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USE OF MOIST SILICA GEL FOR OBTAINING α-ETHYLENIC CARBONYL COMPOUNDS FROM β-ALKYLTHIO OR β-PHENYLTHIO ALLYLIC ALCOHOLS.

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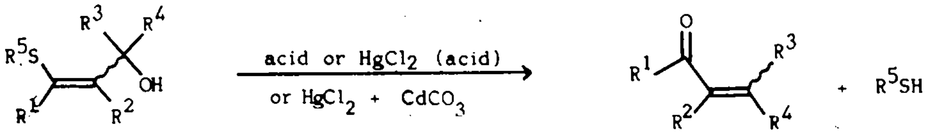
Abstract. The β-alkylthio and β-phenylthio α-ethylenic aldehydes 2, (Z)-6, (E)-6 and 9 were obtained from the corresponding β-chloro α-ethylenic aldehydes, and the α-phenylthiomethylidene ketones (Z)-13 and (E)-13 by Peterson reaction with α,α-dimethoxycyclohexanone followed by deacetalization. Reduction ($NaBH_4$) or addition of organolithium compounds led to allylic alcohols which gave α-ethylenic carbonyl compounds with removal of thiol or thiophenol after treatment by acidic moist silica gel with or without mercuric chloride. The method also worked for oxygenated compounds 21, 22.

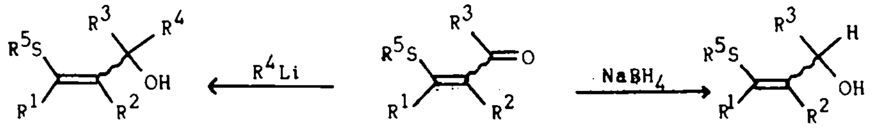
Several previous reports deal with the formation of α-ethylenic carbonyl compounds starting from β-alkylthio or β-arylthio allylic alcohols by treatment with an acid [1] or with mercuric chloride in neutral or acidic medium [2] or with a mixture of mercuric chloride and cadmium carbonate [3], (eq 1), (see also ref quoted in ref 1-4).



(1)

Some of these reactions were fast [1c], but in most cases they worked slowly (15-70 h). Some yields were high [1c,2], but most of them were moderate (30-70%). We have approached this problem with the aim of trying to improve the reaction conditions by using moist silica gel [5].

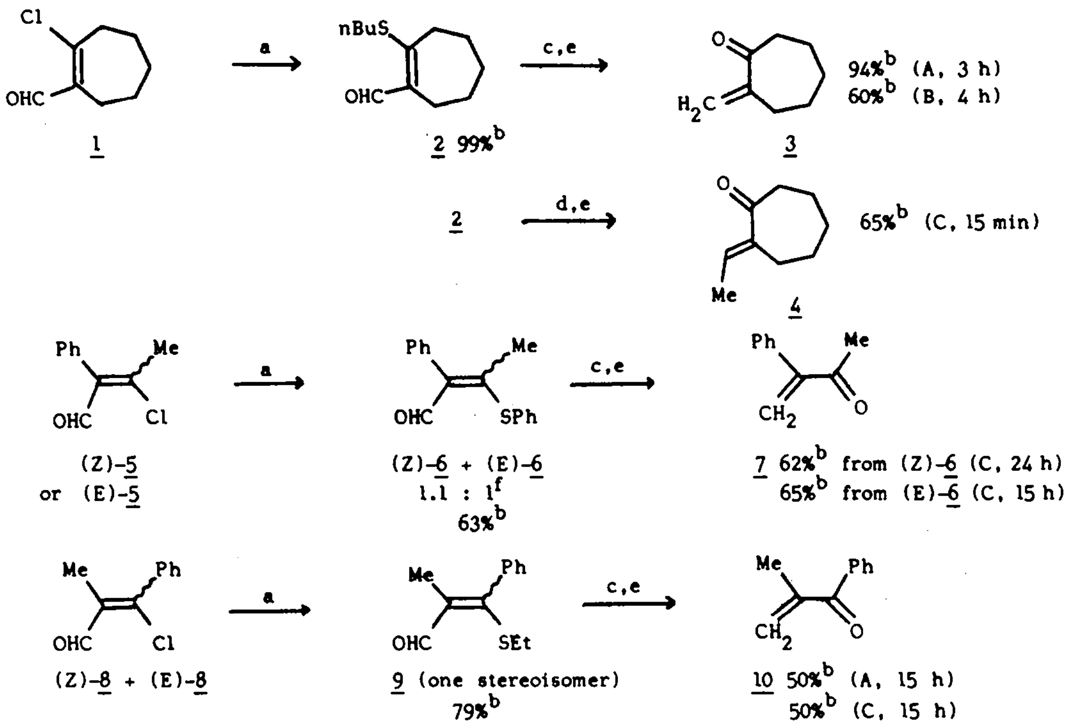
The β-alkylthio and β-phenylthio allylic alcohols were prepared by reduction of the corresponding carbonyl compounds [1a-c,2a] or by addition of organolithium compounds [1c,3], (eq 2). The starting β-alkylthio



