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1,3-BENZODITHIOLE TETRAOXIDE AS A CH_2^{2-} SYNTHON

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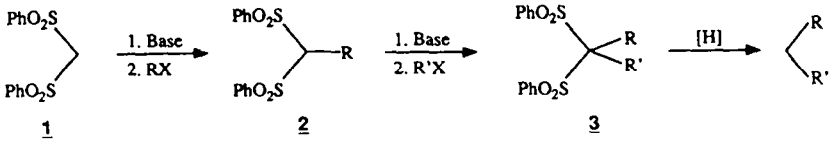
ABSTRACT. 1,3-Benzodithiole tetraoxide (BDT) 4 is more reactive in alkylation reactions than the commonly used bis(benzenesulfonyl)methane (1). This is demonstrated notably in dialkylations with sterically demanding alkyl halides. Besides its ready access and larger scope of applications, BDT has two other advantages over 1, a lower molecular weight and higher crystallinity of its alkylated derivatives. As in 1, the sulfone groups in BDT are readily cleaved by reduction with Mg in methanol.

RESULTS AND DISCUSSION

Bis(benzenesulfonyl)methane (1) is a useful synthon for CH_2^{2-}.[1] Deprotonation of 1 and its monosubstituted derivatives can be achieved under very mild conditions,[2,3] and the resulting anions are readily alkylated with electrophiles. After their employment as electron withdrawing groups, the phenylsulfonyl functionalities can be reductively removed by a variety of methods.



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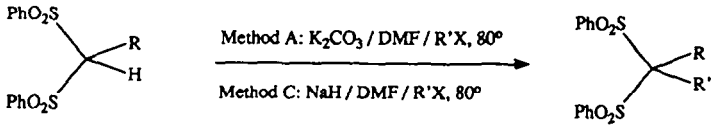
The mono and dialkylation of 1, however, become difficult when sterically demanding electrophiles are used as non-bonded repulsion between the incoming electrophile and the bulky phenylsulfonyl groups prevents efficient alkylation.[4,5] Treatment of the sodium anion of 1 (NaH/DMF/RT) with 2 eq of i-PrI at 80°C (method C) led to a 13:1 mixture of **2a**:1 from which **2a** was obtained in 74% yield after column chromatography (Table 1, entry 1). A similar mixture of **2a** and 1 was obtained by stirring a suspension of K_2CO_3, 1, and 2 eq of i-PrI in DMF (method A) for 7 days.[6] The reactions are accompanied by the formation of a red, polar material resulting from the competitive decomposition of isopropyl iodide. The limitations of this method become even more evident upon alkylation of **2a**. Although methylation of **2a** affords a high yield of the disubstituted derivative **3a**, ethylation proceeds only to 56% conversion after 36 h (mixture of **2a** and **3b**) (Table 1, entries 2 and 3). Increasing the temperature to 110°C has little effect (59% conversion) whereas performing the reaction at 40 °C leads to only 37% conversion after 42 h.

A similar obstacle is encountered upon the attempted reaction of primary monosubstituted derivatives of 2 and secondary electrophiles. 3-Phenyl-1,1-bis(phenylsulfonyl) propane (**2b**) can be obtained in high yield (96%) by method A, but no trace of **3c** is observed after 39 h of reaction with i-propyl iodide (Table 1, entries 4 and 5).

It seemed reasonable that 1,3-benzodithiole tetraoxide 4 could serve as a viable alternative to 1 since the two sulfone functionalities, being part of a fused ring system, are held in the same plane. Steric interactions during intermolecular transformations should therefore be reduced. In addition, the electronic properties of BDT and its derivatives should mimic those of bis(phenylsulfonyl)methane 1 and thus assure the facile reductive cleavage of the sulfonyl groups.[7] BDT can be obtained by the oxidation (H_2O_2/AcOH) of 1,3-benzodithiole,[8] synthesized in three steps from

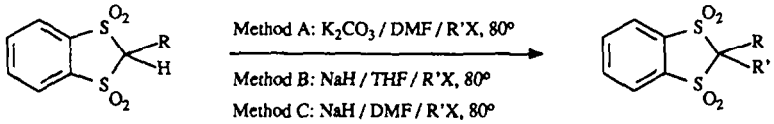
anthranilic acid. Large scale synthesis is viable and the product, BDT, is easily purified by recrystallization from ethanol (mp 186-188°C).

