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A NOVEL SYNTHESIS OF VINYL DITHIOCARBAMATES VIA PHOSPHONIUM YLIDES

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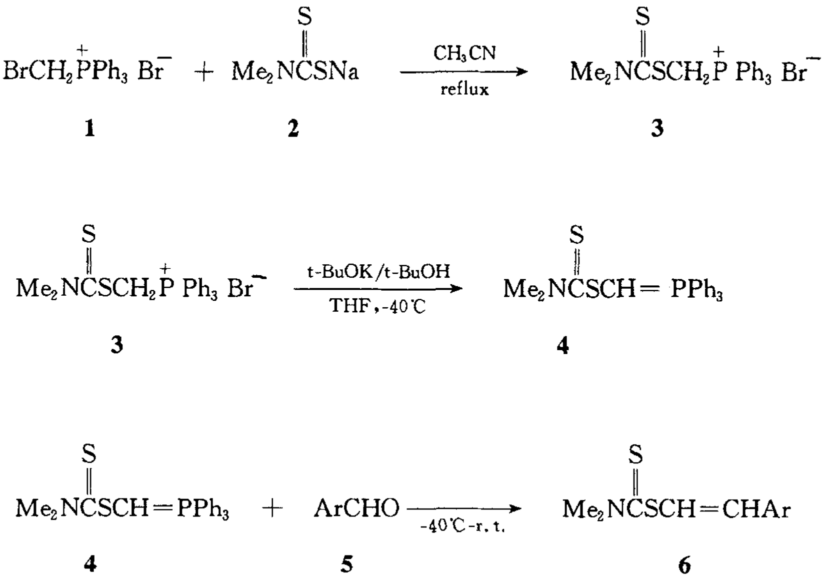
Abstract: In the presence of potassium carbonate, N,N-dimethylamino thiocarbonyl thiomethyl triphenylphosphonium bromide can form the corresponding ylide in situ, which can undergo Wittig reaction with aldehydes to give vinyl dithiocarbamates in high yields. If the esters were hydrolysized in the presence of mercuric chloride, a new method to lengthen aldehydes by one carbon atom was accomplished.

Dithiocarbamates were widely used not only in pharmaceutical and polymer industry, but also in organic synthesis. A lot of methods for the synthesis of alkyl or aryl dithiocarbamates have been reported[1,2,3], but these methods can not be applied to the synthesis of vinyl dithiocarbamates. Recently, vinyl sulfides have become increasingly important in organic synthesis[4,5], thus we considered that vinyl dithiocarbamates should have versatile reactivity. In this paper we have exploited a novel synthesis of vinyl dithiocarbamates and their application.

Because Wittig reaction is an important method for the formation of carbon-carbon double bonds, we used bromomethyl triphenyl phosphonium bromides **1** to react with sodium N, N-dimethylaminodithiocarbamates **2** in acetonitrile and obtained N, N-dimethylaminothiocarbonylthiomethyl triphenyl phosphonium bromides **3**. In the presence of potassium t-butoxide, this salt **3** was converted into the corresponding ylide **4** at -40℃ in situ which can undergo Wittig reaction with aldehydes smoothly, forming vinyl dithiocarbamates in good yields (Method A).



$$BrCH_2\overset{+}{P}Ph_3\ \overset{-}{Br} + Me_2N\overset{\overset{S}{\|}}{C}SNa \xrightarrow[\text{reflux}]{CH_3CN} Me_2N\overset{\overset{S}{\|}}{C}SCH_2\overset{+}{P}Ph_3\ \overset{-}{Br}$$

1 **2** **3**

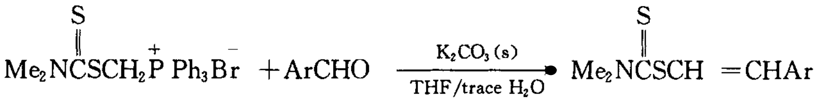
$$Me_2N\overset{\overset{S}{\|}}{C}SCH_2\overset{+}{P}Ph_3\ \overset{-}{Br} \xrightarrow[\text{THF},-40℃]{\text{t-BuOK/t-BuOH}} Me_2N\overset{\overset{S}{\|}}{C}SCH{=}PPh_3$$

