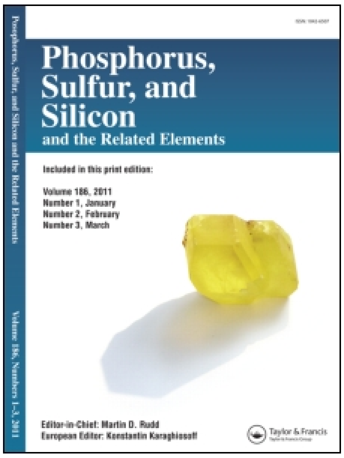

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Synthesis of Bis(arylmethylidene)thiopyranones and Crystal Structure of the Phenyl Derivative

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To cite this Article Abaee, M. Saeed , Mojtahedi, Mohammad M. , Zahedi, M. Mehdi , Mesbah, A. Wahid , Ghandchi, Nafiseh Mohaddes and Massa, Werner(2007) 'Synthesis of Bis(arylmethylidene)thiopyranones and Crystal Structure of the Phenyl Derivative', Phosphorus, Sulfur, and Silicon and the Related Elements, 182: 12, 2891 — 2895

To link to this Article: DOI: 10.1080/10426500701542759

URL: http://dx.doi.org/10.1080/10426500701542759

Phosphorus, Sulfur, and Silicon, 182:2891–2895, 2007
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ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500701542759

Synthesis of Bis(arylmethylidene)thiopyranones and Crystal Structure of the Phenyl Derivative

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A convenient method is offered for double aldol condensation of tetrahydrothiopyran-4-one with aromatic aldehydes under LiBr catalysis. An X-ray analysis verifies the proposed structures.

Keywords Aldol condensation; bis(arylmethylidene)thiopyranones; lithium bromide; thiopyranone

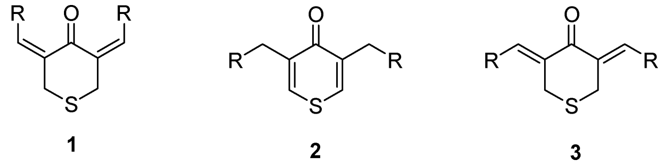
INTRODUCTION

Synthesis of bis(arylmethylidene)cycloalkanones is facilitated via aldol condensation of homocyclic ketones with aromatic aldehydes[1] and several procedures are offered so far for this purpose using Lewis acid catalysis,[2] solid-supported reactions,[3] ionic liquids,[4] microwave irradiation,[3a] and ultrasound mediation.[3b] In contrast, similar chemistry for heterocyclic analogs is much less developed. We recently disclosed the synthesis of several novel bisarylmethylidene derivatives of thiopyranone[5] and pyranone[6] structures using very

Received April 2, 2007; accepted June 5, 2007.

Partial financial support by the Ministry of Science, Research, and Technology of Iran is greatly appreciated.

Address correspondence to Mohammad M. Mojtahedi, Chemistry and Chemical Engineering Research Center of Iran, P. O. Box 14335-186, Tehran, Iran. E-mail: mojtahedi@ccerci.ac.ir facile synthetic methods. The structures were assigned logically based on the spectroscopic characterization of the products. However, to distinguish between the possible isomers (Scheme 1) and verify the proposed structures we decided to determine the crystal structure of a representative compound by X-ray diffraction.



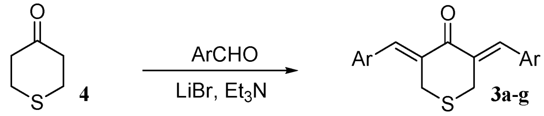
SCHEME 1

In the present article, a convenient and rapid procedure is offered for the synthesis of bis(arylmethylidene)thiopyranones under catalysis of LiBr which has found many applications as a mild Lewis-acid in recent years to ease up various synthetic organic transformations.[7] The X-ray structure analysis of the phenyl derivative confirms the presence of exocyclic double bonds in the products in *Z-Z* configuration (**3**).

RESULTS AND DISCUSSION

An equimolar mixture of thiopyranone **4** and an aldehyde (as listed in Table I) was treated with LiBr (10 mol%) and Et_3N in dichloromethane. Complete conversion of the starting materials to the desired product was observed within a few hours as reactions were monitored by TLC.

TABLE I Alodol Condensation of 4 with Aldehydes under LiBr Catalysis



Entry	ArCHO	M.P. (° C)	Product	Yield%[a]
1	benzaldehyde	142–144	**3a**	95
2	(*p*-Me)benzaldehyde	186–188	**3b**	91
3	(*p*-MeO)benzaldehyde	174–176	**3c**	93
4	(*p*-CI)benzaldehyde	126–128	**3d**	95
5	2-thiophenecarbaldehyde	155–157	**3e**	92
6	furfural	156–158	**3f**	88
7	3-pyridinecarbaldehyde	186–188	**3g**	94

[a] Isolated yields.

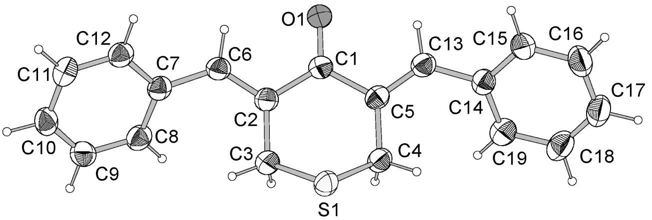


FIGURE 1 Structure of **3a** at 193 K in the crystal. Displacement ellipsoids at 50% probability level. C1–C2 1.495(2), C2–C3 1.498(2), C2–C6 1.344(2), C3–S1 1.802(2), S1–C4 1.799(2), C4–C5 1.499(2), C5–C1 1.503(2), C5–C13 1.331(2) Å.