Table 1: Alkylations of 1 and Monosubstituted Derivatives.



Entry	R	R'(X)	Method	Time (h)	Product	m.p. (°C)	Yield (%)
1	H	*i*-Pr (I)	C	36	**2a**	135-136	74
2	*i*-Pr	Me (I)	C	18	**3a**	130-132	96
3	*i*-Pr	Et (I)	C	36	**3b**		59% conversion
4	H	$PhCH_2CH_2(Br)$	A	24	**2b**	139-140	96
5	$PhCH_2CH_2$	*i*-Pr (I)	C	39	**3c**		0

Table 2. Alkylations of BDT (4) and Monosubstituted Derivatives.



4 (R = H)

Entry	R	R'(X)	Method	Time (h)	Product	m.p. (°C)	Yield (%)
1	H	*i*-Pr (I)	A	24	**5a**	208-210	82
2	H	*i*-Pr (I)	B	38	**5a**	208-210	84
3	*i*-Pr	Me (I)	B	20	**6a**	181-183	88
4	*i*-Pr	Et (I)	B	24	**6b**	209-211	87
5	*i*-Pr	iBu (Br)	C	24	**6c**	191-192	88
6	*i*-Pr	$c\text{-}C_6H_{11}CH_2(Br)$	C	17	**6d**	178-179	81
7	*i*-Pr	*i*-Pr (I)	C	36	**6e**		50% conversion
8	*i*-Pr	$PhCH_2CH_2$ (Br)	B	24	**6f**	162-163	75[a]
9	H	$PhCH_2CH_2$ (Br)	A	36	**5b**	122-123	97
10	$PhCH_2CH_2$	*i*-Pr (I)	C	13	**6f**	162-163	93
11	$PhCH_2CH_2$	Me_3CCH_2 (I)	C	38	**6g**		42% conversion

[a] 25% elimination; reaction driven to completion by 2 subsequent additions of NaH and $PhCH_2CH_2Br$

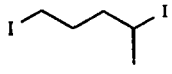
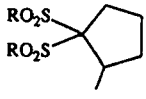
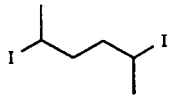
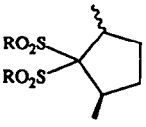
The iso-propylation of BDT can be effected in THF (method B, 38 h) to afford an 84% yield of **5a** after recrystallization. Preparation of **5a** by method A leads to an 82% yield in a shorter period of time (24 h) (Table 2, entries 1 and 2). In contrast to **2a**, the sodium salt of **5a** reacts readily with various sterically demanding electrophiles (Table 2, entries 3 - 6). Methylation and ethylation, to afford **6a** (88%) and **6b** (87%) respectively, can be carried out in THF (method B). The use of alkyl bromides containing β-substituents such as *i*-butyl bromide and cyclohexyl-

methyl bromide also furnishes the expected products, 6c (88%) and 6d (81%), when the reaction is performed in DMF (method C). Treatment of 5a with β-phenethyl bromide leads to a mixture of 6f and 5a due to competitive elimination which affords styrene. Whereas this reaction can be forced to completion by two subsequent additions of NaH and β-phenethyl bromide, it is much more convenient to reverse the order of alkylation. 2-Phenylethyl-1,3-benzodithiole tetraoxide (5b), readily obtained by method A (97%), affords a 93% yield of 6f upon treatment with isopropyl iodide (Table 2, entries 9 and 10). Limitations become apparent with highly hindered systems. Thus isopropylation of 6a only proceeds to 50% completion (mixture of 6e and 5a) after 36 h (entry 7), and the reaction of 5b with neopentyl iodide leads to 42% conversion after 38h (entry 11).

It should be noted here that unlike substituted derivatives of bis(phenylsulfonyl)methane (1) which are often voluminous solids, all BDT derivatives prepared to date are highly crystalline and can be purified by simple recrystallization from ethanol.