(2)

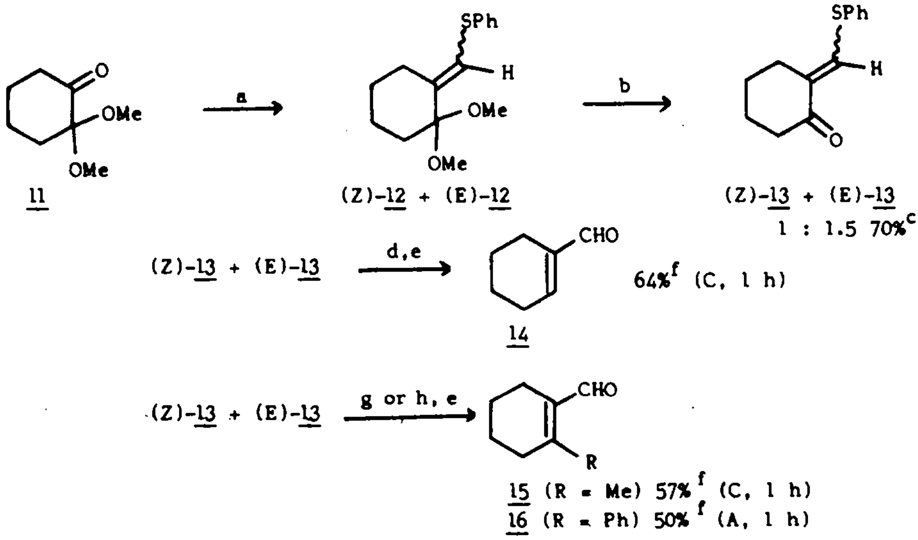
or β-phenylthio α-ethylenic aldehydes (Scheme I) were easily obtained [1c,6] from β-chloro α-ethylenic aldehydes prepared by Vilsmeier-Haack reaction. As it was anticipated, reactions of (Z)-5 or (E)-5 with thiophenol in basic medium were not stereospecific and each isomer gave the same mixture of (Z)-6 and (E)-6. In the case of reaction from (Z)-8 and (E)-8 only one stereoisomer of 9 was isolated. The α-phenylthiomethylidene ketones (Z)-13 and (E)-13 (Scheme II) were obtained from α,α-dimethoxycyclohexanone by Peterson reaction [7] followed by deacetalization with moist silica gel [5].

Scheme I



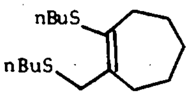
(a) RSH, NaOH, H_2O + THF ; (b) Yield of isolated product(s) ; (c) $NaBH_4$, MeOH ; (d) MeLi, THF + Et_2O; (e) A : SiO_2, H_2O, HOOC-COOH, $HgCl_2$, $CHCl_3$ or CH_2Cl_2 ; B : SiO_2, H_2O, HOOC-COOH, CH_2Cl_2 ; C : SiO_2, H_2O, H_2SO_4, CH_2Cl_2 ; (f) the same result was obtained from (Z)-5 and (E)-5.

