Preparation of 2-Zincio-1,3-Dithianes and Di(1,3-dithian-2-yl)zinc and Their Reaction with Highly Functionalized Halides and α,β-Unsaturated Carbonyl Compounds

Vanda Cerè,[a] Silvia De Angelis,[a] Salvatore Pollicino,[a] Alfredo Ricci,*[a] Ch. Kishan Reddy,[b] Paul Knochel,[b] Gérard Cahiez[c]

[a] Dipartimento di Chimica Organica "A. Mangini", Via Risorgimento N°4, I-40136 Bologna, Italy
Fax +39(51)6443654

[b] Fachbereich Chemie der Phillips-Universität, Hans-Meerwein Strasse, D-35043 Marburg, Germany

[c] Laboratoire de Chimie des Organoélements associè au CNRS, Université Pierre et Marie Curie, 4 Place Jussieu F-75252 Paris, France

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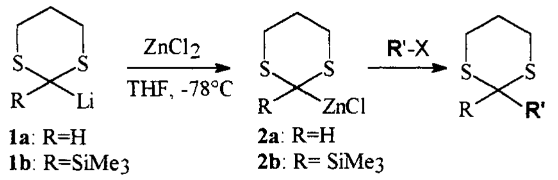
The title compounds were obtained by simple transmetallation of the corresponding lithium derivatives with $ZnCl_2$ or $ZnBr_2$. Contrary to 2-lithio-1,3-dithianes, 2-zincio-1,3-dithianes can react with a number of electrophiles bearing reactive functional groups to afford highly substituted 1,3-dithianes in satisfactory to excellent yields. The synthesis of the new organozinc derivative, di(1,3-dithian-2-yl)zinc, which efficiently adds to enones, is also reported.

Since the discovery of 2-lithio-1,3-dithiane by Corey and Seebach,[1] its use has been ubiquitous in the chemical literature and a number of very thorough reviews[2] on the use of 1,3-dithianes in organic synthesis have been published. Among the standard type of reactions, many examples of displacement reactions between 2-lithio-1,3-dithiane derivatives and a wide range of alkyl halides have appeared in the literature in the last 15 years and in many cases were used in the total synthesis of natural products.

Although good to excellent yields were reported for these alkylation reactions, carried out via normal addition procedures, major side products and poor yields can be a major drawback due to the high reactivity and basicity of this highly polar organolithium derivative[3] which, consequently, cannot be employed in the displacement reactions of halides bearing reactive functional groups. Moreover, autoxidation of 2-lithio-1,3-dithiane in THF has been reported[4] to occur when the reaction is exposed to air.

With the aim of extending and reevaluating the use and the synthetic potential of 2-lithio-1,3-dithianes and being aware that very few studies seem to have been carried out on 1,3-dithiane anions with other counterions, such as potassium, magnesium or copper,[5] an investigation has been undertaken with the purpose of studying the variation of chemoselectivity upon changing the metal counterion. Transmetallation from lithium to zinc was chosen because of the inherently covalent character of the C—Zn bond, a feature which has recently prompted a great deal of selective synthesis with polyfunctionalized organo-metallic reagents.[6] In addition, the preparation and reactivity of polyfunctional zinc compounds bearing sulfur functionalities have been reported,[7] but to our knowledge are unprecedented for the dithianyl systems. The preliminary results of this investigation are reported herein.

After the transmetallation had been performed, according to Yamamoto,[8] by treating the 2-lithio-1,3-dithiane with $ZnCl_2$, the resulting organozinc derivative was used in displacement reactions with functionalized halides as shown in Scheme 1.



Scheme 1

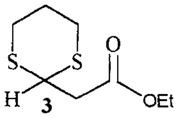
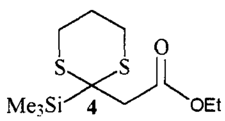
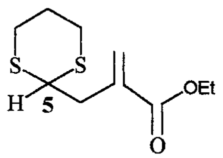
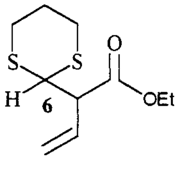
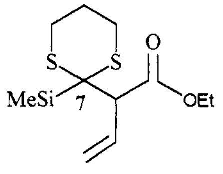
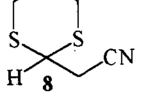
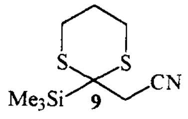
The relevant results obtained when, as a means of comparison, lithio- and zinciodithiane derivatives **1** and **2**, respectively, were employed, are summarized in the Table.

