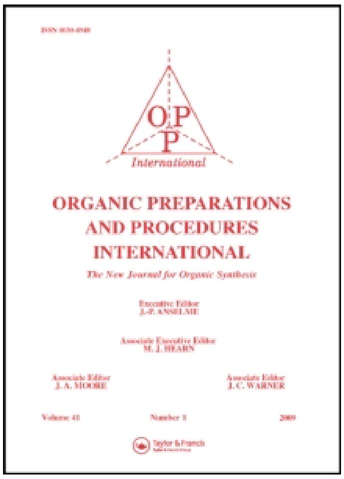

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SINGLE-STEP SYNTHESIS OF 2,3-DIHYDRO-2,2DIMETHYL-1H-PHENOTHIAZIN-4(10H)-ONES

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OPPI BRIEFS

SINGLE-STEP SYNTHESIS OF 2,3-DIHYDRO-2,2DIMETHYL-1H-PHENOTHIAZIN-4 (10H)-ONES

Submitted by
(10/14/92)

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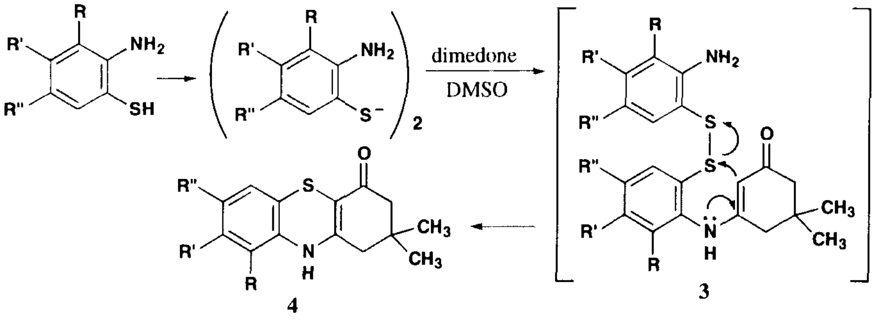
As part of our interest in biologically active heterocycles, it was considered worthwhile to prepare phenothiazin-4-ones (**4**). We now report a one-step synthesis of title compounds by condensation of 2-aminobenzenethiols with dimedone in dimethyl sulfoxide. They were obtained in good yields (56-79%) in pure form by simple crystallization from methanol. However, 2-aminobenzenethiols do not react with *p*-benzoquinone, but undergo condensation with bromochloromethyl *p*-benzoquinone to provides phenothiazin-3-ones[1]in low yields (20-30%) of impure products, which required repeated crystallization. The present method for the title compounds is superior than analogous method used for the preparation of phenothiazin-3-ones.

Substituted 2-aminobenzenethiols (**1**) are readily oxidized under the reaction conditions to *bis*-(*o*-aminophenyl)disulfides (**2**)[2] which undergo condensation with dimedone to afford substituted phenothiazinones (**4**). The reaction is viewed as proceeding *via* the formation of an intermediate enaminoketone (**3**) which cyclizes to the phenothiazinone (**4**) by the scission of sulfur-sulfur bond upon attack by the nucleophilic enaminoketone system (Scheme 1). The structures of all the synthesized compounds were established on the basis of elemental analyses and spectral (IR and NMR) data.



a) $R = CH_3$, R' = R''' = H b) R = R'' = H, $R' = SO_3$ c) R = R' = H, R' = Br
d) R = R' = H, R'' = Cl e) R = R' = H, $R'' = OC_2H_5$ f) R = R' = H, $R'' = CH_3$

EXPERIMENTAL SECTION

The infrared spectra were recorded as KBr pellets on Perkin-Elmer spectrophotometer Model 577. The PMR spectra were recorded on 90 MHz Jeol FX 90Q FT NMR in Polysol-D/DMSO-d_6+$CDCl_3$ using TMS as internal standard. Substituted 2-aminobenzenethiols have been synthesized by the hydrolytic cleavage of substituted 2-aminobenzothiazoles.[3]

Synthesis of Phenothiazin-4-ones. Typical Procedure.- A solution of substituted 2-aminobenzenethiol (**1**, 0.01 mole), dimedone (0.01 mole) in dimethyl sulfoxide (5 mL) was refluxed for 1 hr. Chloroform (2 mL) was added and the product which crystallized out on cooling was collected, dried and recrystallized from methanol. The physical data are summarized in Table 1.

