Clay Catalysis: A Simple and Efficient Synthesis of Enolthioethers from Cyclic Ketones

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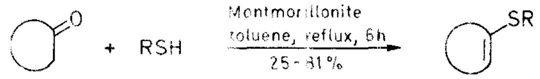
Montmorillonite KSF in refluxing toluene catalyses the synthesis of 1-alkyl- and 1-arylthioalkenes from ketones and thiols (thiophenol or 1-butanethiol).

1-Alkenyl sulfides are versatile and useful reagents in organic synthesis.[1] Multistep methods from ketones using hazardous reagents like cuprous triflate,[2] mercuric salts[1] or peroxides[3] were recently described. Direct conversion of ketones to their enolthioethers involved corrosive and sensitive Lewis acids.[4]

We report here that KSF clay, an acidic montmorillonite type phyllosilicate is a convenient catalyst for the direct conversion of ketones to the corresponding 1-alkyl- and 1-arylthioalkenes. Clay minerals are known to catalyze a variety of organic reactions.[5] Various Montmorillonites were used: KSF (Specific Area (S.A.) = 20–40 m^2/g, Hammett acidity $H_0 \approx -7$), K10SF (S.A. = 150–200 m^2/g, $H_0 \approx -6.8$), and K10 (S.A. = 220–270 m^2/g, $H_0 \approx -6.6$). Similar yields were obtained with KSF, K10SF, and K10 but the reaction takes place faster with KSF, than K10SF, and K10. Montmorillonite KSF is a very acidic clay with no corrosive action.

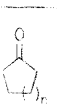
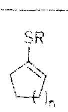
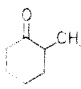
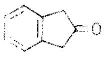
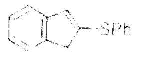
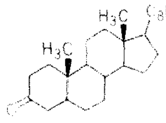
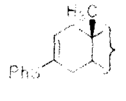
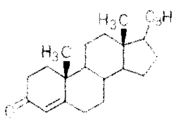
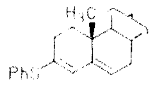
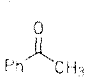
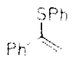


With cyclododecanone (**1e**) and 2-methylcyclohexanone (**3**) a mixture of isomers is obtained (**4**/**5** = 4.14 : 1; **2e** or **2e'**, Z/E = 1 : 1). This shows that the reaction is thermodynamically controlled. With cyclopentanone (**1**) and thiophenol the principal product was 1,1-bis(phenylthio)cyclopentane (yield: 45%) (Table 1).

KSF catalyst is quite inexpensive,[11] stable, and non-corrosive. This new method is remarkably easy, non-hazardous, and inexpensive.

1-Alkyl/arylthioalkenes from Ketones; General Procedure:
A mixture of thiol (10 mmol) and ketone (10 mmol) is stirred and refluxed under nitrogen with montmorillonite KSF (2 g) in toluene (100 mL) for 6 h. Water formed is separated with a Dean-Stark apparatus. After completion of the reaction (TLC, solvent: cyclohexane/EtOAc, 9:1), the mixture is filtered. Ether (80 mL) is added, the organic phase is washed with 10% aq. Na_2CO_3 (2 × 50 mL), water (2 × 50 mL), and dried ($MgSO_4$). The solvent is removed under vacuum, and the