The trend which emerges from the analysis of the data in the Table suggests a general and substantially beneficial effect on the reactions with electrophiles when 2-zincio-1,3-dithianes were employed. Thus, reaction of ethyl bromoacetate with **2a** leads to 45% of the expected product **3** (entry 2) compared with the 10% yield obtained when the lithium derivative **1a** was employed (entry 1). Moreover, in the reaction of the 2-zincio-1,3-dithiane derivative, the unreacted 1,3-dithiane was completely recovered after hydrolytic quenching, thereby indicating the high level of selectivity of this organometallic reagent towards the electrophile. This behavior observed in all the reactions reported in the Table did not hold true when **1a** was employed. In all cases, a number of unidentifiable byproducts, probably due to the unselective attack of the highly reactive and nucleophilic organometallic reagent, were found in the reaction mixture.

An improvement of the reaction yields starting from both of the silylated dithianyl derivatives **1b** (entry 3) and **2b** (entry 4) can also be noted; a likely explanation lies in the higher stabilization of the intermediate carbanion[9] which might inhibit side reactions such as the autoxidation responsible for extensive decomposition of the starting organometallic species mentioned above. The commonly employed[6-8] Zn→Cu transmetallation did not effect any substantial improvement of the reaction yields in the title reactions.

The features outlined thus far in the comparison between **1** and **2** in the reaction with ethyl bromoacetate apply to a number of electrophiles. In particular, the reaction with ethyl (2-bromomethyl)acrylate further highlights the merits of the Li→Zn transmetallation strategy as shown by the dramatic increase in the yields of **5** when going from **1a** (12%, entry 5) to **2a** (91%, entry 6). Accordingly, reaction of ethyl 4-bromocrotonate with 2-lithio-1,3-dithiane derivatives gave, in the most favourable case, only trace amounts of the expected products **6** and **7** (entries

Table. Functionalized Dithianyl Derivatives by the Reaction of 2-Lithio- and 2-Zincio-1,3-dithianes **1a**, **1b**, **2a** and **2b** with Electrophiles

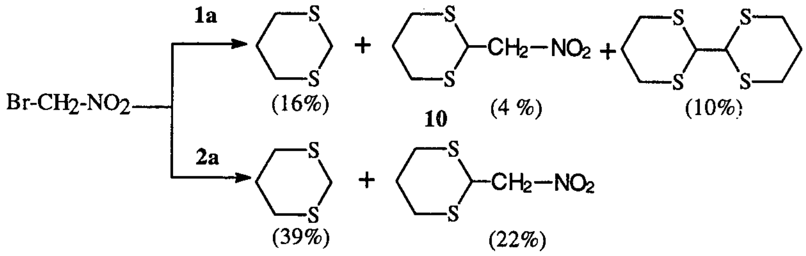
Entry	2-Lithio- or 2-Zincio-1,3-dithiane	Electrophile	Product	Yield[a] (%)
1	**1a**	$BrCH_2CO_2Et$		10
2	**2a**			45
3	**1b**			55
4	**2b**			71
5	**1a**	$BrCH_2C(=CH_2)CO_2Et$		12
6	**2a**			91
7	**1a**	(E)-$BrCH_2CH=CHCO_2Et$		–
8	**2a**			35
9	**1b**			5
10	**2b**			53
11	**1b**	ICH_2CN	–	–
12	**2a**			26
13	**2b**			71

[a] Yield of isolated products.

7 and 9). These products were, on the other hand, isolated in acceptable (35 %, entry 8) to satisfactory (53 %, entry 10) yields from the corresponding 2-zincio-1,3-dithiane reagents. It is worth noting that in these products a γ-regioselectivity was observed, in line with previous[10] findings concerning the reactivity of allylic halides with organometallic reagents.