BDT also proves more effective than 1 in cycloalkylation reactions (Table 3). Reaction of 1 or BDT with 1,4-diiodopentane furnishes the cyclic disulfones (3d and 6h) in identical 82% yields. Cycloalkylation of BDT with the more sterically demanding 2,5-diiodohexane affords a mixture of diastereomeric dimethylcyclopentanes 6l in 71% yield after 48 h at 40°C. After 66 h, under the same conditions, the cycloalkylation of 1 proceeds only to 75% completion. Reactions performed at 80°C leads to lower yields of cyclic products due to competitive decomposition of the diiodide.

Table 3. Cycloalkylations with Sulfones 1 and 4.

Dihalide	Sulfone	Method	Time (h)	Product		Yield
	1	A	40		(3d)	82%
	4 (BDT)	A	24		(6h)	82%
	1	A,40 °C	66			75% conversion
	4 (BDT)	A,40 °C	48		(6l)	71%

Finally, the sulfone functionalities are easily cleaved by reduction with magnesium in methanol.[16] In this fashion, 4-methylpentylbenzene (72%) and 3-methylbutylcyclohexane (50%) were obtained from sulfones 6f and 6d respectively

6f R = CH_2CH_2Ph 7 72%

6d CH_2-c-C_6H_{11} 8 50%

In conclusion, we have introduced 1,3-benzenedithiol tetraoxide (BDT) as a new synthon for CH_2^{2-}. BDT, readily available in large quantities and more reactive than the commonly employed bis(phenylsulfonyl)methane, should find a wide range of practical application in synthetic organic chemistry.

EXPERIMENTAL SECTION

General. THF was distilled from sodium benzophenone ketyl ether. DMF was stirred overnight at 50 °C over CaH_2 and then distilled under reduced pressure. Methanol and ethanol (Merck, analytical grade) were used as supplied. Reagents were purified by standard procedures when deemed appropriate. ^1H NMR spectra were recorded on a Bruker WM 360 (360 MHz) or a Varian XL-200 (200 MHz) spectrometer. Mass spectra were measured on a Varian CH 4 or SM 1 spectrometer at 70 eV. Intensities are given in parenthesis. Melting points were determined on a Büchi 510 apparatus and are not corrected. Elemental analyses were performed by H. Eder, Institute of Pharmaceutical Chemistry, University of Geneva.

1,3-Benzodithiole 1,1,3,3-tetraoxide (BDT) (4).

76 ml of aq. H_2O_2 were added to a mixture of 1,3-benzodithiole[8] (16.58 g, 0.108 mol) in 175 ml of acetic acid and stirred at 20 °C.[9] After 2h, the temperature was raised to 50 °C and stirring was continued overnight (15h). The initially cloudy reaction mixture turned homogeneous after 3h at 50 °C and showed a colorless precipitate after 15 h. The mixture was cooled to 0 °C, the crystalline product collected by suction filtration and washed with water. The crude product (20.39 g, 87%) was recristallized from ethanol (1.4 l) to afford 4 (19.49 g, 83%). m.p. 186-188°C. ^1H NMR (200 MHz, CD_3COCD_3) δ 8.05-8.22 (m, 4H), 5.30 (s, 2H). IR (CH_2Cl_2) 3020, 2950, 1350, 1180, 1120 cm^{-1}. Anal. ($C_7H_6O_4S_2$) C: calcd, 38.52; found, 38.58. H: calcd, 2.77; found, 2.79. S: calcd, 29.38; found, 29.29%.

For the alkylation of the bis-sulfones 1 and 4, three general procedures (A, B and C) were used. They are as follows:

Method A: A mixture of the sulfone (1.0 eq), K_2CO_3 (1.2 eq for monoalkylations, 2.4 eq for dialkylations), and the electrophile (1.05-10 eq) in DMF (0.5 ml/mmol K_2CO_3) was allowed to stir at 80°C until the reaction was complete. The reaction mixture was concentrated, dissolved in CH_2Cl_2, and filtered through a short pad of silica gel. Concentration followed by recrystallization (EtOH) afforded the pure product.

