tures than dispersive spectroscopy. The vibrational assignments made in this work are collectively summarized in Table 1.

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A Simple Synthesis of 3-Substituted 1-Amino-2-thioxo-4-imidazolidinones, Isolation of the Intermediates, N-Amino-N-ethoxycarbonylmethyl-N′-aralkyl-thioureas

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1-Aminothiohydantoin derivatives were prepared in good yields by the reaction of alkyl or arylisothiocyanates with ethyl hydrazinoacetate hydrochloride in presence of triethylamine. The intermediates, N-amino-N-ethoxycarbonylmethyl-N′-aralkylthioureas, which were formed during the reaction and could be transformed into the appropriate 1-aminothiohydantoins, were isolated and characterized.

Introduction

1-Aminothiohydantoin was synthesized first by Traube and Hoffa.[1] Uota[2] synthesized it by heating ethyl hydrazinoacetate·HCl and KCNS at 120℃ for 30 min. 1-Aminohydantoin was prepared by condensation of semicarbazones with ethyl monochloroacetate in presence of sodium alkoxide in dry ethanol by Jack.[3]

The 2-oxo analogues of title compounds, 1-aminohydantoin are important intermediates in the preparation of several hydantoin pharmaceuticals. Nitrofurantoin, the derivatives of 1-aminohydantoin is the most widely used urinary tract antibacterial agent.

In order to discover new useful therapeutic agents, 3-substituted 1-amino-2-thioxo-4-imidazolidinones are synthesized as intermediates of novel NSAIDS. The introduction of a heterocyclic ring in the amide side chain of 1, 2-benzothiazine-3-carboxamide derivatives increases antiinflammatory activity. We will describe a series of related compounds later.

Here we describe a simple synthesis of 3-substituted 1-aminothiohydantoin by reaction of Jacobsen.[4]

Result and Discussion

When ethyl hydrazinoacetate hydrochloride[5] **1** was added to a solution of an equimola of isothiocyanate and a twofold amount of triethylamine in dichloromethane, an intermediate was formed rapidly. The intermediate, N-amino-N-ethoxycarbonylmethyl-N′-aralkyl-thiourea **2** was isolated after about 2 hours and was subsequently transformed into 1-aminothiohydantoin **3** by reaction with triethylamine in dichloromethane for about 4 days. The cyclisation usually required a couple of days and in all cases was not over more than 4 days at room temperature as judged by T.L.C. (silica gel, ethyl acetate : dichloromethane, 1 : 3). This intermediates were reported first by Jacobsen,[4] N-amino-N-ethoxycarbonyl methyl-N′-phenylthiourea was isolated and characterized.

The cyclisation was not accelerated significantly by addition of more than twofold triethylamine. The cyclisation products were characterized by carbonyl absorptions in the

Table 1. N-Amino-N-ethoxycarbonylmethyl-N'-aralkyl-thioureas

Product No.	R	Yield %	Mp. (℃)	Molecular formular	IR (cm^{-1})	NMR($CDCl_3$+DMSO-d_6) δ[ppm]
2a	methyl	48.4	96-98	$C_6H_{13}N_3O_2S$	1720(C=O)	3.18(s, 3H, NCH_3)
2b	allyl	47.3	52-54	$C_8H_{16}N_3O_2S$	1740(C=O)	4.32(s, 2H, $=CH_2CO$), 5.10(m, 1H, CH)
2c	cyclohexyl	52.2	102-104	$C_{11}H_{12}N_3O_2S$	1741(C=O)	1.34(m, 10H, C_6H_{10}), 3.26(m, 1H, CH)
2d	chlorophenyl	67.5	94-96	$C_6H_{14}N_3O_2S$	1751(C=O)	7.52(m, 4H, ClC_6H_4)
2e	benzyl	75.1	78-80	$C_{12}H_{17}N_3O_2S$	1739(C=O)	5.20(s, 2H, NCH_2), 7.32(m, 5H, C_6H_5)
2f	benzoyl	63.4	204-206	$C_{12}H_{15}N_3O_2S$	1753(C=O)	7.26(m, 5H, C_6H_5)
2g	nitrobenzoyl	32.5	82-84	$C_{12}H_{14}N_4O_5S$	1732(C=O)	7.83(AB-system, 4H, C_6H_4)
2h	2-naphtyl	40.2	85-89	$C_{15}H_{17}N_3O_2S$	1730(C=O)	7.17(m, 7H, $C_{10}H_7$)

Table 2. 3-Substituted 1-Amino-2-thioxo-4-imidazolones

Product No.	R	Yield %	Mp. (℃)	Molecular Formular	IR (Cm^{-1})	NMR($CDCl_3$+DMSO-d_6) δ[ppm]
3c	cyclohexyl	70.5	162-166	$C_9H_{15}N_3OS$	1730(C=O)	1.67(m, 10H, C_6H_{10}), 3.26(s, 1H, CH)
3f	benzoyl	29.5	217-218	$C_{10}H_9N_3O_2S$	1760(C=O)	7.65-7.84(m, 5H, C_6H_5)
3g	nitrobenzoyl	24.6	200-202	$C_{10}H_9N_4O_4S$	1740(C=O)	7.47(AB-system, 4H, C_6H_4)
3h	2-naphtyl	45.3	185-187	$C_{13}H_{11}N_3OS$	1740(C=O)	7.5-7.85(m, 7H, $C_{10}H_7$)

