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A new, unexpected synthesis of 1,3-dithietanones

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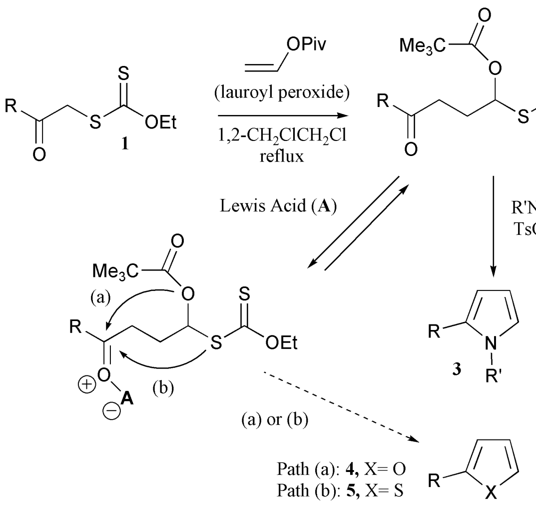
Treatment of a geminal pivaloxy xanthate, prepared by an intermolecular radical addition of a xanthate to vinyl pivalate, gives a 1,3-dithietanone, a little known class of compounds.

We recently described a practical and flexible synthesis of pyrroles outlined in Scheme 1.[1] It is based on the radical addition of an acetonyl xanthate **1** to vinyl pivalate[2] followed by heating of the adduct **2** with an amine. Not unexpectedly, treatment of the **2** with acid in the absence of amine produced the corresponding furan **4** but this reaction was somewhat capricious in our hands. Thiophene **5** was also formed in small amounts in certain cases.

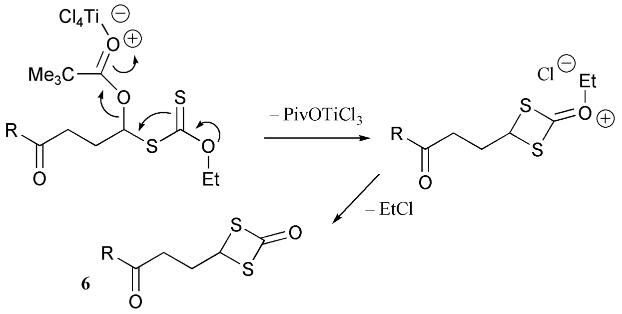
In order to improve the access to either the furans or the thiophenes, we examined the effect of a Lewis acid in a non-protic solvent. We reasoned that activation of the ketone by the Lewis acid would provoke a nucleophilic attack either by the oxygen of the pivalate to give the furan (path a) or by the sulfur of the xanthate to furnish ultimately the thiophene (path b).

In the event, exposure of xanthate **2a** to the action of titanium tetrachloride in dichloromethane gave neither the furan nor the thiophene in significant amounts.† The major product, isolated in quite good yield (81%), had lost both the xanthate and pivalate groups and exhibited, in addition to the ketone stretch band at 1690 cm^{-1}, a strong band at 1775 cm^{-1} suggesting the presence of a strained carbonyl group. All the spectral and analytical data were consistent with 1,3-dithietanone **6a**. 1,3-Dithietanones are very rare and only a few have been described in the past. Most are halogenated derivatives, accessible by partial hydrolysis of thiophosgene photodimers.[3] 4-Alkylidene-1,3-dithietanones are somewhat more common since these can be made by reacting the dianion of dithiocarboxylic acids with phosgene.[4]

This unexpected reaction proceeds presumably through an initial complexation of the Lewis acid with the carbonyl of the pivalate group which triggers a nucleophilic attack by the xanthate sulfur followed by cleavage of the intermediate with concomitant formation of ethyl chloride, as depicted in Scheme 2. With a convenient and highly efficient access to the precursors by the radical addition of a xanthate to vinyl pivalate, we could easily explore the generality of this transformation. As indicated by the examples collected in Table 1, both aromatic and aliphatic structures can be made and groups other than ketones (*e.g.* nitrile in **6j**) can be present. The reaction was not clean in the case of adduct **2g** containing a simple methyl ketone. A better result was observed with **2h** where the aliphatic ketone is sterically shielded. The relative sensitivity of cyclopropyl ketones to Lewis acids may have been one of the

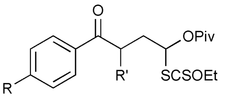
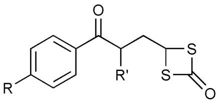
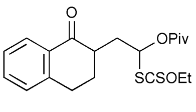
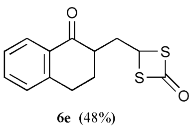
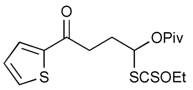
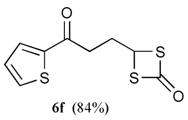
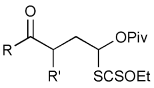
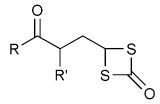
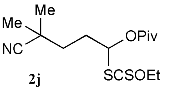
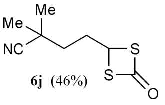


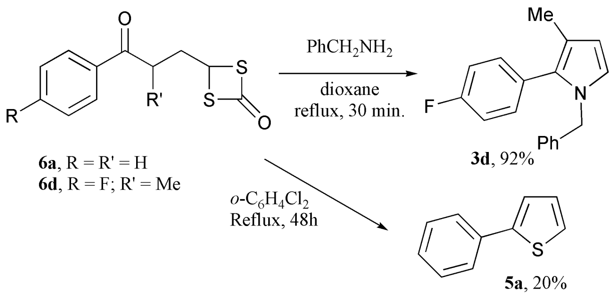
Scheme 1 Synthesis of pyrroles, furans, and thiophenes.