TABLE 1. Yields, Spectral and Analytical Data of Compounds **4a-f**

Cmpd.	Yield (%)	mp. (°C)	IR (cm^{-1})	NMR (δ)	Elemental Analyses Calcd. (Found) C	H	N
4a	58	241	3300(NH) 1575(CO)	9.16 (s, 1H), 6.56-7.44 (m, 3H), 2.21 (s, 2H), 2.18 (s, 2H), 2.12 (s, 3H), 1.07 (s, 6H)	69.33 (69.11)	6.56 (6.53)	5.40 (5.37)
4b	56	235	3230(NH) 1570(CO) 1300(SO_3H)	9.12 (s, 1H), 7.86 (s, 1H), 6.49-7.10 (m, 3H),2.28 (s, 2H), 2.18 (s, 2H),1.04 (s, 6H)	51.69 (51.81)	4.61 (4.59)	4.30 (4.27)
4c	70	255	3260(NH) 1570(CO)	9.03 (s, 1H),6.46-7.35 (m, 3H), 2.31 (s, 2H), 2.21 (s, 2H), 1.04 (s, 6H).	51.98 (52.20)	4.32 (4.33)	4.32 (4.28)
4d	72	257	3260(NH) 1570(CO) 740(C-Cl)	9.12 (s, 1H),6.46-7.60 (m, 3H), 2.21 (s, 2H), 2.12 (s, 2H), 1.04 (s, 6H).	59.94 (59.72)	5.00 (4.98)	5.00 (4.97)
4e	66	263	3230(NH) 1595(CO) 1035-2280 (C-O-C)	9.09 (s, 1H), 6.37-7.03 (m, 3H), 3.64-4.05(q,2H), 2.28 (s, 2H), 2.21 (s, 2H), 1.17-1.39 (t, 3H), 1.07 (s, 6H).	66.43 (66.21)	6.57 (6.55)	4.84 (4.82)
4f	79	260	3230(NH) 1590(CO)	9.06(s, 1H),6.40-6.87(m,3H), 2.28(s,2H),2.21(s,2H), 2.12(s,3H) ,1.04(s,6H).	69.49 (69.11)	6.56 (6.54)	5.40 (5.43)

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AN IMPROVED SYNTHESIS OF THIENO(2,3-b)QUINOLINES *via* S-OXIDES

Submitted by
(02/03/93)

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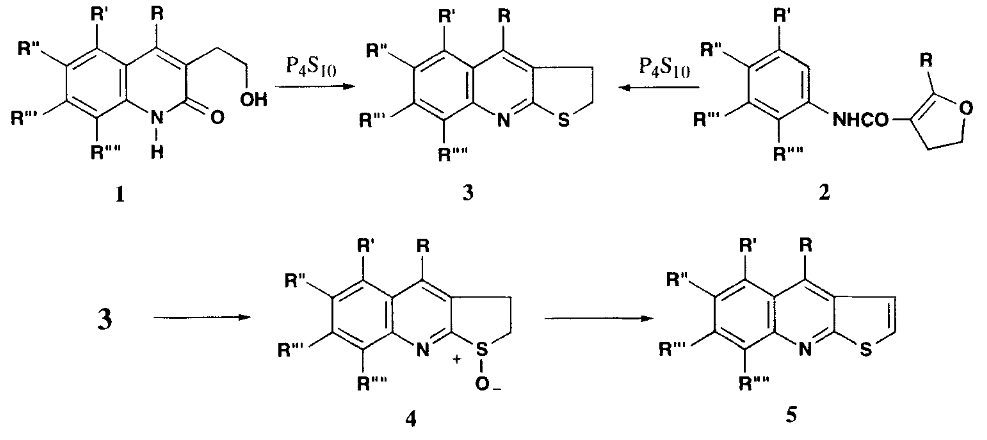
Earlier, we reported two convenient methods for the preparation of 2,3dihydrothieno(2,3-b)quinoline (**3**) and its derivatives.[1,2] These involved heating 3-(2'-hydroxyethyl)quinolin-2(1H)-one (**1**) or 4,5-dihydrofuran-3-carboxanilide (**2**) with tetraphosphorus decasulfide.[1] Of these two procedures, the former based on the use of quinolonyl ethanols (**1**) is quite useful, particularly since a variety of quinolonyl ethanols are available.[3,4] Kuwayama[5] prepared the parent thienoquinoline **5a** *via*



a) $R = R' = R'' = R''' = R'''' = H$ b) $R = R' = R''' = R'''' = H, R'' = CH_3$
c) $R = R'' = R''' = H, R' = R'''' = OCH_3$ d) $R = R'' = R''' = H, R' = R'''' = CH_3$
e) $R = R'' = R''' = H, R' = Cl, R'''' = OCH_3$ f) $R = R' = R'' = H, R''' = R'''' = CH{=}CH{-}CH{=}CH$
g) $R = CH_3, R' = R'' = R''' = R'''' = H$ h) $R = C_6H_5, R' = R'' = R''' = R'''' = H$
i) $R = C_6H_4(p\text{-}CH_3), R' = R'' = R''' = R'''' = H$

S-oxidation of **3a** with perphthalic acid and refluxing the S-oxide with acetic anhydride.[5] However in the perpthalic acid oxidation, the yield of S-oxide was only 46% and the product was contaminated with S,S-dioxide, S,S,N-trioxide and N-oxide. It was felt that a clean conversion of **3a** to its S-oxide