Control experiments confirmed the combined promoting and catalytic effects of LiBr; an alternative reaction in the absence of the catalyst led to formation of less than 10% of **3a** after 24 h.

The structure of the products was assigned with spectroscopic methods and compared with the literature data.[5,8] In order to verify this structure, a single crystal of **3a** was prepared and investigated by X-ray diffraction. The result, as depicted in the Figure 1, clearly supports the proposed structure with exocyclic double bonds C2–C6 and C5–C13. The experimental data and crystal parameters are given in the Table II.

The atoms of the central moiety C1, O1, C2, C3, C4, C5, C6, C7, C13, and C14 are almost coplanar (maximum deviation from the best plane 0.065(2) Å). The folding angle of this main plane and the C3, S1, C4 plane is 122.8(6)°. The planes of the phenyl rings are rotated out of the main plane as documented in torsion angles C5-C13-C14-C15 –143.0(2)° and C2-C6-C7-C12 147.3(2)°, resulting in a molecule conformation resembling a landing bird (Fig. 2).

In summary, a LiBr promoted aldol condensation of thiopyran **4** with various aldehydes was carried out within few hours. Reactions proceeded with catalytic amounts of the Lewis acid, and the use of harsh conditions and tedious work up procedures were avoided. High yields of the products and rapid completion of the reactions are among other advantages of this methodology. The proposed structure was confirmed for the first time by single crystal X-ray diffraction analysis.

EXPERIMENTAL

Typical Procedure for the Synthesis of 3a

A mixture of **4** (5.0 mmol), benzaldehyde (5.0 mmol), LiBr (0.5 mmol), and Et_3N (10.0 mmol) in CH_2Cl_2 (15 mL) was stirred in a flask. The course of the reaction was monitored by TLC and complete

TABLE II Crystal and Experimental Data for the Structure Determination of 3a

Empirical formula	$C_{19}\ H_{16}\ O\ S$
Formula weight	292.38
Habitus, color	column, colorless
Crystal size	$0.33 \times 0.15 \times 0.12\ \text{mm}^3$
Crystal system	monoclinic
Space group	$P2_1/n$, Z = 4
Unit cell dimensions	a = 10.035(1) Å
	b = 9.540(1) Å $\beta = 95.32(1)^\circ$.
	c = 15.595(1) Å
Volume	1486.55(15) Å^3
Wavelength	0.71073 Å
Temperature	193(2) K
Density (calculated)	1.306 Mg/m^3
Absorption coefficient	0.213 mm^{-1}, no correction
F(000)	616
Theta range for data collection	2.32 to 25.87°.
Index ranges	$-12<=h<=12$, $-11<=k<=11$, $-19<=l<=19$
Reflections collected	14181
Independent reflections	2870 [R(int) = 0.0308]
Completeness to theta = 25.87°	99.6 %
Refinement method	Full-matrix least-squares on F^2
Treatment of hydrogen atoms	refined with isotropic displacement parameters
Data / restraints / parameters	2870 / 0 / 254
Goodness-of-fit on F^2	0.715
Final R indices [I>2sigma(I)]	R1 = 0.0307, wR2 = 0.0758
R indices (all data)	R1 = 0.0505, wR2 = 0.0828
Largest diff. peak and hole	0.185 and −0.159 e.Å^{-3}

disappearance of the starting materials was observed within few hours. The mixture was diluted by dichloromethane (20 mL) and washed twice by water (20 mL portions). The organic phase was dried over Na_2SO_4, the solvent was removed at reduced pressure and the product was precipitated after removal of the volatile portion. The NMR, and IR spectra and melting point of the product were obtained and compared perfectly with those existing in the literature.[5,8]

(3Z,5Z)-3,5-Dibenzylidene-tetrahydrothiopyran-4-one (3a)

Yellow crystals were obtained in 95% yield. M.p. 142–144°C; IR (KBr, cm^{-1}) 1599, 1444, 1269; ^{1}H NMR ($CDCl_3$)δ 3.84 (s, 4H), 7.30 (s, 10H), 7.72 (s, 2H); ^{13}C NMR ($CDCl_3$)δ0.0, 128.4, 128.7, 129.8, 133.7, 134.9, 136.6, 188.6; MS (70 eV) m/z (%) 292 (M^+), 147, 115.

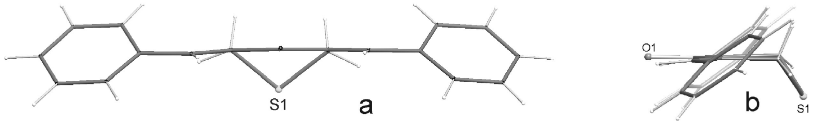


FIGURE 2 Side views of the structure of **3a** in the crystal showing the molecular conformation.

X-Ray Crystal Structure Analysis of 3a

A crystal of **3a**, grown from hexane, was investigated on an IPDS area detector system (Stoe) at −80°C using MoKα-radiation. Crystal and experimental data are given in the Table II. The structure was solved by direct methods and refined using the SHELX97 programs. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-637988. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. Code +44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk or via www.ccdc.cam.ac.uk/conts/retrieving.html]

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