

THE SYNTHESIS OF METAL COMPLEXES OF SOME DIOSPHENOLS THIO CARBAMATES AND EXAMINATION OF ITS PROPERTIES

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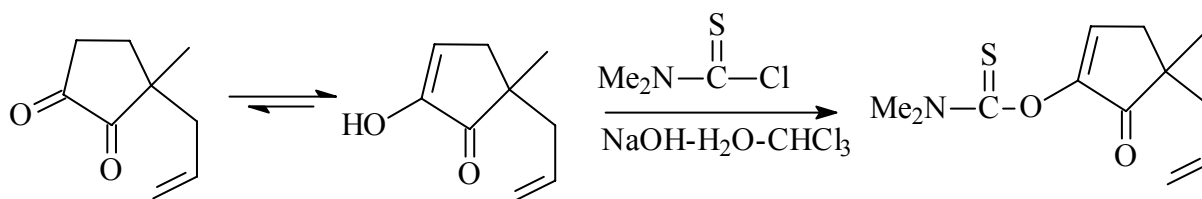
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ABSTRACT

Diosphenols (α -hydroxyl- α , β -unsaturated ketones) are major materials as both intermediate and natural compounds in natural product chemical. Diosphenols functional groups take place in the constitution of numerous complex compounds. In this study, diosphenolsthiocarbamates and metal complexes of diosphenolsthiocarbamates have been investigated by using five different diosphenols.

In the first part of the study, synthesis of five different diosphenolsthiocarbamates have been realized by using methods of Ponaras and Zaim. In this method, enolic hydroxyl dimethylthiocarbamates of diosphenols have been synthesized by using dimethylthiocarbonyl chloride as an activating group:



In the second part of the study, metal complexes of obtained diosphenolsthiocarbamates have been investigated by using acetate, sulfate, nitrate, perchlorate and chloride salts of four different metals:



L: Diosphenolsthiocarbamates, Me: Zn, Cu, Co, Ni acetate, sulfate, nitrate, perchlorate and chloride salts.

Finally, the structural characteristics of the products obtained by these methods have been analyzed with IR and NMR spectrums.

INTRODUCTION

The diosphenol (enolized α -diketone) array is found in diverse natural products [1-5] and has synthetic utility for Claisen rearrangements [6], aldol and Michael additions [7], Wittig reactions [8], ring-cleavage reactions [9], ring-contraction reactions [10] and photochemical reactions [11]. α,β -Epoxyketones have been used as precursors of diosphenols via isomerization with strong acid in a hydroxylic solvent [12]. This procedure, however, gives variable results [13] and is incompatible with many functional groups. Treatment of α,β -epoxyketones with methoxide often gives acceptable yields of diosphenol methyl ethers [14], but hydrolysis to the parent diosphenols requires harsh conditions [15]. The apparently simpler route, namely treatment of an α,β -epoxyketone with hydroxide ion is unsatisfactory since any diosphenol produced undergoes benzilic acid rearrangement [16].

Diosphenolthiocarbamates have been realized by using methods of Ponaras and Zaim. In this method, enolic hydroxyl dimethyl thio carbamates of diosphenols have been synthesized by using dimethyl thio carbonyl chloride as an activating group.

EXPERIMENTAL

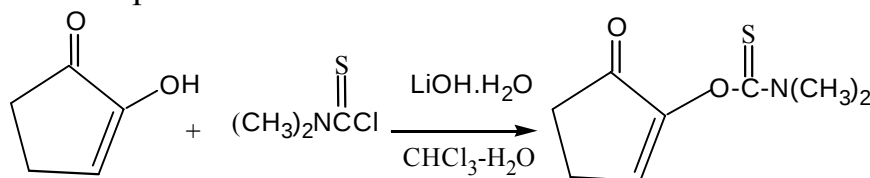
Materials and Aparatus

All of the analytical reagents grade were provided from Merck and Aldrich and in the experimentals were used electro-mag sterilizer (300 °C), Chittern scientific magnetic stirrer heater, electrothermal heater, Buchi labarotecnic AG, R-114A29 B-480 evaporator, Nüve EV 018 vacuum sterilizer, Brook Crompton vachum pump, Desaga Sarstedt-Gruppe Min UVIS 254/366 nm UV lamp, Shimadzu IR 470 IR spectrophotometer, Varian 300 MHz NMR spectrophotometer and Gec Avery balance.