Method B: The solid sulfone (1.0 eq) was added to a suspension of NaH (1.1 eq) in dry THF (3 ml/mmol). After hydrogen evolution had ceased, the electrophile was added and the reaction mixture was heated at 80°C until the reaction was complete. The reaction mixture was concentrated, dissolved in CH_2Cl_2, and filtered through a short pad of silica gel. Concentration followed by recrystallization (EtOH) afforded the pure product.

Method C: Same as method B, except that dry DMF was used as solvent.

1,1-Bis(phenylsulfonyl)-2-methylpropane (2a). 2a was obtained in 74% yield from 1 and isopropyl iodide according to method C. (Table 1, entry 1). m.p. 135-136°C. ^1H NMR (200 MHz, $CDCl_3$) δ 7.99-8.00 (m, 4H), 7.48-7.73 (m, 6H), 4.47 (br d, 1H, J = 1.3 Hz), 2.81 (dd, 1H, J = 7.2, 1.3 Hz), 1.27 (d, 6H, J = 7.2 Hz). MS (m/z) 323(4), 149(24), 141(43), 125(69), 77(100), 55(57), 51(57). High Res Mass Spec. ($C_{16}H_{18}O_4S_2$) Calcd, 338.0646; found, 338.0645.

2,2-Bis(phenylsulfonyl)-3-methylbutane (3a). 3a was obtained in 96% yield from 2a and methyl iodide according to method C. (Table 1, entry 2). m.p. 130-132°C. ^1H NMR (200 MHz, $CDCl_3$) δ 8.05-8.15 (m, 4H), 7.53-7.77 (m, 6H), 2.54 (septet, 1H, J = 6.7 Hz), 1.67 (s, 3H), 1.21 (d, 6H, J = 6.7 Hz). MS (m/z) 352(7), 211(31), 143(100), 125(39), 77(81), 69(82), 55(40). High Res Mass Spec. ($C_{17}H_{20}O_4S_2$) Calcd, 352.0803; found, 352.0800.

1,1-Bis(phenylsulfonyl)-3-phenylpropane (2b). 2b was obtained in 96% yield from 1 and β-phenethyl bromide according to method A. (Table 1, entry 4). m.p. 139-140°C. ^1H NMR (200 MHz, $CDCl_3$) δ 7.82-7.97 (m, 4H), 7.47-7.75 (m, 6H), 7.14-7.33 (m, 3H), 6.95-7.10 (m, 2H), 4.36 (t, 1, J = 5.8 Hz), 2.93 (t, 2H, J = 7.3 Hz), 2,48 (q, 2H, J = 7.3 Hz). MS (m/z) 400(6), 259(7), 117(100), 91(62), 77(46), 51(8). High Res Mass Spec. ($C_{21}H_{20}O_4S_2$) Calcd, 400.0803; found, 400.0807.

2-Isopropyl-1,3-benzodithiole-1,1,3,3-tetraoxide (5a). 5a was obtained in 82% yield from 4 and isopropyl iodide according to method A. (Table 2, entry 1). m.p. 208-210°C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.83-8.07 (m, 4H), 4.09 (d, 1H, J = 10.9 Hz), 2.58 (dd, 1H, J = 10.9, 6.8 Hz), 1.43 (d, 6H, J = 6.8 Hz). MS (m/z) 260(5), 245(4), 218(8), 130(18), 96(26), 76(35), 55(100), 50(46). High Res Mass Spec. ($C_{10}H_{12}O_4S_2$) Calcd, 260.0156; found, 260.0154.

2-Isopropyl-2-methyl-1,3-benzodithiole-1,1,3,3-tetraoxide (6a). 6a was obtained in 88% yield from 5a and methyl iodide according to method B. (Table 2, entry 3). m.p. 181-183°C. ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.86-8.04 (m, 4H), 3.16 (septet, 1H, J = 7 Hz), 1.62 (s, 3H), 1.24 (d, 6H, J = 7 Hz). MS (m/z) 274(2), 188(30), 124(15), 96(48), 69(100), 55(53), 50(31). High Res Mass Spec. ($C_{11}H_{14}O_4S_2$) Calcd, 274.0333; found, 274.0333.