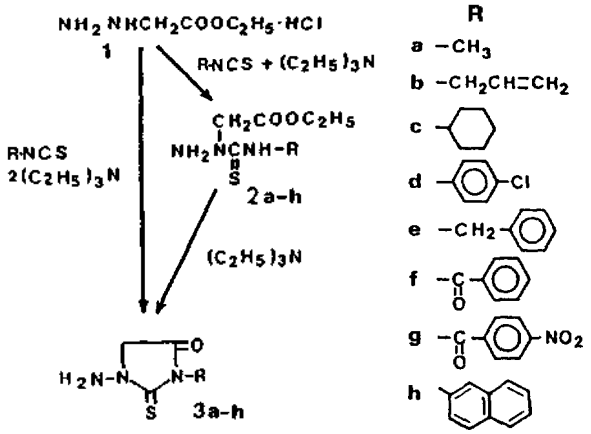
1730-1760 cm^{-1} and ^{1}H-NMR spectra (Table 1)-notably the presence of one NH_2 signal.

Experimental

General. Melting points were determined in open capillary tubes on a Büchi 535 melting point apparatus. The NMR spectra were recorded on a JEOL UNM-PMX 60 SI NMR spectrometer. IR spectra were recorded with a Bomen Michelson FT-IR spectrometer.

1-Amino-2-thioxo-3-methyl-4-imidazolone 3a. Ethyl hydrazinoacetate hydrochloride (3.11 g, 20 mmol) is added to a stirred solution of methyl isothiocyanate (14 m*l*, 20 mmol) and triethylamine (40 mmol) in dichloromethane (80 m*l*). When the solution becomes homogeneous, it is left for 4 days at room temperature. The solvent is then evaporated and the residue is washed with a minimum of cold water, filtered. The residue is dissolved in a minimum of boiling methanol, the hot solution is filtered and cooled to −20℃. A white crystalline is separated from methanol. Yield: 2.04 g (69.5%), mp. 117-118℃. Formular $C_4H_7N_3OS$(Mol. W. 145); NMR($CDCl_3$+DMSO-d_6 : δ) 3.17(s, 3H, CH_3), 4.26(s, 2H, CH_2), 4.99(s, 2H, NH_2); IR(KBr, cm^{-1}) 3444(NH_2), 3316(NH), 2939(CH), 1740(C=O), 1627(C=O), 937(C=S).

N-Amino-N-ethoxycarbonylmethyl-N'-methyl-thiourea 2a. Ethyl hydrazinoacetate hydrochloride (1.56 g, 10 mmol) is added to a stirred solution of methyl isothiocyanate (0.7 m*l*, 10 mmol) and triethylamine (20 mmol) in dichloromethane (40 m*l*). When the solution becomes homogeneous, it is left for 2 hours. The solvent is then evaporated and the residue is washed with water, filtered and dissolved in methanol (30 m*l*). Upon standing at −20℃ white needles of **2a** separated are filtered and washed with cold methanol. Yield: 0.94 g (48.4%), mp. 96-98℃. Formular $C_6H_{13}N_3O_2S$ (Mol. W. 191); NMR ($CDCl_3$+DMSO-d_6, δ) 1.32(t, 3H, CH_3), 3.18(s, 3H, NCH_3), 4.14(q, 2H, CH_2), 4.29(s, 2H, CH_2), 5.03(m, 2H, NH_2); IR(KBr, cm^{-1}) 3420(NH_2), 3311(NH), 2951(CH), 2870(CH), 1720(C=O), 1615(C=O), 931(C=S).



Scheme 1. Synthetic routes of N-Amino-N-ethoxycarbonylmethyl-N'-aralkyl-thioureas and 1-Amino-2-thioxo-3-aralkyl-4-imidazolones.

Ethyl hydrazinoacetate monohydrochloride 1. To the boiling solution of 98% hydrazine hydrate (20 g, 0.4 mol) in abs. ethanol (120 m*l*) is added monochloroacetic acid (9.4 g, 0.1 mol) in abs. ethanol (94 m*l*) dropwise.

The mixture is refluxed for 30 minutes. After cooling the reaction mixture dry HCl gas is introduced for 4 hours. Then the reaction mixture is boiled again for 30 minutes, filtered hot, and cooled. A white crystals is separated from the filtrate. The mother liquor concentrated in vacuo below 40℃ also afforded crystals. The combined crystals is recrystallized from ethanol. Yield: 4.1 g (26.6%), mp. 152-154℃. Formular $C_4H_{11}ClN_2O_2$(Mol. W. 154); NMR(DMSO-d_6, δ) 1.32(t, 3H, CH_3), 3.93(s, 2H, N-CH_2), 4.65(q, 2H, $COOCH_2$); IR(KBr, cm^{-1}) 3225(NH), 2890(CH), 1710(C=O), 1575(C=O), 1360 (SO_2), 1220(CH_2).

