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An Unusual Reaction of Lawesson's Reagent with 1,8-Diketones: A Synthesis of Fused 1,4-Dithiins and Thiophenes

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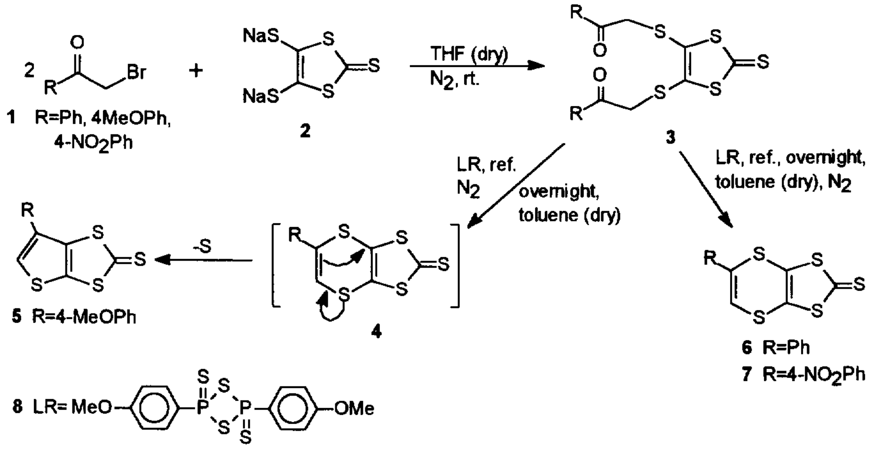
Abstract. Reaction of 1,8-diketones **3** with Lawesson's reagent **8** resulted in the formation of five and six-membered rings **5-7**, **18**, depending on the nature of the substituents. Product **6** is converted in two steps to the unsymmetric 'ET' analogue **20**, containing an extra double bond. Copyright © 1996 Elsevier Science Ltd

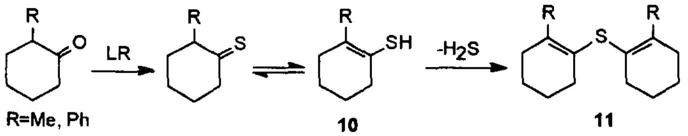
Use of Lawesson's reagent (LR) **8** for the chemical conversion of carbonyl to thiocarbonyl compounds has been well investigated.[1] One of its important applications involves the synthesis of thiophenes from 1,4-dicarbonyls. It was reported that the reaction mechanism presumably involves the formation of a 1,4-dithioxo intermediate which subsequently undergoes spontaneous *in situ* cyclization to give the corresponding thiophene.[2a] Although this reaction has been well investigated,[2] there is no example of its reaction with 1,8-dicarbonyl species.

In this letter, an unusual reaction of LR with 1,8-dicarbonyls is reported, which has been uncovered during the efforts to synthesise new superconducting derivatives of bis(ethylenedithio)tetrathiafulvalene, 'BEDT-TTF" or 'ET' **22**.[3]