Scheme II

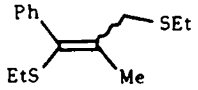


(a) PhSCH(Li)$SiMe_3$, THF + hexane ; (b) SiO_2, H_2O, CH_2Cl_2 ; (c) Yield of isolated product from 11 ; (d) $NaBH_4$, MeOH ; (e) see Scheme I ; (f) Yield of isolated product ; (g) MeLi, THF + Et_2O ; (h) PhLi, THF + C_6H_6 + Et_2O.

When the crude alcohol arising from reduction of 2 was treated with 1M sulfuric acid [1c] (1h, -6°C), the starting material was recovered and when the reaction was run with 10% hydrochloric acid in ethanol [1a] (24 h, room temp.), a small amount of 2-methylene cycloheptanone 3 (ca 2%) was obtained beside the starting material and 15% dithioether 17 (such by products were previously obtained under similar conditions[1d]). The results were much better in the presence of mercuric chloride [2b] as the α-enone 3



17



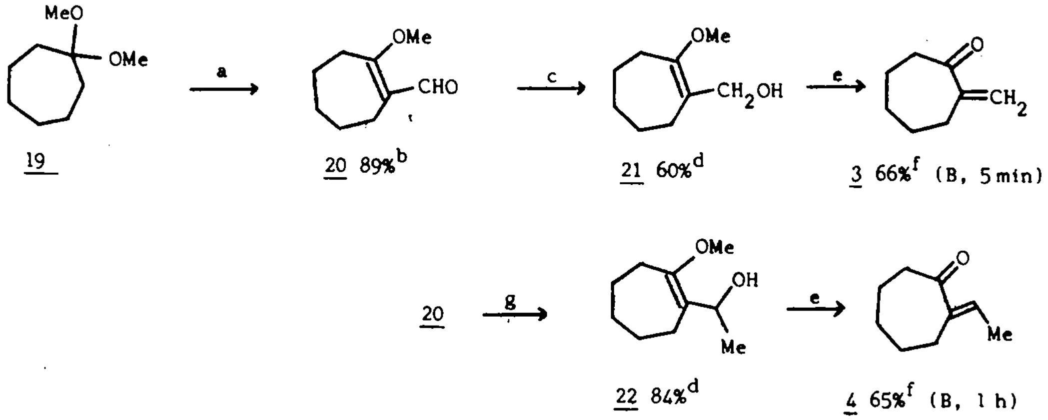
(Z)-18 and (E)-18

was then obtained in 58% yield from 2 in 17 h. However the use of moist silica gel greatly improved the reaction conditions as the α-enone 3 was thus obtained in 60% yield (4 h) in the presence of a small amount of oxalic acid and in 94% yield (3 h) when mercuric chloride was added to the reaction mixture (Scheme I). Moreover we observed that removing the mercuric derivatives at the end of the reaction was easier in these conditions than without silica gel.

Compounds 4, 7 and 10 (Scheme I) were obtained from the crude alcohols derived from 2, (Z)-6, (E)-6 and 9 by using moist silica gel acidified with oxalic acid. In these conditions 10 was obtained along with 41% of dithioethers (Z)-18 and (E)-18 but the yield was not improved when the reaction was run in the presence of mercuric chloride. Reactions from the crude alcohols corresponding to (Z)-13 and (E)-13 (Scheme II) led to 14 or 15 in moderate yield when using moist silica gel acidified with sulfuric acid. In the case of 16 the yield was improved when the reaction was conducted in the presence of mercuric chloride.

We were also interested in checking the method for oxygenated compounds [4,8]. Therefore we prepared the β-methoxy α-ethylenic aldehyde 20 by Vilsmeier reaction [9] from the acetal 19 (Scheme III). The expected β-methoxy α-ethylenic alcohols 21 and 22 were easily obtained from 20 by reduction or reaction with methyllithium. However these products are less stable than the corresponding sulfur compounds and they must be used quickly. When treated with moist silica gel acidified with oxalic acid they led to the expected α-enones 3 and 4.