Displacement reactions between metallated 1,3-dithianes and electrophiles bearing a cyano moiety as the reactive functional group are, to our knowledge, unprecedented since only addition reactions to nitriles by 2-lithio-1,3-dithiane have been reported so far in the synthesis of aminoketene dithioacetals.[11] The milder reactivity of type-**2** metallated dithianes allowed once more for a displacement process to prevail over an undesired addition. In the reaction using iodoacetonitrile, products **8** (entry 12, 26 %) and **9** (entry 13, 71 %) were isolated in reasonable yields starting from **2a** and **2b**, respectively, whereas the corresponding reaction run with **1b** failed, as only byproducts originating mainly from addition to the cyano group were detected.

A final attempt to evaluate the reactions features of zinciodithiane derivatives was focused on the use of nitro-containing reactive electrophiles in the displacement



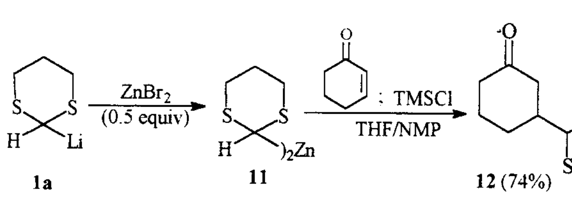
Scheme 2

process. In the reaction between nitroarenes and lithiodithianes competition between addition and redox processes has been reported[12] to occur via a single electron transfer (SET) which gives rise, through a dithian-2-yl radical, to a complex reaction mixture in which 1,3-dithianes and 2,2′-bi(1,3-dithianes) are detectable, among other products.

In order to keep the metallated dithiane concentrations low with respect to the reacting electrophile, **1a** and **2a** were reacted with bromonitromethane according to the inverse addition procedure. As shown in Scheme 2, these reactions afforded mixtures of different compositions.

Interestingly, in addition to a quite sizeable improvement in the yields of the target product **10** and the recovery of a larger amount of the unreacted 1,3-dithiane, the reaction with **2a** does not result in formation of the dimeric byproduct, 2,2′-bi(1,3-dithiane), thus indicating the lower efficiency of the SET processes.[13]

Addition of **2a** and **2b** to enones failed since only starting materials were recovered. Taking into account the higher reactivity of diorganozinc derivatives[14] and the beneficial effect of cosolvents as promoters of conjugate additions,[15] a modified procedure was devised based on the preparation of di(1,3-dithian-2-yl)zinc (**11**). Thus the reaction of 1,3-dithian-2-yllithium (**1a**) with 0.5 equivalents of zinc bromide at −50 °C followed by warming up to room temperature furnishes a THF solution of the new reagent **11** which undergoes a smooth Michael addition to cyclohex-2-enone in the presence of one equivalent of chlorotrimethylsilane in a 1:1 mixture of THF/NMP (*N*-methylpyrrolidinone) leading to the 1,4-addition product **12** in 75% yield.



Scheme 3

In summary, we have prepared zincated dithiane derivatives **2a–b** and **11** and have demonstrated their synthetic utility in alkylation, allylation and 1,4-addition. On account of its efficiency, flexibility and operational simplicity, this method should find further practical use in the synthesis of a wider range of highly functionalized new, synthetically valuable 1,3-dithianyl derivatives.

^{1}H NMR spectra were recorded in $CDCl_3$ on a Varian Gemini (300 MHz) spectrometer using TMS as internal standard. Coupling constants are reported in Hz. ^{13}C NMR spectra were recorded in $CDCl_3$ on a Varian Gemini 300 (75.5 MHz) spectrometer. Chemical shifts are reported as δ in units of parts per million (ppm) relative to $CDCl_3$ ($\delta = 77.2$) as an internal reference. GC mass spectra were recorded at 70 eV on a Carlo Erba QMD 1000 (electron impact, EI) or on a VG-7070-E high resolution (HR) spectrometer. GC analysis were carried out with a Hewlett Packard 5890 gas chromatograph. All reactions were performed under an atmosphere of dry Ar. THF was distilled under Ar from sodium/benzophenone ketyl before use. NMP was purified by distillation over CaH_2. The purity of the commercially available BuLi was checked according to Gilman.[16] Reactions were monitored by GC or TLC analysis of hydrolyzed reaction aliquots. $ZnCl_2$ (0.7 M) solution in anhyd Et_2O (from $LiAlH_4$) was prepared and titrated as previously described.[17] Petroleum ether used had bp 40–60 °C. Satisfactory microanalysis obtained (**4–6, 8, 12**): C ± 0.3; H ± 0.22.