3 **4**

$$Me_2N\overset{\overset{S}{\|}}{C}SCH{=}PPh_3 + ArCHO \xrightarrow[-40℃\text{-r.t.}]{} Me_2N\overset{\overset{S}{\|}}{C}SCH{=}CHAr$$

4 **5** **6**

Considering phosphonium salt itself has the property of phase transfer, we think that, in the presence of potassium carbonate and trace water, phosphomium salt can also be changed into phosphonium ylide in situ, which react with aldehydes to afford vinyl dithiocarbamates immediatly. The experimental results show that, in the presence of potassium carbonate, N, N-dimethylaminothiocarbonylthiomethyl triphenyl phosphonium bromide **3** and aldehydes **5** in THF with trace water can undergo phase transfer catalytic reaction at 50-60℃ to form vinyl dithiocarbamates (Method B).

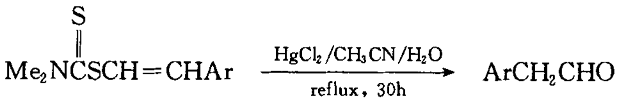


$$\mathrm{Me_2N\overset{\overset{S}{\|}}{C}SCH_2\overset{+}{P}Ph_3\overset{-}{Br}} + \mathrm{ArCHO} \xrightarrow[\mathrm{THF/trace\ H_2O}]{\mathrm{K_2CO_3\,(s)}} \mathrm{Me_2N\overset{\overset{S}{\|}}{C}SCH=CHAr}$$

3 **5** **6**

The advantages of this method are availability of starting materials, mild reaction conditions and being a simple one pot reaction.

Vinyl dithiocarbamates **6** are very useful synthetic intermediates. In the presence of mercuric chloride, vinyl dithiocarbamate **6** was refluxed in acetonitrile-water for 30h, it was hydrolysized into aldehyde **7** as a novel method for increasing one carbon atom from the original aldehyde.



$$\mathrm{Me_2N\overset{\overset{S}{\|}}{C}SCH=CHAr} \xrightarrow[\mathrm{reflux,\ 30h}]{\mathrm{HgCl_2/CH_3CN/H_2O}} \mathrm{ArCH_2CHO}$$

6 **7**

68-81%

EXPERIMENTAL SECTION

Melting points are uncorrected. IR spectra were recorded as KBr discs on Perkin Elmer 683 spectrophotometer. ^{1}H-NMR spectra were obtained with a Varian Em-360A, Fx-90Q spectrometer in $CDCl_3$ using TMS as internal standard. Chemical shifts are expressed in δ (ppm). The microelemental analyses were carried out on Carlo Erba 1106 instrument. N, N-Dimethylaminothiocarbonylthiomethyl triphenyl phosphonium bromide **3** was prepared as described.[6]

Synthesis of Vinyl Dithiocarbamates 6

Method A: N, N-Dimethylaminothiocarbonylthiomethyl triphenyl phosphonium brimide **3** (1. 2g, 2. 5mmol) in dry THF(20ml) was syringed into a solution of potassium ter-butoxide (3. 4g, 3mmol) in THF(15ml) at -40℃ under nitrogen. After stirred for 30 minuts, the solution of aldehyde (2. 5mmol) in THF(6ml) was added. The mixture was stirred for 2h at -40℃. Then the temperature was raised to r. t.. The mixture was continuously stirred about 1h. The reaction was monitored by TLC. A saturated solution of sodium chloride (30ml) was added to the reaction mixture and extracted with ether(3 × 25ml). The combined ethetr solution was dried with $MgSO_4$ and concentrated under vacuumn to give crude prodrct, which was purified by chromatography on silica gel (n-hexane : ethyl acetate 5 : 1).