Scheme III



(a) $POCl_3$, DMF ; (b) Yield of isolated product ; (c) $NaBH_4$, Et_2O ; (d) Yield of crude product ; (e) B: SiO_2, H_2O, HOOC-COOH, CH_2Cl_2 ; (f) Yield of isolated product calculated from crude 13 or 14 ; (g) MeLi, THF + Et_2O.

The main purpose of this work was to test the usefulness of moist silica gel for conversion of α-ethylenic β-sulfenylated alcohols, which can be prepared by various routes, into α-ethylenic carbonyl compounds. Our results effectively show an improvement as increased yields and reaction rates with regard to usual work up are observed. Moreover the experimental conditions are attractive as solutions of the crude products are obtained without extraction, simply by removing of the moist silica gel by filtration. In several cases, mercuric chloride was added to the reaction mixture to assist the carbon-sulfur bond cleavage, thus reducing the amount of by products. Even in these cases, the use of moist silica gel improved the results and made it easier to remove the mercuric derivatives at the end of the reaction. Finally the method also works for oxygenated compounds. It is also worth mentioning that the preceeding four step sequence for obtaining α-methylene ketones, which led, for instance to 2-methylene cycloheptanone in 75.4% overall yield from cycloheptanone, (Scheme I) [10] may be a valuable alternative to useful general methods (see ref 11a-d for other recent preparations of the same product in lower overall yield and ref 11e for another preparation in better yield).

Experimental Section

Proton NMR spectra were obtained on a Perkin Elmer R32 (90 MHz) instrument. Mass spectra were recorded on a Girdel-Nermag R10-10 mass spectrometer. High resolution mass spectra were measured on a Kratos MS 50 instrument (12). IR spectra were determined on a Perkin Elmer 682 instrument. Microanalyses were performed by the Service de Microanalyses, CNRS, ICSN, Gif-sur-Yvette.

β-Chloro α-ethylenic aldehydes 1, (Z)-5, (E)-5, (Z)-8 + (E)-8

The β-chloro α-ethylenic aldehydes were prepared by the literature procedures (13,14). Both isomers of 3-chloro-2-phenyl-but-2-enal (Z)-5 and (E)-5 were separated by column chromatography on silica gel (ether/pentane, 7:93). Both isomers of 3-chloro-3-phenyl-2-methyl-propenal (Z)-8 and (E)-8 were not separated.

2-n-Butylthio-cyclohept-1-ene-carbaldehyde 2

A solution of 1.54 g (9.71 mmol) of 1 in tetrahydrofuran (18 mL) was added dropwise (-10°C) to a stirred solution of butanethiol (1.49 g, 16.5 mmol) in tetrahydrofuran (18 mL). After 15 min of stirring at -10°C, 14.56 mL of aqueous solution of 1M NaOH (14.56 mmol) were added dropwise (10 min ; -8°C to +5°C) and the reaction mixture was allowed to warm up slowly to room temperature (25 min). Extraction (3 x 60 mL of ether), washing (3 x 20 mL of water), drying (Na_2SO_4) and evaporation gave the crude product which was chromatographed on 40 g of silica gel (ether/pentane, 7:93). Aldehyde 2 was thus obtained in 99% yield (2.04 g). ^1H NMR (CCl_4) δ 0.95 (t, J = 5.4 Hz, 3H), 1.15 - 2.01 (m, 10H), 2.33- 2.95 (m, 6H), 10.31 (s, 1H) ; IR (CCl_4) 1670, 1575 cm^{-1} ; MS, m/e (relative intensity) (EI) 41 (55), 93 (34), 155 (100), 212 (M^+, 13). Anal. Calcd for $C_{12}H_{20}OS$: C, 67.87 ; H, 9.49 ; S, 15.10. Found : C, 67.50; H, 9.57 ; S, 14.90.