METHODS

The synthesis of 2-(dimethylthiocarbamoyloxy)-2-cyclopentene-1-one

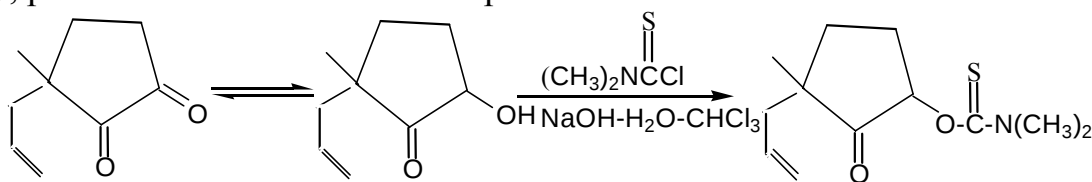
A solution of 2.94 g (20 mmol) cyclopentanediene in 20 mL chloroform was placed in a magnetically stirred 250 mL round bottom flask and the solutions 1.26 g (30 mmol) LiOH.H₂O in 30 mL water and 3.72 g (30 mmol) dimethylcarbamoylchloride in 20 mL chloroform were added. System was stirred two hours, aqueous phase was removed and washed with ether, evaporated slowly, product was dried at room temperature. Yield: 85 %.



The synthesis of 5-allyl-5-methyl-2-(dimethylthiocarbamoyloxy)-2-cyclopentene-1-one

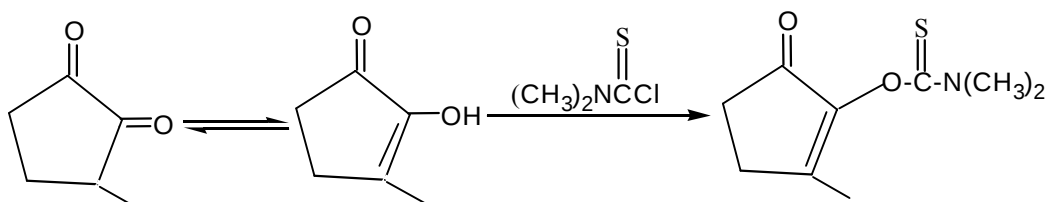
A solution of 0.8 g (20 mmol) NaOH in 20 mL water was placed in a magnetically stirred 250 mL round bottom flask and the solutions 3.04 g (20 mmol) 5-allyl-5-methyl-2-hydroxy-2-cyclopentene-1-one in 15 mL chloform and 2.84 g (20 mmol) dimethylcarbamoylchloride in 10 mL chloroform were added. System was

stirred two hours, aqueous phase was removed and washed with ether, evaporated slowly, product was dried at room temperature. Yield: 97 %.



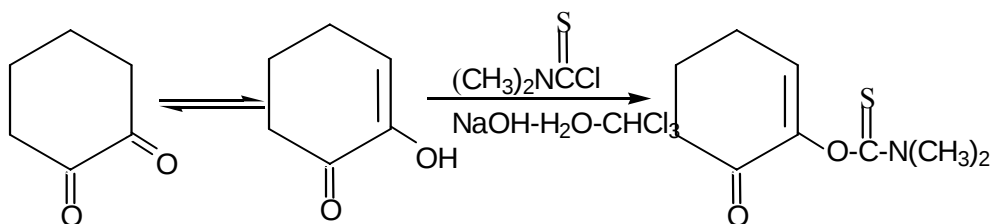
The synthesis of 3-methyl-2-(dimethylthiocarbamoyloxy)-2-cyclopenten-1-one

A solution of 0.8 g (20 mmol) cyclopentanedione in 20 mL water was placed in a magnetically stirred 250 mL round bottom flask and the solutions 2.8 g (25 mmol) cycloten in 15 mL chloroform and 3.08 g (25 mmol) dimethylcarbamoylchloride in 20 mL chloroform were added. System was stirred two hours, aqueous phase was removed and washed with ether, evaporated slowly, product was dried at room temperature. Yield: 85 %.