Method B: N, N-Dimethylaminothiocarbonylthiomethyl tripheny phosphonium bromide **3** (1. 2g, 2. 5mmol), aldehyde(2. 5mmol) and potassium carbonate(0. 55g, 4mmol) in THF(25ml) and trace water(30μl) were stirred at 50-60℃ about 6h. The reaction was monitored by TLC and the remaining work up was similar to Method A.

6a(Ar=C_6H_5): Yield 66%(Method A), 74%(Method B). E/Z=5/2. IR: 1532, 1382, 1260, 753, 687 cm^{-1}. ^{1}H NMR($CDCl_3$):δ, 3. 48(br, 6H, CH_3), 6. 78(d, 0. 72H, J=16Hz, E-isomer), 6. 82(d, 0. 28H, J=11Hz, Z-isomer), 7. 20~7. 62(m, 6H, H Ar and vinylic). Ms, m/z: 223(M^+, 68), 88(100).

6b(Ar=4-ClC_6H_4): Yield 81%(Method A), 78%(Method B). E/Z=3/1. IR: 1541, 1380, 1241, 852 cm^{-1}. ^{1}H NMR($CDCl_3$): δ, 3. 46(br, 6H, CH_3), 6. 76(d, 0. 75H, J=16Hz, E-isomer), 6. 70(d, 0. 25H, J=11Hz, Z-isomer), 7. 26~7. 58(m, 5H, H Ar and vinylic). MS, m/z: 257(M^+, 7), 88(100).

6c(Ar=4-BrC_6H_4): Yield 75%(Method A), 76%(Method B). E/Z=5/2. IR: 1539, 1381, 1242, 851 cm^{-1}. ^{1}H NMR($CDCl_3$): δ, 3. 47(br, 6H,

CH_3), 6. 68(d, 0. 72H, J=16Hz, E-isomer), 6. 73(d, 0. 28H, J=11Hz, E-isomer), 7. 26~7. 60(m, 5H, H Ar and vinylic). MS, m/e: 802(M^+, 8), 88(100).

6d (Ar=4-$HO_2C_6H_4$): Yield 84%(Method A), 80%(Method B). E/Z =2/1. IR: 1550, 1478, 1342, 862 cm^{-1}^{1}H NMR($CDCl_3$): δ, 3. 54(br, 6H, CH_3), 6. 80(d, 0. 67H, J=16Hz, E-isomer), 6. 82(d, 0. 33H, J=11Hz, Z-isomer), 7. 55~8. 20(m, 5H, H Ar and vinylic). MS, m/2: 268 (M^+,10)), 88(100).

6e(Ar=2,4,$Cl_2C_6H_4$): Yield 73%(Method A),75%(Method B), E/2 =2/1. IR: 1538,1340,1268,852cm^{-1}. ^{1}H NMR($CDCl_3$): δ,3. 50(br,6H, CH_3), 6. 87(d,0. 67H,J=16H_2,E-isomer), 6. 90(d,0. 33H,J=11H_2,Z-isomer), 7. 28~7. 65(m,4H,H Ar and vinylic).

Hydrolysis of Vinyl Dithiocarbamates 6 **(Typical Procedure)**

To a solution of vinyl dithiocarbamate 6d (0. 27g, 1mmol) in 10ml of 3 : 1 acetonitrile-water was added mercuric chloride (0. 54g, 2mmol) in 10ml of same solvent mixture. The solution was reflux for 30 hr. The milky mixture was filtered, with thorough ether washing. The filtrate was washed with aqueous sodium bicarbonate and then with brine, dried over anhydrous magnesium sulfate, and concentrated under vacumn, to give crude product, which was purified by chromatography on silicagel (methylene chloride eluent) to give pure 4-nitrophenyl acetaldehyde **2d** 0. 13g, yield 76%, mp. 84-86℃ (Lit[7] 85-86℃).

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