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Synthesis of 4*H*-1,3-Oxathiin-4-ones by Reaction of α-Diazo-β-diketone with Thiones

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ABSTRACT: *A series of 2,2-disubstituted 5,6-diphenyl-4*H*-1,3-oxathiin-4-ones was synthesized by cycloaddition of thiones with benzoylphenylketene, which was generated by the thermal Wolff rearrangement of 2-diazo-1,3-diphenyl-1,3-propanedione.* © 2001 John Wiley & Sons, Inc. Heteroatom Chem 12:630–632, 2001

INTRODUCTION

α-Diazo-β-diketones, diacyldiazomethanes, are very important and suitable precursors for the generation of acylketenes via thermal, photolytic, or metal catalytic elimination of nitrogen accompanied by Wolff rearrangement [1–3]. The acylketenes are also generally generated in situ by flash vacuum pyrolysis of 2,3-dihydrofuran-2,3-diones [4]. The acylketenes are highly reactive and useful synthons for the synthesis of oxy-containing six-membered heterocyclic compounds [3]. They show a pronounced tendency to form [2 + 4] Diels–Alder adducts when treated with dienophiles. They exhibit excellent and predictable regioselectivity, and as electron-deficient oxy-containing dienes, they participate preferentially as the 4π component in inverse (diene LUMO controlled) Diels-Alder reactions with electron-rich and/or dipolar dieneophiles [5–10]. They are especially prone to undergo [2 + 4] cycloadditions with heterodienophiles, such as imines [5–8] or nitriles [9] for synthesis of 2,3-dihydro-1,3-oxazin-4-one or 1,3-oxazin-4-one derivatives; carbonyl groups for 4*H*-1,3-dioxin-4-one derivatives [10,11] as well as electron-rich alkenes or alkynes, for example, enamines [11] or enol ethers [12] for synthesis of 2,3-dihydro-4-pyranone derivatives; and alkoxyacetylenes [13] for synthesis of 1,4-pyrone derivatives. The acylketenes can also react with some heterocumulenes [14], such as carbodiimides and isocyanates, to yield 2,3-dihydro-1,3-oxazine derivatives. Recently we studied reactions of α-diazo-β-diketones with aldehydes and ketones [10], and imines in 1,5-benzodiazepines and 1,5-benzothiazepines [7,8]. In a continuation of this study, we investigated the reaction of α-diazo-β-diketone with thiones.

RESULTS AND DISCUSSION

Thiones were obtained by thionation of ketones. Tetraphosphorus decasulfide is a long known thionating reagent for the conversion of carbonyl groups into thiocarbonyl groups [15,16]. We followed the normal procedure of refluxing ketones with a large excess of P_4S_{10} in an insert solvent, such as toluene. The reaction times are long and the yields low. Lawesson's reagent, 2,4-bis-(4-methoxy)-1,3-dithiadiphosphetane-2,4-disulfide, is another general thionating reagent and the one used extensively for the conversion of carbonyl groups into thiocarbonyl groups [17,18]. After refluxing ketones with Lawesson's reagent in toluene for 3 h, thiones and toluene were codistilled from the reaction mixtures. Pure thiones were obtained in good yields after chromatographic separation on silica gel columns.

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TABLE 1 Physical and Spectral Data

Compd.	*R*^{1}	*R*^{2}	*Yield* %	*m.p* (°C)	^{1}*H NMR (CDCl$_3$/TMS)* *δ(ppm), J (Hz)*	*IR* *cm*$^{-1}$ *C=O*	*MS/FAB* *m/z* *(MH*$^+$*)*
4a	Ph	Me	81	179–180	7.76–6.94 (15H, m, aromatic), 2.32 (3H, s, Me)	1727.1	359
4b	Ph	CH$_2$Ph	78	155–156	7.46–6.86 (20H, m, aromatic), 3.59 (1H, d, *J* = 13.8 Hz, H in CH$_2$), 3.51 (1H, d, *J* = 13.8 Hz, H in CH$_2$)	1727.1	435
4c	(CH$_2$)$_4$		86	143–144	7.49–7.10 (10H, m, aromatic), 2.35 (4H, m, 2CH$_2$), 1.93 (4H, m, 2CH$_2$)	1718.9	323
4d	Et	Et	90	101–102	7.36–7.13 (10H, m, aromatic), 2.20 (4H, q, *J* = 7.2 Hz, 2CH$_2$), 1.13 (6H, t, *J* = 7.2 Hz, 2Me)	1716.9	325
4e	Pr	Pr	92	88–89	7.45–7.15 (10H, m, aromatic), 2.13 (4H, m, 2CH$_2$), 1.63 (4H, m, 2CH$_2$), 0.99 (6H, t, *J* = 7.3 Hz, 2Me)	1716.9	353
4f	*t*-Bu	Me	84	185–186	7.35–7.20 (10H, m, aromatic), 1.87 (3H, s, Me), 1.20 (9H, s, CMe$_3$)	1714.4	339