Reactions of Lithiodithianes 1a–b with Electrophiles; General Procedure I:

To a solution of 1,3-dithiane or 2-trimethylsilyl-1,3-dithiane (2.5 mmol) in THF (8 mL) under Ar and at −40 °C was added slowly a 1.6 M solution of BuLi (1.56 mL, 2.5 mmol) with stirring, leading to the formation of **1a** or **1b**. After 1.5 h at −25 °C, the mixture was cooled at −78 °C and the appropriate electrophile (2.5 mmol) in THF (2 mL) was added by means of a syringe. After stirring overnight at r.t., aq sat. NH_4Cl soln (4 mL) was added and the aqueous layer extracted with Et_2O (2 × 20 mL). The combined organic layers were washed with brine and dried ($MgSO_4$). Removal of the solvent afforded a crude product which was purified by flash chromatography with silica gel (Table).

Reactions of Zinciodithianes 2a–b with Electrophiles; General Procedure II:

To a solution of 1,3-dithiane or 2-trimethylsilyl-1,3-dithiane (2.5 mmol) in THF (8 mL) under Ar and at −40 °C was added slowly a 1.6 M solution of BuLi (1.56 mL, 2.5 mmol) with stirring. After 1.5 h at −25 °C, the mixture was cooled to −78 °C and a 0.7 M solution of $ZnCl_2$ in Et_2O (3.6 mL, 2.5 mmol) was added with a syringe, leading to formation of **2a** or **2b**. After 1 h at 0 °C, the mixture was cooled to −78 °C and the appropriate electrophile (2.5 mmol) in THF (2 mL) was added. After stirring overnight at r.t., aq sat. NH_4Cl soln (4 mL) was added and the aqueous layer extracted with Et_2O (2 × 20 mL). The combined organic layers were washed with brine and dried ($MgSO_4$). Removal of the solvent afforded a crude product which was purified by flash chromatography with silica gel (Table).

Ethyl (1,3-Dithian-2-yl)acetate (**3**):

The product was obtained starting from **2a** (2.5 mmol) and with ethyl bromoacetate as the electrophile (2.5 mmol, 0.280 mL) following the general procedure II. The crude was purified by flash chromatography (eluent: Et_2O/petroleum ether, 10:40) affording 0.231 g (45%) of **3** as a pale yellow oil.

^{1}H NMR: $\delta = 1.2$ (3 H, t, $J = 7.0$ Hz), 1.8 (1 H, m), 2.1 (1 H, m), 2.7 (2 H, d, $J = 7.5$ Hz), 2.8 (4 H, m), 4.1 (2 H, q, $J = 7.0$ Hz), 4.3 (1 H, t, $J = 7.5$ Hz).

^{13}C NMR: $\delta = 14.2, 25.3, 29.5, 40.7, 42.0, 61.1, 170.1$.

MS: m/z (%) = 206 (M^+, 77), 132 (96), 119 (100).

HRMS: m/z calc. for $C_8H_{14}O_2S_2$: 206.0435; found: 206.0468.

Ethyl (2-Trimethylsilyl-1,3-dithian-2-yl)acetate (**4**):

The product was obtained starting from **2b** (2.5 mmol) and using ethyl bromoacetate (2.5 mmol, 0.280 mL) as the electrophile, following the general procedure II. Flash chromatography (eluent: Et_2O/petroleum ether, 10:40) of the crude, afforded 0.493 g (71 %) of the product **4** as a pale yellow oil.

^{1}H NMR: δ = 0.3 (9 H, s), 1.3 (3 H, t, J = 7.5 Hz), 1.8 (1 H, m), 2.1 (1 H, m), 2.5–3.1 (4 H, m), 3.2 (2 H, s), 4.1 (2 H, q, J = 7.5 Hz, 2 H).

^{13}C NMR: δ = 2.6, 14.3, 23.8, 24.9, 34.2, 42.6, 60.7, 168.3.

MS: m/z (%) = 278 (M^+, 26), 205 (95), 73 (100).

$C_{11}H_{22}O_2S_2Si$	calc.	C 47.47	H 7.97
(278.1)	found	47.28	7.94

Ethyl 2-(1,3-Dithian-2-ylmethyl)acrylate (**5**):

The product was obtained according to the general procedure II starting from **2a** (2.5 mmol) and using ethyl 2-(bromomethyl)-acrylate as the electrophile (2.5 mmol, 0.350 mL). Flash chromatography (eluent: Et_2O/petroleum ether, 10:90) afforded 0.528 g (91 %) of the product **5** as a colorless oil.