(Z)- and (E)-2-phenyl-3-phenylthio-but-2-enals, (Z)-6 and (E)-6

The procedure was the same as described above for 2. The reaction from (Z)-5 (0.520 g, 2.88 mmol) led to the crude product which was chromatographed on 25 g of silica gel (ether/pentane, 10:90). Compounds (Z)-6 (0.241 g, 33%) and (E)-6 (0.219 g, 30%) were successively eluted. The reaction from (E)-5 gave the same result. (Z)-6 : ^1H NMR (CCl_4) δ1.85 (s, 3H), 6.96 - 7.56 (m, 10H), 10.33 (s, 1H) ; IR (CCl_4) 1680 cm^{-1} ; MS, m/e (relative intensity) (EI) 110 (94) ; 115 (100), 116 (63), 254 (M^+, 48). Anal. Calcd for $C_{16}H_{14}OS$: C, 75.56 ; H, 5.55 ; S, 12.61. Found : C, 75.57 ; H, 5.55 ; S, 12.64. (E)-6 : ^1H NMR δ 2.21 (s, 3H) 7.09 - 7.52 (m, 10H), 9.85 (s, 1H) ; IR (CCl_4) 1672 cm^{-1} ; MS, m/e (relative intensity) (EI) 110 (94), 115 (100), 116 (63), 254 (M^+, 48). Anal. Calcd for $C_{16}H_{14}OS$: C, 75.56 ; H, 5.55 ; S, 12.61. Found : C, 75.70 ; H, 5.53 ; S, 12.63.

3-Ethylthio-2-methyl-3-phenyl-propenal, 9

The procedure was the same as described above for 2. The reaction from (Z)-8 + (E)-8 (1.500g, 8,30 mmol) led to the crude product which was chromatographed on 30 g of silica gel (ether/pentane, 10:90). Compound 9 was thus obtained in 79% yield (1.35 g). ^1H NMR (CCl_4) δ1.05 (t, J = 8 Hz, 3H), 1.93 (s, 3H), 2.28 (q, J = 8 Hz, 2H), 7.08 - 7.62 (m, 5H), 9.09 (s, 1H) ; IR (CCl_4) 1670, 1575 cm^{-1} ; MS, m/e (relative intensity) (EI) 115 (39), 177 (100), 206 (M^+, 20), accurate mass (EI) m/e 206.0763 (calcd for M^+, $C_{12}H_{14}OS$: 206.0765) ; Anal. Calcd for $C_{12}H_{14}OS$: C, 69.86 ; H, 6.84 ; S, 15.54. Found : C, 69.59; H, 6.84 ; S, 15.53.

(Z)- and (E)-2-[(phenylthio)methylidene]cyclohexanone, (Z)-13 and (E)-13

n-Butyllithium (6.50 mmol ; 4.42 mL of a solution 1.47M in hexane) was added dropwise at 0°C with stirring and under argon to a solution of 1.28 g (6.52 mmol) of [(phenylthio)methyl]trimethylsilane in THF (15 mL). After 15 min. of stirring at 0°C, a solution of 2,2-dimethoxycyclohexanone (15) (1.00g, 6.35 mmol) in THF (10 mL) was added dropwise. After 15 min. of stirring the mixture was allowed to warm up to room temperature and stirred during 2 h at this temperature. Then 25 mL of brine was added with stirring and the aqueous phase was extracted with ether (3 x 20 mL). The combined organic phases were dried (Na_2SO_4) and evaporated to leave a mixture of crude (Z)-12 + (E)-12. ^1H NMR (CCl_4) δ1.33- 1.92 (m, 6H), 1.98 - 2.60 (m, 2H), 3.11 (s, 3H), 3.22 (s, 3H), 6.18 (br s, 0.4H), 6.54 (br s, 0.6H), 7.01 - 7.57 (m, 5H) ; MS, m/e (relative intensity) (EI) 67 (46), 95 (35), 110 (100), 264 (M^+, 39). The crude preceding mixture was deacetalized by the following procedure : 12 g of silica gel SDS 70-230 mesh, 30 mL of CH_2Cl_2 and 1.2 g of water were stirred at room temperature (ca 2 min). The mixture of (Z)-12 + (E)-12 was added and the reaction mixture was stirred during 1 h. The solid phase was separated by suction filtration on a sintered glass funnel and washed several times with CH_2Cl_2. Evaporation of the solvent gave the crude product which was chromatographed on 45 g of silica gel (ether/pentane, 6:94). The mixture of (Z)-13 + (E)-13 was thus obtained in 70% overall yield (1.24 g). ^1H NMR (CCl_4) δ 1.52 - 2.05 (m, 4H), 2.18 - 2.69 (m, 4H), 6.75 (t, J = 1.33 Hz, 0.4H, isomer Z), 7.10 - 7.65 (m, 5H), 7.55 (t, J = 1.33 Hz, 0.6H; isomer E) (the stereochemical assignements were verified by spectra in the presence of $Eu(fod)_3$ (16)); IR (CCl_4) 1715, 1675 cm^{-1} ; MS, m/e (relative intensity) (EI) 79 (38), 81 (73), 109 (46), 218 (M^+, 100). One of these compounds has been previously reported (17).