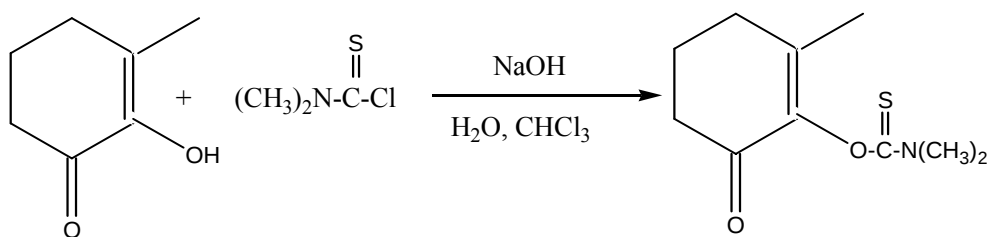
The synthesis of 2-(dimethylthiocarbamoyloxy)-2-cyclohexene-1-one

A solution of 1.12 g (10 mmol) 1,2-cyclohexanedione in 10 mL chloroform was placed in a magnetically stirred 250 mL round bottom flask and the solutions 0.4 g (10 mmol) NaOH in 10 mL water and 1.488 g (12 mmol) dimethylcarbamoylchloride in 20 mL chloroform were added. System was stirred two hours, aqueous phase was removed and washed with ether, evaporated slowly, product was dried at room temperature. Yield: 84 %.



The synthesis of 3-methyl-2-(dimethylthiocarbamoyloxy)-2-cyclohexene-1-one

A solution of 2.52 g (10 mmol) diophenol in 10 mL chloroform was placed in a magnetically stirred 250 mL round bottom flask and the solutions 0.8 g NaOH in 20 mL water and 2.48 g dimethylcarbamoylchloride in 15 mL chloroform were added. System was stirred two hours, aqueous phase was removed and washed with ether, evaporated slowly, product was dried at room temperature. Yield: 85 %.



The synthesis of metal complexes of diosphenolthiocarbamates in the presence Co (II), Cu(II), Ni(II), Zn(II) acetate, sulfate, nitrate, perchlorate and/or chloride salts.

A solution of calculated amount diosphenolthiocarbamates in proper solvent was placed in a magnetically stirred 50 mL round bottom flask. An addition funnel filled with a solution of calculated amount salt of metal in proper solvent was connected with one of the necks. System was heated to reflux while solution metal salt was added dropwise within 20-24 minute. After the addition the mixture was stirred for two days under reflux. The heating was stopped and the reaction mixture was poured in a extraction funnel. Finally, black, oily precipitates achieved, desired complexes weren't obtained.



Me: Salts of Co (II), Cu (II), Ni (II), Zn (II) acetate, sulfate, nitrate, perchlorate, chloride

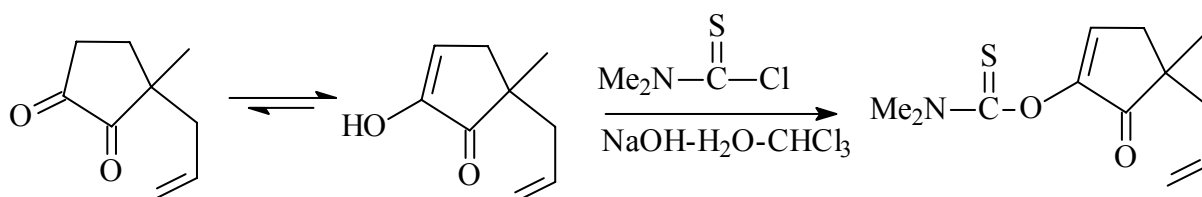
L: 2-(dimethylthiocarbamoyloxy)-2-cyclopentene-1-one, 5-Allyl-5-methyl-2-(dimethylthiocarbamoyloxy)-2-cyclopentene-1-one, 3-Methyl-2-(dimethylthiocarbamoyloxy)-2-cyclopentene-1-one, 2-(dimethylcarbamoyloxy)-2-cyclohexene -1-one, 3-Methyl-2-(dimethylcarbamoyloxy)-2-cyclohexene -1-one.

Solvents: Methyl alcohol (Merck), Ethyl alcohol (Merck), Chloroform (Merck), Acetone (Merck), Acetonitrile (Merck), Benzene (Merck), Petroleum ether (Merck), Diethyl ether (Merck), Dichloro methane (Merck), Carbon tetrachloride (Merck), Tetrahydrofuran (Merck), n-hexane (Merck), Ethyl acetate (Merck).

RESULTS AND DISCUSSION

In this study, diosphenolthiocarbamates and metal complexes of diosphenolthiocarbamates have been investigated by using five different diosphenols.