^{1}H NMR: δ = 1.3 (3 H, t, J = 7.1 Hz), 1.8 (1 H, m), 2.1 (1 H, m), 2.68 (CHCH_2, 2 H, d, J = 7.6 Hz), 2.8 (4 H, m), 4.15 (2 H, q, J = 7.1 Hz), 4.2 (CH, 1 H, t, J = 7.6 Hz), 5.6 (=CH_2, 1 H, d, J = 1.4 Hz), 6.3 (=CH_2, 1 H, d, J = 1.4 Hz).

^{13}C NMR: δ = 14.2, 25.8, 30.0, 38.1, 45.5, 60.9, 127.9, 136.1, 166.4.

MS: m/z (%) = 232 (M^+, 5.7), 119 (100).

IR (neat): ν = 2981, 2934, 1713, 1629, 1188, 1133 cm^{-1}.

$C_{10}H_{16}O_2S_2$	calc.	C 51.69	H 6.94
(232.4)	found	51.67	7.23

Ethyl 2-(1,3-Dithian-2-yl)but-3-enoate (**6**):

The product was prepared following procedure II starting from **2a** (2.5 mmol) and using ethyl 4-bromocrotonate (2.5 mmol, 0.460 mL) as the electrophile. The crude product was purified by flash chromatography (eluent: Et_2O/petroleum ether, 10:90) affording 0.203 g (35 %) of **6** as a pale yellow oil.

^{1}H NMR: δ = 1.2 (3 H, t, J = 7.1 Hz), 1.8 (1 H, m), 2.1 (1 H, m), 2.7 (4 H, m), 3.3 (1 H, dd, J = 9.6 Hz), 4.1 (2 H, q, J = 7.1 Hz), 4.2 (1 H, d, J = 9.6 Hz), 5.2 (2 H, m), 5.7 (1 H, m).

^{13}C NMR: δ = 14.0, 25.3, 28.8, 29.1, 47.1, 55.2, 61.0, 119.7, 132.6, 170.6.

MS: m/z (%) = 232 (M^+, 48), 145 (100).

$C_{10}H_{16}O_2S_2$	calc.	C 51.69	H 6.94
(232.4)	found	51.75	7.19

Ethyl 2-(2-Trimethylsilyl-1,3-dithian-2-yl)but-3-enoate (**7**):

The product was prepared from **2b** (2.5 mmol) and ethyl 4-bromocrotonate (2.5 mmol, 0.460 mL) following the general procedure II. Purification of the crude product by flash chromatography (eluent: Et_2O/petroleum ether, 5:95) afforded 0.402 g (53 %) of **7**.

^{1}H NMR: δ = 0.3 (9 H, s), 1.3 (3 H, t, J = 7.1 Hz), 1.8 (1 H, m), 2.1 (1 H, m), 2.3–2.5 (2 H, m), 2.9 (1 H, m), 3.2 (1 H, m), 3.97 (CHCH=, 1 H, d, J = 9.2 Hz), 4.1 (2 H, q, J = 7.1 Hz), 5.15 (=CH_2, 2 H, m, J_{trans} = 11.8 Hz, J_{cis} = 4.1 Hz, J_{vic} = 9.2 Hz), 6.03 (CHCH=CH_2, 1 H, m).

^{13}C NMR: δ = −0.74, 14.1, 23.5, 24.1, 29.7, 38.7, 57.8, 60.7, 118.1, 135.2, 171.9.

MS: m/z (%) = 304 (M^+, 2), 191 (38), 73 (100).

HRMS: m/z calc. for $C_{13}H_{24}O_2S_2Si$: 304.0987; found: 304.0877.

(1,3-Dithian-2-yl)acetonitrile (**8**):

The product was obtained according to procedure II starting from **2a** (2.5 mmol) and using iodoacetonitrile (2.5 mmol, 0.185 mL) as the electrophile. After flash chromatography (eluent: Et_2O/petroleum ether, 30:70), 0.111 g (26 %) of the product were recovered.