2-Methoxy-cyclohept-1-ene carbaldehyde 20

The reaction of 1,1-dimethoxycycloheptane with $POCl_3$ + DMF according to ref. 9 (introduction of 1,1-dimethoxycycloheptane below 4°C then the reaction was allowed to proceed at room temperature during 15 h). The crude product was chromatographed on silica gel (ether/pentane, 50:50). Compound 20 was thus obtained in 89% yield. ^1H NMR (CCl_4) δ1.31 - 2.05 (m, 6H), 2.16 - 2.68 (m, 4H), 3.73 (s, 3H), 9.95 (s, 1H) ; IR (film) 1660, 1620 cm^{-1} ; MS, m/e (relative intensity) (EI) 54 (67), 55 (63), 84 (93), 95 (66), 154 (M^+, 100), accurate mass (EI) m/e 154.0990 (calcd for M^+, $C_9H_{14}O_2$: 154.0994).

Reduction of β-alkylthio and β-arylthio α-ethylenic carbonyl compounds 2, (Z)-6, (E)-6, 9, (Z)-13+(E)-13 with $NaBH_4$

The reduction according to ref. 2a (2 h, room temperature for aldehydes, 24 h for ketones ; solvent, MeOH) gave the crude alcohols which were used in the following step without purification. Spectral data : 2-n-butylthio-1-hydroxymethyl-cyclohept-1-ene : ^1H NMR (CCl_4) δ0.94 (t, J = 5.4 Hz, 3H), 1.20 - 1.91 (m, 10H), 2.24 - 2.81 (m, 6H), 3.88 (m, 1H), 4.37 (br s, 2H) ; IR (CCl_4) 3620, 3450, 1620 cm^{-1} ; MS, m/e (relative intensity) (EI) 41 (39), 67 (20), 95 (24), 157 (100), 214 (M^+, 16) ; (Z)-2-phenyl-3-phenylthiobut-2ene-1-ol : ^1H NMR (CCl_4) δ1.58 (s, 1H), 2.02 (s, 3H), 4.33 (br s, 1H), 7.04 - 7.47 (m, 10H) ; IR (CCl_4) 3618, 3450, 1620 cm^{-1} ; MS, m/e (relative intensity) (EI) 77 (94), 91 (82), 115 (100), 147 (58), 256 (M^+, 65) ; (E)-2-phenyl-3-phenylthio-but-2-ene-1-ol : ^1H NMR (CCl_4) δ1.74 (s, 1H), 1.77 (s, 3H), 4.58 (br s, 2H), 7.02 - 7.47 (m, 10H) ; IR (CCl_4) 3618, 3450, 1620 cm^{-1} ; MS, m/e (relative intensity) (EI) 77 (93), 91 (83), 110 (64), 115 (100), 145 (74), 147 (88), 256 (M^+, 99) ; (E)- or (Z)-2-ethylthio-2-methyl-3-phenyl-prop-2-ene-1-ol ; ^1H NMR (CCl_4) δ1.00 (t, J = 7 Hz, 3H), 2.00 (s, 3H), 2.13 (q, J = 7 Hz, 2H), 3.31 (s, 1H), 3.77 (s, 2H), 7.11 - 7.37 (m, 5H) ; IR (CCl_4) 3628, 3475, 1620 cm^{-1} ; MS, m/e (relative intensity) (EI) 115 (40), 117 (54), 121 (48), 179 (100), 208 (M^+, 30) ; (E)- + (Z)-2-[(phenylthio)methylidene]cyclohexane-1-ol : ^1H NMR (CCl_4) δ1.20 - 2.24 (m, 6H), 2.33 - 2.86 (m, 2H), 4.10 (m, 1H), 4.88 (m, 1H), 5.89 (s, 0.4H), 6.18 (s, 0.6H), 6.98 - 7.46 (m, 5H) ; IR (CCl_4) 3620, 3460, 1625 cm^{-1}.