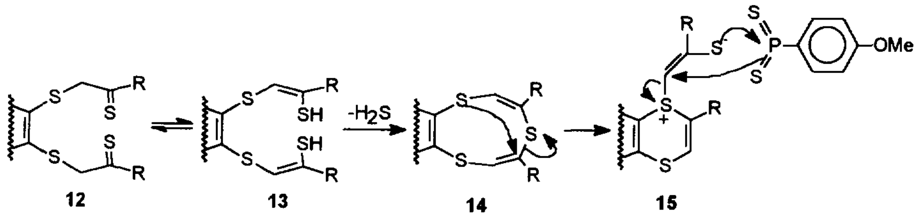
SCHEME I

As outlined in Scheme I, α-haloketones **1** were reacted with the readily available dithiolate salt **2**[4] in dry THF to obtain diketones **3** (72% R=Ph, 68% R=4-MeOPh and 52% R=4-NO_2Ph). Treatment of 1,8-diketones **3** with LR in refluxing toluene led to the formation of six-membered rings **6**[5] and **7**[6], when R=Ph (67%) and 4-NO_2Ph (42%), respectively, and to the fused thiophene **5**[7], when R=4-MeOPh (58%). The structure of **5** was proved by a X-ray diffraction analysis (to be published elsewhere) and showed that the loss of sulfur is adjacent to the R group.[8] Formation of two different products, five- and six-membered rings, shows that when R is electron donating group such as 4-MeOPh, an electrocyclic process is favoured, but when R is electron withdrawing such as Ph and 4-NO_2Ph, it stabilises the dithiin ring by delocalization of the π electron density.



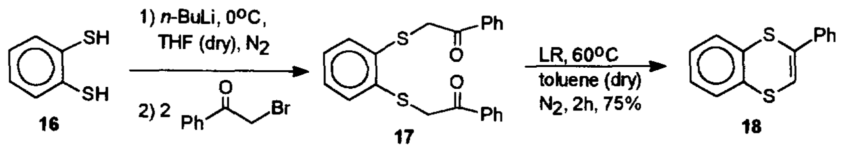
SCHEME II

In order to understand the mechanism of this unusual reaction of LR, **3** (R=Ph) was refluxed in dry toluene under nitrogen in the absence of LR. Even after five days, starting material was recovered. This proved that the presence of LR is vital. In the light of this result, it was considered that reaction goes via the 1,8-dithioxo intermediate **12** analogous to the synthesis of thiophenes from 1,4-dicarbonyls.[2a] It has been reported that ketones **9**, bearing α-hydrogens on treatment with LR form the enethiols **10** which, on standing for some days, gave sulfides **11** (Scheme II).[9] Hence, a possible explanation was then focused on the formation of the nine-membered ring **14** which results from cyclization of the dienedithiols **13** (Scheme III). Rearrangement of **14** gives the six-membered ring **15**, a zwitterion, which reacts with LR to give free six-membered-ring. Treatment of **3** (R=Ph) with LR at various temperatures 50 and 80°C in an attempt to isolate any intermediate which forms during the reaction, resulted in either isolation of starting material or slow conversion to the six-membered ring, respectively.



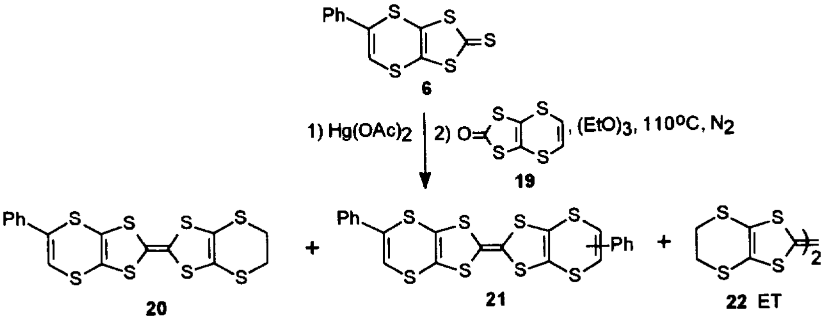
SCHEME III

In an other attempt, 1,8-diketone **17**, which was synthesised from the reaction of 1,2-benzenedithiol **16** with α-bromoketone, was treated with LR. Compared to the 1,8-diketones **3**, **17** gave the six-membered ring **18**[10] in a shorter time, 2 h, and at a lower temperature, 60°C (Scheme IV). Again, all attempts to isolate any stable intermediate failed.



SCHEME IV

Thione **6** was subsequently converted to a dehydro-ET analogue **20** (Scheme V). After replacement of thione sulfur with oxygen using $Hg(OAc)_2$, the product was coupled with **19** according to a standard procedure with $(EtO)_3P$ at 110°C to give four products.[11] Successful separation was achieved by silica column chromatography eluting with dichloromethane which resulted in pure cross-coupled product **20**[12] (32%), the mixture of diphenyl self-coupled products **21** (28%) and ET **22** (20%).



