (6.0 mmoles) in absolute ethanol (50 ml), a solution of sodium ethoxide (10.0 mmoles) in absolute ethanol (10 ml) is added and the whole mixture refluxed for 20 minutes. The precipitated faint yellow product is filtered off, washed with cold dilute methanol and recrystallised from the suitable solvent to give compounds **1** (cf. Table I).

2,3-Diaryl-5-phenylmethylene-4-oxo-1,3-thiazolidine-1-oxides **2a-c.** Finely powdered **1a, b** or **c** (1.0 gm) is added portionwise to a stirred cold solution of peracetic acid (30 ml of 1 M solution), and the whole mixture is stirred for 2–3 hours during which the temperature is kept below 40°. The reaction mixture is allowed to stand overnight in the refrigerator and the precipitated faint yellow solid is filtered off, washed thoroughly with cold water, dried and recystallised from the proper solvent to give the title compounds (cf. Tables I and II).

TABLE I

The newly synthesised compounds

Product	Yield (%)	M.P. (°C)	Mol. formula Mol. Wt.	Analysis% C	H	N
1a	70	185–188[a]	$C_{22}H_{17}NOS$	76.96	4.95	4.08
			(343)	76.85	4.90	4.00
1b	70	185–187[b]	$C_{23}H_{19}NOS$	77.31	5.32	3.92
			(357)	77.30	5.10	3.80
1c	65	193–194[a]	$C_{22}H_{16}ClNOS$	69.93	4.24	3.70
			(377.5)	70.00	4.10	3.60
2a	65	210–212[c]	$C_{22}H_{17}NO_2S$	73.53	4.73	3.90
			(359)	73.60	4.52	3.70
2b	65	174–176[d]	$C_{23}H_{19}NO_2S$	74.00	5.09	3.75
			(373)	74.10	5.00	3.85
2c	65	180–181[c]	$C_{22}H_{16}ClNO_2S$	67.09	4.06	3.55
			(393.5)	67.00	4.00	3.55
3a	40	185–187[e]	$C_{29}H_{26}N_2O_2S$	74.67	5.58	6.00
			(466)	74.40	5.50	5.80
3b	45	190–192[a]	$C_{30}H_{28}N_2O_2S$	75.00	5.83	5.83
			(480)	74.80	5.60	6.00
4a	45	195–197[d]	$C_{29}H_{25}NO_2S$	77.16	5.54	3.10
			(451)	76.95	5.50	3.00
4b	45	195–197[d]	$C_{30}H_{27}NO_2S$	77.42	5.80	3.01
			(465)	77.55	5.80	3.10
4c	40	205–207[d]	$C_{28}H_{22}ClNO_2S$	71.26	4.66	2.97
			(471.5)	70.95	4.30	2.95

[a] Benzene/light petroleum, [b] Ethanol, [c] Benzene, [d] Ethanol/toluene, [e] Ethanol/water.

TABLE II

Spectral data of compounds **2–4**

Product	^{1}H-NMR, J(Hz)
2a*	6.52 (s, 1H, heteroring CH), 7.30–7.90 (m, 15H aromatic), 8.33 (s, 1H, =CH–).
2b	6.55 (s, 1H, heteroring CH), 7.20–7.90 (m, 14H, aromatic); 8.35 (s, 1H, =CH–).
2c	6.70 (s, 1H, heteroring CH), 7.30–7.85 (m, 14H, aromatic); 8.35 (s, 1H, =CH–).
3b	2.30 (s, 3H, CH_3), 3.05 (broad s, 1H, NH); 3.60 (s, 2H, CH_2Ph), 3.72–4.20 (partially splitted AB_q, 2H, H_A and H_B), 6.40 (s, 1H, heteroring CH), 7.10–7.70 (m, 19H. aromatic), upon deuteration the signal at 3.05 ppm disappeared
4a	3.05 (m, 3H, $PhCH_2 + H_A$), 4.05 broad s, 1H, H_B), 6.22 (s, 1H, heteroring CH), 7.20–7.80 (m, 20H, aromatic).

* MS: m/e (relative intensity) 359(7), 343(15), 182(18), 181(100), 180(47), 178(38), 134(35), 77(22).

2,3-Diaryl-5-(α-phenylmethylaminobenzyl)-4-oxo-1,3-thiazolidine-1-oxides **4a-b.** Benzylamine (10 mmole) is added to a suspension of **2a** or **b** (5 mmoles) in benzene (20 ml) and the whole mixture is refluxed over a boiling water bath for 60 minutes. The reaction mixture is treated with charcoal, concentrated, allowed to stand overnight and the precipitated solid is recrystallised from the suitable solvent to give compounds **3** (cf. Tables I and II).

2,3-Diaryl-5(α-phenylmethylbenzyl)-4a-b and 2-(4-chlorophenyl)-2-phenyl-5-diphenylmethyl-4c 4-oxo-1,3-thiazolidine-1-oxides. An ethereal solution of benzylmagnesium chloride or phenylmagnesium bromide [from benzyl chloride or bromobenzene (30 mmoles) and magnesium turnings (35 mmoles)] is added dropwise to a supension of **2a, b** or **c** (5 mmoles) in anhydrous toluene (100 ml) and the whole mixture is refluxed for 10 hours. The yellow to orange reaction mixture is left to stand overnight, hydrolysed with saturated ammonium chloride solution containing few drops of hydrochloric acid and steam distilled. The residual semisolids are dissolved in ethanol, treated with charcoal, concentrated and left to stand overnight. The precipitated solid is recrystallised from the suitable solvent to give the title compounds (cf. Tables I and II).

REFERENCES

1. A. R. A. Raouf, M. T. Omar, M. M. El-Attal, *Acta Chimica* (Budapest), **83,** 367 (1975; A. R. A. Raouf, M. T. Omar, M. M. El-Attal, *Acta Chimica* (Budapest), **87,** 187 (1975); M. T. Omar, M. M. Habashy, A. El-Khamry, *Aust. J. Chem.*, **33,** 619 (1980); M. T. Omar, F. A. Sherif, *Synthesis,* 742 (1981); M. T. Omar, M. M. Habashy, A. M. Youssef, F. A. Sherif, *J. Prakt. Chem.*, **331,** 393 (1989).
2. M. T. Omar, A. E. El-Khamry and F. A. Sherif, *J. Heterocyclic Chem.*, **18,** 633 (1981).
3. S. Karoly, B. Castro and D. Balde, German Patent 2,620,101; *Chem. Abstr.*, **86,** 89 842x (1977).
4. W. Paul Anthony, R. William George and S. Margaret Claire, Eur. Pat. Appl. 4,129; *Chem. Abstr.*, **92,** 110995k (1980).
5. S. P. A. Montedison, Jpn Kokai Tokkyo Koho 8187,547; *Chem. Abst.*, **95,** 187236h (1981).
6. T. H. Pieter and W. Shirley Beatrice, Eur Pat. Appl. EP 91,148; *Chem. Abst.*, **100,** 139089n (1984).
7. C. P. Lo, E. Y. Shropshire and W. J. Croxall, *J. Am. Chem. Soc.*, **75,** 4845 (1953).
8. F. C. Brown, R. S. Jones and M. Kent, *Can. J. Chem.*, **41,** 817 (1963).
9. T. W. Findley, D. Swern and J. T. Scanlan, *J. Am. Chem. Soc.*, **67,** 412 (1945).
10. J. M. McIntosh and R. K. Leavitt, *Can. J. Chem.*, **63,** 3313 (1985).