2-Isopropyl-2-ethyl-1,3-benzodithiole-1,1,3,3-tetraoxide (6b). 6b was obtained in 87% yield from 5a and ethyl iodide according to method B. (Table 2, entry 4). m.p. 209-211°C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.83-8.04 (m, 4H), 3.13 (septet, 1H, J = 6.8 Hz), 2.36 (q, 2H, J = 7.5 Hz), 1.27 (d, 6H, J = 6.8 Hz), 0.85 (t, 3H, J = 7.5 Hz). MS (m/z) 289(0.5), 246(2), 231(6), 188(11), 96(9), 83(100), 79(10), 55(92). Anal. ($C_{12}H_{16}O_4S_2$) C: calcd, 49.98; found, 49.99. H: calcd, 5.59; found, 5.59%.

2-Isobutyl-2-isopropyl-1,3-benzodithiole-1,1,3,3-tetraoxide (6c). 6c was obtained in 88% yield from 5a and isobutyl bromide according to method C. (Table 2, entry 5). m.p. 191-192°C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.82-8.03 (m, 4H), 3.00 (septet, 1H, J = 6.8 Hz), 2.24 (d, 2H, J = 5.7 Hz), 1.67-1.92 (m, 1H), 1.19 (d, 6H, J = 6.8 Hz), 0.99 (d, 6H, J = 6.8 Hz). MS (m/z) 317(1), 301(6), 252(37), 188(31), 143(31), 111(50), 85(52), 69(100), 55(52). High Res Mass Spec. ($C_{14}H_{20}O_4S_2$) Calcd, 316.0803; found, 316.0760.

2-Cyclohexylmethyl-2-isopropyl-1,3-benzodithiole-1,1,3,3-tetraoxide (6d). 6d was obtained in 81% yield from 5a and cyclohexylmethyl bromide according to method C. (Table 2, entry 6) m.p. 178-179°C. ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.86-8.04 (m, 4H), 3.03 (septet, 1H, J = 7 Hz), 2,18 (d, 2H, J = 5.5 Hz), 1.70-1.86 (m, 2H), 1.30-1.70 (m, 5H), 1.19 (d, 6H, J = 7 Hz), 0.90-1.12 (m, 4H). MS (m/z) 357(0.5), 189(24), 172(30), 151(32), 95(36), 86(40), 69(62), 55(100). Anal. ($C_{17}H_{24}O_4S_2$) C: calcd, 57.28; found, 57.22. H: calcd, 6.79; found, 6.74%.

2-(2-Phenylethyl)-1,3-benzodithiole-1,1,3,3-tetraoxide (5b). 5b was obtained in 97% yield from 4 and β-phenethyl bromide according to method A. (Table 2, entry 9) m.p. 122-123°C. ^{1}H NMR (200MHz, $CDCl_3$) δ 7.85-8.08 (m, 4H), 7.20-7.40 (m, 5H), 4.33 (t, 1H, J = 7.0 Hz), 3.09 (t, 2H, J = 7.3 Hz), 2.63 (q, 2H, J = 7.3 Hz). MS (m/z) 322(6), 172(18), 117(100), 105(29), 91(100), 77(24), 65(68), 50(29). High Res Mass Spec. ($C_{15}H_{14}O_4S_2$) Calcd, 322.0333; found, 322.0322.

2-Isopropyl-2-(2-phenylethyl)-1,3-benzodithiole-1,1,3,3-tetraoxide (6f). 6f was obtained in 93% yield from 5b and isobutyl bromide according to method C. (Table 2, entry 10). m.p. 162-163°C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.84-8.11 (m, 4H), 7.09-7.32 (m, 5H), 3.19 (septet, 1H, J = 6.8 Hz), 2.38-2.57 (m, 4H), 1.28 (d, 6H, J = 6.8 Hz). MS (m/z) 364(5), 300(6), 245(19), 211(15), 172(60), 159(80), 91(100), 71(48), 65(57). High Res Mass Spec. ($C_{18}H_{20}O_4S_2$) Calcd, 364.0803; found, 364.0780.