2-Methoxy-1-hydroxymethyl-cyclohept-1-ene 21

The reduction of aldehyde 20 with $NaBH_4$ according to ref. 18 (10 min at 0°C then 24 h at room temperature, solvent : Et_2O) gave the crude alcohol 21 (60% crude yield) which was used in the following step without purification. ^1H NMR (CCl_4) δ1.20 - 2.10 (m, 6H), 2.20 - 2.65 (m, 4H), 3.84 (s, 3H), 4.48 (d, J = 6 Hz, 1H) ; IR (film) 3400, 2930, 1450 cm^{-1}. MS, m/e (relative intensity) (EI) 41 (67), 55 (65), 84 (87), 95 (58), 154 (100), 156 (M^+, 1.5)

Reaction of carbonyl compounds 2 and 20 with MeLi and of (Z)-13 + (E)-13 with MeLi and PhLi

These reaction were run in THF + Et_2O (ca 2 mmol of organolithium compound per mmol of carbonyl compound) by the usual procedure (2, (Z)-13 + (E)-13 : 10 min at -75°C then the reaction mixture was allowed to warm up to -60°C during 40 min ; 20 : 4 h at -78°C). The crude alcohols were used in the following step without purification. Spectral data : 1-(2'n-butylthio-cyclohept-1'-ene)ethane-1-ol : ^1H NMR (CCl_4) δ0.83 - 2.03 (m comprising one d (1.13, J = 6.7 Hz), 16H), 2.18 - 2.80 (m, 6H), 3.74 (m, 1H), 5.30 (q, J = 6.7 Hz, 1H) ; IR (CCl_4) 3622, 3460, 1450 cm^{-1} ; MS, m/e (relative intensity) (EI) 41 (25), 43 (100), 95 (24), 171 (80), 228 (M^+, 16) ; (Z)- + (E)-1-methyl-2-[(phenylthio)methylidene]cyclohexane-1-ol : ^1H NMR (CCl_4) δ1.25 - 2.09 (m, 6H), 1.37 (s, 1.8H), 1.41 (s, 1.2H), 3.30 (m, 1H), 2.07 - 2.78 (m, 2H), 5.94 (s, 0.4H), 6.32 (s, 0.6H), 7.10 - 7.77 (m, 5H) ; IR (CCl_4) 3615, 3460, 1622 cm^{-1} ; MS, m/e (relative intensity) (EI) 43 (76), 110 (35), 125 (100), 234 (M^+, 33) ; (Z)- + (E)-1-phenyl-2-[(phenylthio)methylidene]cyclohexane-1-ol : ^1H NMR (CCl_4) δ1.18 - 2.91 (m, 9H), 6.14 (s, 0.4H), 6.19 (s, 0.6H), 6.95 - 7.57 (m, 10H); IR (CCl_4) 3615, 3480, 1625 cm^{-1} ; MS, m/e (relative intensity) (EI) 77 (52), 105 (71), 187 (100), 278 (70), 296 (M^+, 30); 1-(cyclohept-1'-ene-2'-methoxy)ethane-1-ol 22 : ^1H NMR (CCl_4) δ1.13 (d, J = 7 Hz, 3H), 1.30 - 1.82 (m, 6H), 1.98 - 2.48 (m, 4H), 3.50 (s, 3H), 4.77 (q, J = 7 Hz, 1H) ; IR (film) 3410, 1450 cm^{-1}; MS, m/e (relative intensity) (EI) 67 (76), 68 (100), 81 (89), 82 (71), 170 (M^+, 2).