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Synthesis of Tetradecker Sandwich Complex with 1,4-Dialkyl-1,4-dibora-2,5-cyclohexadiene

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A tetradecker sandwich compiex (**7a**) was synthesized in low yield by the reaction of a tripledecker, bis (η^5-cyclopentadienyl)-μ-(η^6-1,2,3,4-tetramethyl 1,4-dibora-2,5-cyclohexadiene) dinickel (**5a**) with potassium and $FeCl_2 \cdot 2THF$. The reaction of another tripledecker, bis-(η^5-cyclopentadienyl)-μ-(η^6-2,3-diethyl-1,4-dimethyl-1,4-dibora-2,5-cyclohexadiene) dicobalt (**4a**) with potassium and $FeCl_2 \cdot 2THF$ at room temperature produced a doubledecker complex (**2b**) *via* the decomposition of the dark green crystal.

Introduction

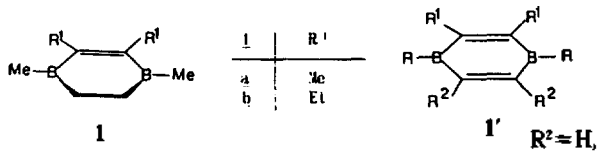
An unstable 1,4-dialkyl-1,4-dibora-2,5-cyclohexadiene (**1'**) rearranges to give a nido-tetracarbahexaborane because the electron-deficient boron atoms are included in it[1]. We synthesized the stable 1,2,3,4-tetraalkyl-1,4-dibora-2-cyclohexene (**1**) acted as the precursor **1'** by the elimination of two hydrogen atoms[3]. The complexes of **1'** with transition metals are comparatively stable to be separated and identified under inert gas atmosphere at room temperature. These stable doubledecker and tripledecker sandwich complexes were reported by Herberich[2] and our research team[3] for the first time. However the multidecker complexes over tetradecker have not been known until now. On the other hand Siebert and his coworkers synthesized another kinds of multidecker compounds including many kinds of tetradeckers with the 1,3-diborolene as a ligand[4]. In this paper we report the preparation of tetradecker complex with 1,2,3,4-tetraalkyl-1,4-dibora-2,5-cyclohexadiene.

Experimental

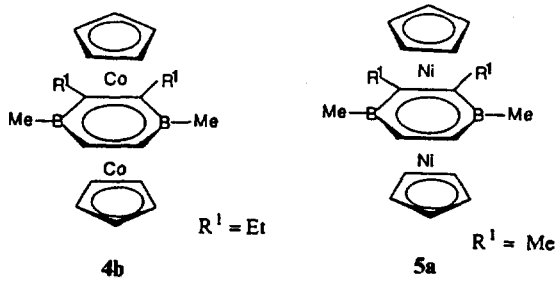
All reactions and manipulation were carried out under an atmosphere of purified and dried nitrogen or argon by using Schlenk type glassware. The solvents for preparation were dried by standard methods, distilled over potassium and benzophenone under argon atmosphere.

^{1}H-NMR spectra (δ, Me_4Si) were recorded on a Bruker AM 300, Bruker WP 80 SY spectrometer, ^{11}B-NMR (δ, $BF_3 \cdot OEt_2$) spectra were obtained on a JEOL FX-90Q. Mass spectra were recorded on a Varian MATCH 7 and a Kratos MS 25RFA in EI method. Melting points were determined on a Gallen Kamp M.P. Apparatus.

2,3-Dialkyl-1,4-dimethyl-1,4-dibora-2-cyclohexene (**1**) was synthesized by the reported methods[3]. (η^5-Cyclopentadienyl) bis (ethylene) cobalt (Jonas reagent) was synthesized by the



Jonas method[5]. Cobalt tripledecker complex (**4b**), bis-[(η^5-cyclopentadienyl)-μ-(carbonyl) nickel] and nickel tripledecker complex (**5a**) were synthesized by the previously described methods[6-8].



Reaction of 4b with Potassium and $FeCl_2 \cdot 2THF$. A 100 m*l* Schlenk tube was mirrored with 57 mg of potassium (1.46 mmol) in vacuum and was filled with argon gas. The solution of 270 mg of **4b** (0.66 mmol) in 20 m*l* THF was put into this tube and stirred vigorously at room temperature. After 5 hours this reaction solution was filtered to remove the excess potassium and reacted with solid 280 mg of $FeCl_2 \cdot 2THF$ (1.03 mmol). After 2 more hours reaction, the solvent was removed and the residue was extracted with petroleum ether (PE) and a dark brown solution was obtained. The product was separated by column chromatography on silicagel eluting with PE. A dark green solid was obtained and recrystallized at −30℃. The product amounted to 80 mg. This decomposed to an orange-colored solid at room temperature during identification.