^{1}H NMR: δ = 2.0 (2 H, m), 2.7–3.2 (4 H, m), 2.9 (2 H, d, J = 7.5 Hz), 4.2 (1 H, t, J = 7.5 Hz).

^{13}C NMR: δ = 24.8, 25.3, 26.6, 46.7, 118.

MS: m/z (%) = 159 (M^+, 36), 119 (100).

$C_6H_9NS_2$	calc.	C 45.25	H 5.69
(159.3)	found	45.23	5.93

(2-Trimethylsilyl-1,3-dithian-2-yl)acetonitrile (**9**):

The reaction was performed according to procedure II starting from **2b** (2.5 mmol) and using iodoacetonitrile (2.5 mmol, 0.185 mL) as the electrophile. Flash chromatography (eluent: Et_2O/petroleum ether, 30:70) afforded 0.320 g (71 % yield) of **9** as a colorless oil.

^{1}H NMR: δ = 0.3 (9 H, s), 1.8 (1 H, m), 2.0 (1 H, m), 2.4 (1 H, m), 2.45 (1 H, m), 3.0 (2 H, m), 3.2 (2 H, s).

^{13}C NMR: δ = −3.5, 23.5, 24.3, 27.6, 33.5, 118.3.

MS: m/z (%) = 231 (M^+, 10), 132 (100).

HRMS: m/z calc. for $C_9H_{17}NS_2Si$: 231.0571; found: 231.0623.

2-Nitromethyl-1,3-dithiane (**10**):

The product was prepared with an inverse addition procedure with respect to procedure II by adding with a cannula a THF solution (10 mL) of **2a** (2.6 mmol) to a solution of bromonitromethane (0.349 g, 2.5 mmol) in THF (5 mL). The crude product was purified by flash chromatography (eluent: Et_2O/petroleum ether, 30:70) affording 0.098 g (22 %) of **10**. NMR analysis of the product revealed the presence of the nitro and *aci*-nitro forms in a 3:1 ratio.

^{1}H NMR: δ = (nitro) 1.8–2.2 (2 H, m), 2.7–3.0 (4 H, m), 4.5 (1 H, t, J = 7.5 Hz), 4.7 (2 H, d, J = 7.5 Hz); (*aci*-nitro) 1.8–2.2 (2 H, m), 2.8–3.3 (4 H, m), 4.2 (1 H, d, J = 10.5 Hz), 5.2 (1 H, s), 6.2 (1 H, d, J = 10.5 Hz).

Di(1,3-dithian-2-yl)zinc (11):

A three-necked 100-mL flask was charged with 1,3-dithiane (2.4 g, 20 mmol) in anhyd THF (35 mL), cooled to −60 °C, and BuLi (14.6 mL, 20 mmol) was added slowly. After stirring for 2 h at −30 °C, $ZnBr_2$ (2.25 g, 10 mmol) in THF was added at −50 °C. The mixture was allowed to reach r.t. and was stirred for 0.5 h.

3-(1,3-Dithian-2-yl)cyclohexanone (12):

A three-necked 100-mL flask was charged with THF (5 mL) and NMP (5 mL) and cooled to −30 °C. Cyclohex-2-enone (480 mg, 5 mmol) and TMSCl (500 mg, 5 mmol) were added, followed by the above prepared zinc reagent **11** in THF. The mixture was allowed to reach r.t., stirred for 6 h and was poured into aq 10 % HCl soln (5 mL) in THF (20 mL). The resulting mixture was stirred for 5 min and worked up as usual. After evaporation of the solvents, the crude product was purified by flash chromatography (eluent: hexane/Et_2O, 80:20) to give **12** (850 mg, 75 %) as a colorless oil.

^{1}H NMR: δ = 4.01 (1 H, d, J = 4.9 Hz), 2.86–2.79 (4 H, m), 2.48–2.01 (8 H, m), 1.77–1.15 (3 H, m).

^{13}C NMR: δ = 210.1, 53.3, 45.0, 43.4, 40.9, 30.8, 28.3, 25.9, 24.6.

IR (neat): ν = 2935, 1710, 1421, 1224, 910, 764 cm^{-1}.

MS: m/z (%) = 216 (M^+, 9.5), 119 (100).

$C_{10}H_{16}OS_2$	calc.	C 55.51	H 7.45
(216.4)	found	55.20	7.47

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