General procedure to obtain the α-ethylenic carbonyl compounds by method A ; preparation of 2-methylenecycloheptanone 3

Silica gel SDS 70-230 mesh (2.1 g) $CHCl_3$ or CH_2Cl_2 (6 mL) and 10% aqueous solution of oxalic acid (0.21 g) were stirred at room temperature (ca 2 min). $HgCl_2$ (542 mg, 2.00 mmol) then the crude alcohol obtained by reduction of 422 mg (1.99 mmol) of 2 were successively added to this mixture under stirring. The reaction mixture was stirred during 3 h (TLC monitoring). The solid phase was separated by suction filtration on a sintered glass funnel and washed several times with CH_2Cl_2. Evaporation of the solvent gave a crude product which was chromatographed on 4 g of silica gel (ether/pentane, 8:92). 2-Methylenecycloheptanone 3 was thus obtained in 94% yield from 2 (232 mg) (spectral data in agreement with literature (11d)).

General procedure to obtain the α-ethylenic carbonyl compounds by methods B and C

In the case of method B the procedure was the same as for method A (ca 5 g of silica gel and 0.5 g of 10% aqueous solution of oxalic acid per g of α-ethylenic alcohol) but the reaction was run without $HgCl_2$. In the case of method C the reaction was run without $HgCl_2$ and 10% aqueous solution of sulfuric acid was used instead of oxalic acid.

In both methods CH_2Cl_2 was used as solvent but $CHCl_3$ could also be used.

Spectral data for α-ethylenic carbonyl compounds 4, 7, 10, 14, 15, 16 and for dithioethers 17, 18 (for method, reaction time and yield see Schemes I, II and III or text for 17 and 18)

The spectral data for 4, 7, 10, 14, 15 are in agreement with literature (ref. 11d for 4 ; ref. 19 for 7 ; ref. 20 for 10; ref. 21 for 14 and 15). Cyclohex-1-ene-2-phenylcarbaldehyde 1 : ^1H NMR (CCl_4) δ1.57 - 1.92 (m, 4H), 2.12 - 2.64 (m, 4H), 6.88 - 7.69 (m, 5H), 9.42 (s, 1H) ; IR (CCl_4) 1675, 1628 cm^{-1}; MS (22), m/e (relative intensity) (EI) 129 (23), 185 (100), 186 (M^+, 85) ; accurate mass (EI) m/e 186.1045 (calcd for M^+ $C_{13}H_{14}O$: 186.1044) ; 1-n-butylthio-2-(n-butylthio)methyl-cyclohept-1-ene 17 : ^1H NMR (CCl_4) δ0.72 - 1.11 (m, 6H), 1.11 - 1.95 (m, 14H), 2.11 - 2.55 (m, 8H), 3.44 (s, 2H) ; IR (film) 1625 cm^{-1}; MS m/e (relative intensity) (EI) 41 (32), 79 (32), 197 (100), 286 (M^+, 25) ; Anal. Calcd for $C_{16}H_{30}S_2$: C, 67.07; H, 10.55 ; S, 22.38. Found : C, 67.23 ; H, 10.25 ; S, 22.21 ; (Z)- + (E)-1-ethylthio-2 (ethylthio)methyl-1-phenylpropene (Z)-18 + (E)-18 : ^1H NMR (CCl_4) δ0.98 (t, J = 8 Hz, 1.5H), 1.01 (t, J = 8 Hz, 3H), 1.28 (t, J = 8 Hz, 1.5H), 1.74 (s, 1.5H), 2.11 (s, 1.5H), 2.15 (q, J = 8 Hz, 1H), 2.24 (q, J = 8 Hz, 1H), 2.52 (q, J = 8 Hz, 1H); 3.07 (s, 1H), 3.60 (s, 1H), 7.04 - 7.44 (m, 5H) ; IR (CCl_4) 1600 cm^{-1} ; MS, m/e (relative intensity) (EI) 75 (31), 129 (100), 191 (86), 252 (M^+, 24), accurate mass (EI) m/e 252.1005 (calcd for M^+, $C_{14}H_{20}S_2$: 252.1006).

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