In the first part of the study, synthesis of five different diosphenolthiocarbamates have been realized by using methods of Ponaras and Zaim. In this method, enolic hydroxyl dimethylthiocarbamates of diosphenols have been synthesized by using dimethylthiocarbonyl chloride as an activating group:



IR and NMR spectrums of obtained diosphenolthiocarbamates:

IR bands (cm^{-1}) of 2-(dimethylcarbamoyloxy)-2-cyclopentene-1-one: 3072, 2944, 1721, 1635, 1545, 1449, 1395, 1280, 1251, 1174, 1129, 780.

^1H NMR data (ppm) of 2-(dimethylcarbamoyloxy)-2-cyclopentene-1-one: 1.52 (s, 3H), 2.52 (m, 2H), 2.68 (m, 2H), 3.27 (s, 3H), 3.40 (s, 3H).

^{13}C NMR data of 2-(dimethylcarbamoyloxy)-2-cyclopentene-1-one: 23, 33, 39, 44, 148, 153, 201.

IR bands (cm^{-1}) of 5-allyl-5-methyl-2-(dimethylthiocarbamoyloxy)-2-cyclopentene-1-one: 2960, 1715, 1638, 1542, 1392, 1315, 1264, 1225, 1177, 1123, 1017, 992, 835.

^1H NMR data (ppm) of 5-allyl-5-methyl-2-(dimethylthiocarbamoyloxy)-2-cyclopentene-1-one: 1.2 (s, 3H), 2.30-2.70 (dd, $J=2.929\text{ Hz}$, $J=18.745\text{ Hz}$, 2H), 2.17-2.31 (m, 2H), 3.2 (s, 2H), 3.4 (s, 2H), 5.1 (m, 2H), 5.7-5.8 (m, 1H), 7.1 (t, $J=3.1\text{ Hz}$, 1H).

^{13}C NMR data of 5-allyl-5-methyl-2-(dimethylthiocarbamoyloxy)-2-cyclopentene-1-one: 24, 37, 39, 42, 44, 46, 119, 134, 145, 151, 205.

IR bands (cm^{-1}) of 3-methyl-2-(dimethylthiocarbamoyloxy)-2-cyclopentene-1-one: 2944, 1721, 1664, 1542, 1395, 1382, 1331, 1273, 1203, 1132.

^1H NMR data of 3-methyl-2-(dimethylthiocarbamoyloxy)-2-cyclopentene-1-one: 1.5 (s), 2.1 (s), 2.4-2.6 (dd), 3.25 (s), 3.4 (s), 7.2 (t).

IR bands (cm^{-1}) of 2-(dimethylthiocarbamoyloxy)-2-cyclohexene-1-one: 2944, 1686, 1638, 1539, 1398, 1350, 1280, 1241, 1180, 1145.

^1H NMR data (ppm) 2-(dimethylthiocarbamoyloxy)-2-cyclohexene-1-one: 2.1 (q, 2H), 2.57 (m, 4H), 3.26 (s, 3H), 3.4 (s, 3H), 6.5 (t).

^{13}C data NMR 2-(dimethylthiocarbamoyloxy)-2-cyclohexene-1-one: 22.8, 25.2, 38.6, 39, 43.4, 135.9, 192.6.

IR bands (cm^{-1}) of 3-methyl-2-(dimethylthiocarbamoyloxy)-2-cyclohexene-1-one: 2944, 1721, 1664, 1542, 1395, 1382, 1331, 1273, 1203, 1132.

^1H NMR data (ppm) of 3-methyl-2-(dimethylthiocarbamoyloxy)-2-cyclohexene-1-one: 1.5 (s), 2.1 (s), 2.4-2.6 (dd), 3.25 (s), 3.4 (s), 7.2 (t).

These values have been proved the rightness of obtained diosphenolthiocarbamates. Figure 1, Figure 2, Figure 3, Figure 4 and Figure 5 have been demonstrated spatial configurations of diosphenolthiocarbamates.