SCHEME V

In conclusion, an unusual reaction of LR with 1,8-diketones has been uncovered. Further exploration of cyclization of various diketone systems, and synthesis and properties of new ET analogues are under investigation and will be reported in due course.

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5 5-Phenyl-1,3-dithiolo[4,5-*b*]-1,4-dithiin-2-thione **6**: mp. 97°C (dec.); expected C:44.29%, H:2.01%; found C:44.14%, H:1.98%; EIMS (*m/z*) 298 (M^+); FABMS (*m/z*) 298 (M^+); ^1H NMR (270 MHz, $CDCl_3$) δ 6.66 (1H, s), 7.39 (3H, m), 7.54 (2H, m); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 213.79, 142.37, 134.97, 129.75, 129.31, 128.93, 128.76, 127.33, 117.60.

6 5-(4-nitrophenyl)-1,3-dithiolo[4,5-*b*]-1,4-dithiin-2-thione **7**: mp. 75°C (dec.); EIMS (*m/z*) 343 (M^+), 311 (M^+-S), 221 (M^+-Ph); FABMS (*m/z*) 343 (M^+); ^1H NMR (270 MHz, $CDCl_3$) δ 6.92 (1H, s), 8.25 (2H, d, J=8.93 Hz), 7.27 (2H, d, J=8.93 Hz); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 214.0, 141.0, 132.79, 132.58, 128.11, 126.02, 124.72, 124.22, 122.55.

7 4-(4-methoxyphenyl)thieno[2,3-*d*]-1,3-dithiol-2-thione **5**: mp. 137-139°C; expected C:48.64, H:2.70; found C:48.51, H:2.62; EIMS (*m/z*) 296 (M^+); FABMS (*m/z*) 297 ($M^+ + 1$); ^{1}H NMR (270 MHz, CDCl$_3$) δ 3.85 (3H, s), 6.97 (2H, d, J=8.79 Hz), 7.42 (2H, d, J=8.79 Hz), 7.54 (1H, s); ^{13}C NMR (67.8 MHz, CDCl$_3$) δ 214.73, 159.90, 136.15, 128.25, 127.83, 126.84, 126.20, 124.01, 114.62, 55.41.

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10 2-Phenyl-1,4-benzodithiin **18**: viscous liquid; EIMS (*m/z*) 242 (M^+), 210 (M^+-S), 165 (M^+-Ph); ^{1}H NMR (270 MHz, CDCl$_3$) δ 7.81 (1H, dd, J=1.5 Hz, J=8.64 Hz), 7.59 (2H, m); 7.42 (1H, m), 7.33 (3H, m), 7.20 (2H, dd, J=3.29 Hz, J=5.77 Hz), 6.64 (1H, s); ^{13}C NMR (67.8 MHz, CDCl$_3$) δ 118.19, 126.83, 127.52, 127.59, 127.74, 127.77, 128.16, 128.30, 128.48, 128.53.

11 Ozturk, T.; Rice, C. R.; Wallis, J. D. *J. Mater. Chem.*, **1995**, *5*, 1553.

12 2-(5,6-dihydro-1,3-dithiolo[4,5-*b*]-1,4-dithiin-2-ylidene)-5-phenyl-1,3-dithiolo[4,5-*b*]-1,4-dithiin **20**: mp. 62°C (dec.); expected C:41.92, H:2.18; found C:41.67, H:2.25; EIMS (*m/z*) 458 (M^+); FABMS (*m/z*) 459 ($M^+ + 1$); ^{1}H NMR (270 MHz, CDCl$_3$) δ 3.29(4H, s), 6.60 (1H, s), 7.35 (3H, m), 7.52 (2H, m); ^{13}C NMR (67.8 MHz, CDCl$_3$) δ 30.20, 118.59, 121.36, 123.08, 126.50, 127.22, 128.06, 128.76, 128.97, 129.03, 129.32, 135.48, 142.37.

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