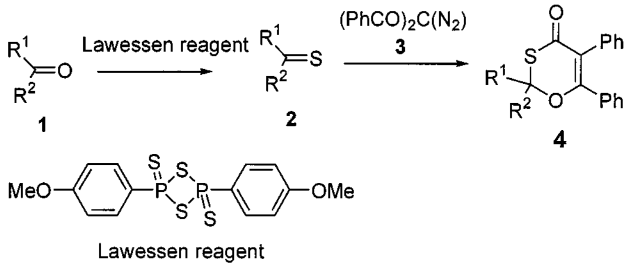
2-Diazo-1,3-diphenyl-1,3-propanedione reacted with thiones in refluxing anhydrous toluene for 1–2 h to give colorless cycloadducts, 4*H*-1,3-oxathiin-4-ones, in yields of 78–92%. All cycloadducts described in the present study were fully characterized by ^{1}H NMR, MS, and IR spectroscopies and by elemental analysis. Compared with the yields in the reaction with ketones [10], the yields in the reaction of thiones with 2-diazo-1,3-diphenyl-1,3-propanedione are higher (Tables 1 and 2).

EXPERIMENTAL

Melting points were obtained on a Yanaco melting point apparatus and are uncorrected. Elemental analyses were carried out on an Elementar Vario EL elemental analyzer. The ^{1}H NMR spectra were recorded in CDCl$_3$ solution on a Varian Inova 300 spectrometer with TMS as an internal standard. The IR spectra were taken on a Brucker Vector 22 FT-IR spectrophotometer in KBr. Mass spectra were obtained on a VG ZAB-HS mass spectrometer. TLC separations were performed on silica gel G plates with petroleum ether (30–60°C)/ethyl acetate (5:1) as the eluent, and the plates were visualized with UV light and/or iodine vapor.

TABLE 2 Elemental Analysis Data

			Cald.		*Found*	
Compd.	*Mol. Formula*	*Mol. Weight*	*C*	*H*	*C*	*H*
4a	C$_{23}$H$_{18}$O$_2$S	358.45	77.07	5.06	76.93	4.95
4b	C$_{29}$H$_{22}$O$_2$S	434.55	80.15	5.10	80.36	5.38
4c	C$_{20}$H$_{18}$O$_2$S	322.42	74.50	5.63	74.72	5.85
4d	C$_{20}$H$_{20}$O$_2$S	324.44	74.04	6.21	73.86	6.18
4e	C$_{22}$H$_{24}$O$_2$S	352.49	74.96	6.86	75.08	6.90
4f	C$_{21}$H$_{22}$O$_2$S	338.46	74.52	6.55	74.45	6.47



SCHEME 1 Synthesis of 2,2-disubstituted 5,6-diphenyl-4*H*-1,3-oxathiin-4-ones.

Synthesis of 2,2-Disubstituted 5,6-Diphenyl-4H-1,3-oxathiin-4-ones

General Procedure. Thione (**2**) (1 mmol) and 2-diazo-1,3-diphenyl-1,3-propanedione (**3**) (0.275 g, 1.1 mmol) were dissolved in anhydrous toluene (10 ml). The resulting mixture was refluxed for 1–2 h, the optimum reaction time being determined by TLC monitoring (silica gel). The solvent was evaporated under reduced pressure to give a residue that was crystallized from a mixture of petroleum ether (30–60°C) and ethyl acetate or separated on a silica-gel column with use of petroleum ether (30–60°C)/ethyl acetate (5:1) as the eluent to give colorless crystals **4** (Scheme 1).

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