Scheme 2 Unexpected formation of 1,3-dithietanones.

Table 1 Synthesis of 1,3-dithietanones **6** from radical adducts **2**

Xanthate adduct **2**	1,3-Dithietanone **6**
 **2a**, R = R' = H **2b**, R = OMe; R' = H **2c**, R = Cl; R' = H **2d**, R = F; R' = Me	 **6a**, R = R' = H (81%) **6b**, R = OMe; R' = H (51%) **6c**, R = Cl; R' = H (71%) **6d**, R = F; R' = Me (67%)
 **2e**	 **6e** (48%)
 **2f**	 **6f** (84%)
 **2g**, R = R' = Me **2h**, R = Me$_3$C; R' = H **2i**, R = cyclopropyl; R' = H	 **6g**, R = R' = Me (—) **6h**, R = Me$_3$C; R' = H (47%) **6i**, R = Cyclopropyl; R' = H (10%)
	



Scheme 3 Some reactions of 1,3-dithietanones.

causes of the poor yield of **6i**. The conditions we have used in this initial study have not been optimised; nevertheless, the yields are synthetically useful. Lowering the temperature did not result in appreciable improvement and replacing titanium tetrachloride with $BF_3 \cdot OEt_2$ did not prove very satisfactory: relatively complex mixtures were obtained containing furan and thiophene among other compounds. The nature of the Lewis acid is clearly important but further, more extensive screening is still needed.

Little is known of the chemistry of the [1,3]dithietanone group. Heating compound **6d** with benzylamine in refluxing dioxane resulted in a good yield of pyrrole **3d** (Scheme 3). In contrast, heating dithietanone **6a** in refluxing dichlorobenzene for two days gave rise to thiophene **5a** in a disappointing 20% yield. The resistance to heat of the dithietanone motif was surprising.

This preliminary study has provided a simple, flexible, and convergent access to an unusual class of compounds. Further work is necessary to better delineate the scope of this approach and explore its synthetic potential.

Notes and references

† Typical example: a solution of xanthate **1a** (**1**, R = Ph; 1.00 g, 4.2 mmol) and vinyl pivalate (1.23 mL, 8.4 mmol) in 1,2-dichloroethane (4.2 mL) was heated under nitrogen for 15 min. A first batch of lauroyl peroxide (5 mol%) was added followed by another batch (2.5 mol%) after 90 min. and heating was continued until almost complete consumption of the xanthate (further amounts of lauroyl peroxide may be added if necessary). The solvent was then removed under vacuum and the residue purified by flash chromatography over silica gel (ethyl acetate–petroleum ether 5 : 95; a small layer of basic alumina is placed on top of the silica column to remove any lauric acid present). Adduct **2a** was obtained as a yellowish oil (1.40 g; 93%) and was used as such in the next step; ^1H NMR (400 MHz; $CDCl_3$): 1.19 (s, 9H), 1.39–1.42 (m, 3H), 2.40–2.44 (m, 2H), 3.12–3.16 (m, 2H), 4.61–4.68 (m, 2H), 6.72 (t, *J* 6.4, 1H), 7.47 (d, *J* 6.8, 2H), 7.49–7.57 (m, 1H), 7.95 (d, *J* 7, 2H); ^{13}C NMR (100 MHz; $CDCl_3$) δ (ppm): 13.7, 28.6, 34.2, 43.6, 70.3, 80.3, 128.1, 128.7, 133.4, 136.5, 176.8, 197.9, 210.1; IR (CCl_4, cm^{-1}): 1739 (C=O), 1692 (C=O), 1227 (C=S), 1051(C–S); *m*/*z* (CI) 385 ($M + NH_4^+$).

To a stirred solution of $TiCl_4$ (0.1 mL, 1 mmol) in freshly distilled dichloromethane (1 mL) was added a solution of adduct **2a** (200 mg, 0.5 mmol) in dichloromethane (1 mL). After stirring for 1 hour at room temperature and under an inert atmosphere, the reaction mixture was cooled in an ice bath and water was slowly added. The organic layer was separated, dried over sodium sulfate, and concentrated under reduced pressure. The residue was purified by flash chromatography over silica gel (ethyl acetate–petroleum ether 5 : 95) to give 1,3-dithietanone **6a** as a white solid (102 mg, 81%); it was recrystallised from dichloromethane–petroleum ether; mp 110–112 °C; ^1H NMR (400 MHz; $CDCl_3$) 2.61 (q, *J* 6.8, 2H), 3.23 (t, *J* 6.6, 2H), 4.35 (t, *J* 6.8, 1H), 7.49 (t, *J* 7.4, 2H), 7.61 (t, *J* 7.6, 1H), 7.97 (d, *J* 7.6, 2H); ^{13}C NMR (100 MHz; $CDCl_3$) δ (ppm): 26.9, 31.8, 36.2, 128.2, 128.9, 133.8, 136.3, 173.7, 197.8; IR (CCl_4, cm^{-1}): 1775 (C=O), 1690 (C=O); *m*/*z* (CI) 239 ($M + H^+$). Calc. for $C_{11}H_{10}O_2S_2$ (%): C, 48.44; H, 3.33. Found (%): C, 48.68; H, 3.45.

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