1,1-Bis(phenylsulfonyl)-2-methylcyclopentane (3d). 3d was obtained in 82% yield from 1 and 1,4-diiodo pentane according to method A. (Table 3) m.p. 157-157°C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.10-8.21 (m, 4H), 7.53-7.80 (m, 6H), 2.39-2.93 (m, 3H), 1.55-2.05 (m, 4H), 1.05 (d, 3H, J = 7 Hz). MS (m/z) 364(1), 223(3), 143(8), 125(8), 97(5), 81(100), 67(7), 53(8). High Res Mass Spec. ($C_{18}H_{20}O_4S_2$) Calcd, 364.0803; found, 364.0823.

1,3-Benzodithiole-1,1,3,3-tetraoxide-2-spiro-2'-methylcyclopentane (6h). 6h was obtained in 82% yield from 4 and 1,4-diiodo pentane according to method A. (Table 3). m.p. 161-162°C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.82-8.07 (m, 4H), 3.10 (sextet, 1H, J = 7 Hz), 2.63-2.81 (m, 1H), 2.35-2.51 (m, 1H), 1.77-2.23 (m, 4H), 1.21 (d, 3H, J = 7Hz). MS (m/z) 286(5), 205(5), 188(6), 172(5), 98(9), 81(100), 79(48), 67(13). High Res Mass Spec. ($C_{12}H_{14}O_4S_2$) Calcd, 286.0333; found, 286.0320.

1,3-Benzodithiole-1,1,3,3-tetraoxide-2-spiro-2',5'-dimethylcyclopentane (6i). 6i was obtained as a 2:1 mixture of diastereomers in 71% yield from 4 and 2,5-diiodo hexane according to method A (at 40 °C). (Table 3). m.p. 189-199°C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.80-8.04 (m, 4H), 3.17-3.35 (m, 0.67H), 2.85-3.10 (m, 0.33H), 1.65-2.37 (m, 4H), 1.21 (d, 2H, J = 6.8Hz), 1.15 (d, 4H, J = 6.8 Hz). MS (m/z) 300(1), 245(21), 125(20), 95(99), 81(80), 67(92), 55(100), 53(85). Anal. ($C_{13}H_{16}O_4S_2$) C: calcd, 51.93; found, 51.78. H: calcd, 5.32; found, 5.32%.

Reduction of the BDT derivatives 6d and 6f with Mg/MeOH: To a solution of the sulfone (1.0 eq) in methanol (24 ml/mmol) at 50°C were added in 3 portions over a 3 h period Mg turnings (total of 470 mg/mmol). Gas evolution occurred throughout the reaction as the Mg was oxidized and it was sometimes necessary to cool the reaction mixture. After all the Mg had reacted (~4 h), the reaction mixture was concentrated and the solid residue extracted with CH_2Cl_2 (or pentane). Concentration of the extracts and chromatography on silica gel afforded the pure hydrocarbon.

3-Methylbutylcyclohexane (8) (from the reduction of 6d): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.45-1.90 (m, 6H), 1.00-1.45 (m, 8H), 0.86 (d, 6H, J = 6.8 Hz), 0.72-1.00 (m, 2H). IR (CH_2Cl_2) 2960, 2930, 2860, 1470, 1450, 1380, 1360. MS (m/z) 154(12), 111(11), 97(28), 83(100), 81(60), 69(22), 55(79). High Res Mass Spec. ($C_{11}H_{22}$) Calcd, 154.1722; found, 154.1720.

4-Methylpentylbenzene (7) (from the reduction of 6f): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.10-7.34 (m, 5H), 2.59 (br t, 2H, J = 7.8 Hz), 1.42-1.65 (m, 3H), 1.18-1.24 (m, 2H), 0.88 (d, 6H, J = 6.8 Hz). IR (CH_2Cl_2) 3170, 3160, 3030, 2960, 2930, 2880, 1600, 1500, 1470, 1450, 1380, 1360, 1030. MS (m/z) 162(29), 119(8), 105(11), 92(80), 91(100), 78(7), 65(11), 55(6). High Res. Mass Spec. ($C_{12}H_{18}$) Calcd, 162.1409; found, 162.1410.

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