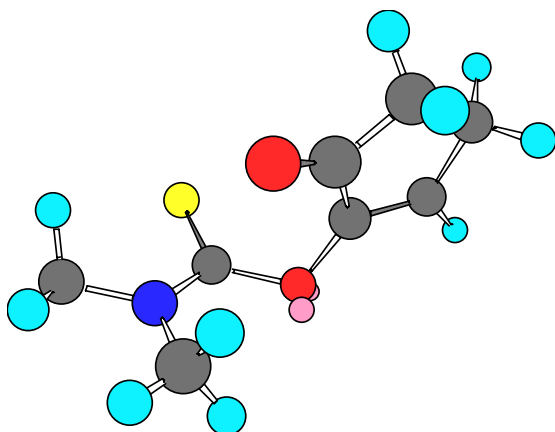


Figure 1. Spatial configuration of 2-(dimethylthiocarbamoyloxy)-2-cyclopentene-1-one

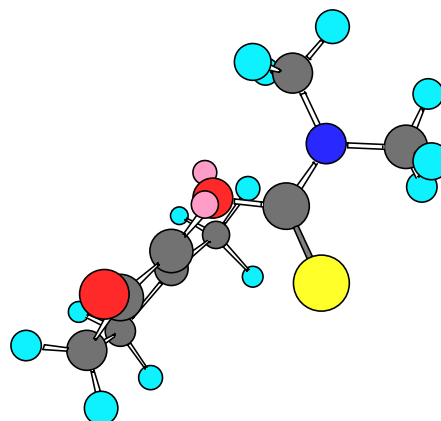


Figure 2. Spatial configuration of 5-allyl-5-methyl-2-(dimethylthiocarbamoyloxy)-2-cyclopentene-1-one

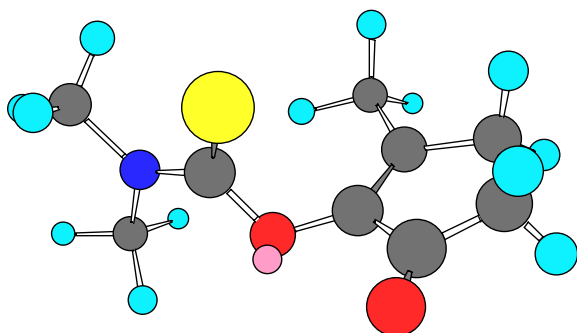


Figure 3. Spatial configuration of 3-methyl-2-(dimethylthiocarbamoyloxy)-2-cyclopentene-1-one

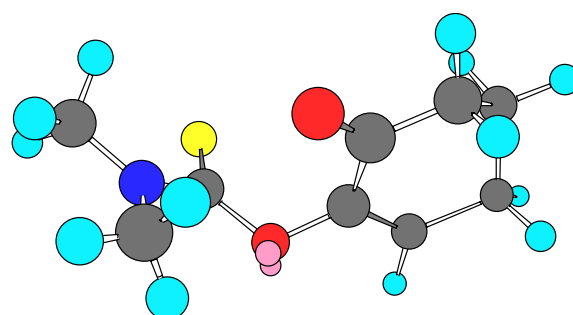


Figure 4. Spatial configuration of 2-(dimethylthiocarbamoyloxy)-2-cyclohexene-1-one

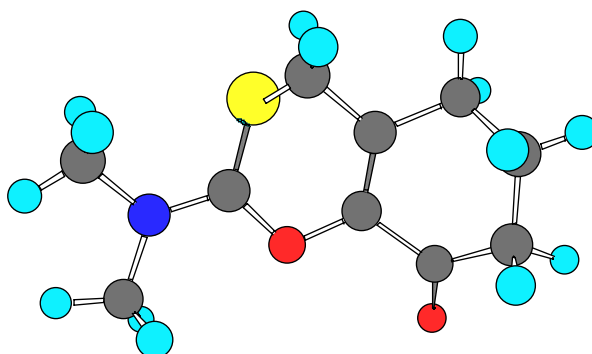


Figure 5. Spatial configuration of 3-methyl-2-(dimethylthiocarbamoyloxy)-2-cyclohexene-1-one

In the second part of the study, metal complexes of obtained diosphenolthiocarbamates have been investigated by using acetate and chlorate salts of four different metals:



L: Diosphenols thio carbamates, Me: Zn, Cu, Co, Ni acetates and chlorates

Finally, desired complexes weren't obtained. We observed that didn't reaction of diosphenolthiocarbamates from TLC and spatial configurations of diosphenolthiocarbamates demonstrated that weren't proper position. That's why those diosphenolthiocarbamates can not bandage metals.

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