Table 1. Synthesis of 1-Alkyl/arylthioethers from Ketones and Thiols

Ketone	Thiol	Product		Yield[a] (%)	mp (°C) or bp (°C)/mbar[b]	Molecular Formula[c] or Lit. Data
	PhSH					
1a		**2a**	n = 1, R = Ph	25	110/0.1	bp 110/0.1[1]
1b		**2b**	n = 2, R = Ph	60	145/0.7	bp 115/0.1[1]
1c		**2c**	n = 3, R = Ph	70	90–91/0.15	bp 95/0.2[6]
1d		**2d**	n = 4, R = Ph	73	110–120/0.1	bp 110–115/0.05[7]
1e		**2e**	n = 8, R = Ph (Z/E = 1 : 1)	70	160–170/0.1	bp 164/0.1[1]
1b	*n*-BuSH	**2b'**	n = 2, R = *n*-Bu	70	95/0.1	$C_{10}H_{18}S$ (170.2)
1c		**2c'**	n = 3, R = *n*-Bu	43	100/0.1	$C_{11}H_{20}S$ (184.2)
1d		**2d'**	n = 4, R = *n*-Bu	81	95/0.15	$C_{12}H_{22}S$ (198.2)
1e		**2e'**	n = 8, R = *n*-Bu (Z/E = 1 : 1)	62	200/0.15	$C_{16}H_{30}S$ (254.3)
3 	PhSH	**4** + **5**		58 14	170–175/10 170–175/10	$C_{13}H_{16}S$ (204.2) $C_{13}H_{16}S$ (204.2)
6 	PhSH	**7**		30	185–190/0.2	–[8,d]
8 	PhSH	**9**		62	82[e]	mp 83–85[9]
10 	PhSH	**11**		40	70[f]	mp 67–68[9]
12 	PhSH	**13**		40	90–91/0.12	bp 90–92/0.11[10]

[a] Yield of isolated products based on starting ketone.
[b] Uncorrected.
[c] Satisfactory microanalyses obtained: C ±0.30, H ±0.30, S ±0.30.
[d] Product **7** is described in Ref. 8, but no bp is reported.
[e] Recrystallized from CH_3OH/EtOAc.
[f] Recrystallized from CH_3OH.

Table 2. IR and ^{1}H-NMR Spectra of Enolthioethers

Compound	IR (neat)[a] ν (cm^{-1})	^{1}H-NMR (CCl_4/TMS)[b] δ, J (Hz)
2a	1645, 1580	1.8 (m, 2H, CH_2); 2.3 (m, 4H, $=CCH_2$); 5.6 (s, 1H, $=CH$); 7.2 (m, 5H, Ph)
2b	1635, 1590	1.5 (m, 4H, CH_2); 2.08 (m, 4H, $=CCH_2$); 5.9 (t, 1H, $=CH$, $J = 7$); 7.1 (m, 5H, Ph)
2c	1630, 1590	1.4 (m, 6H, CH_2); 2.18 (m, 4H, $=CCH_2$); 6.02 (t, 1H, $=CH$, $J = 6.5$); 7.1 (m, 5H, Ph)
2d	1630, 1590	1.52 (m, 8H, CH_2); 2.23 (m, 4H, $=CCH_2$); 5.6 (t, 1H, $=CH$, $J = 8$); 7.2 (m, 5H, Ph)
(*E*)-2e	1630, 1595	1.1–1.56 (m, 16H, CH_2); 2.1–2.2 (m, 2H, $=CCH_2$); 2.25–2.45 (m, 2H, $=CCH_2$); 5.9 (t, 1H, $=CH$, $J = 8$); 7.14 (m, 5H, Ph)
(*Z*)-2e	1630, 1595	1.1–1.7 (m, 16H, CH_2); 2.3 (m, 4H, $=CCH_2$); 5.8 (t, 1H, $=CH$, $J = 8$); 7.15 (5H, Ph)
2b′	1630, 1450	0.9 (t, 3H, CH_3, $J = 5$); 1.5 (m, 8H, CH_2); 2.0 (m, 4H, $=CCH_2$); 2.5 (t, 2H, SCH_2, $J = 6$); 5.45 (m, 1H, $=CH$)
2c′	1625, 1460	0.95 (t, 3H, CH_3, $J = 5$); 1.55 (m, 10H, CH_2); 2.15 (m, 4H, $=CCH_2$); 2.5 (t, 2H, SCH_2, $J = 6$); 5.45 (t, 1H, $=CH$, $J = 6.5$)
2d′	1620, 1465	0.9 (t, 3H, CH_3, $J = 6$); 1.45 (m, 12H, CH_2); 2.1 (m, 4H, $=CCH_2$); 2.55 (t, 2H, SCH_2, $J = 7$); 5.22 (t, 1H, $=CH$, $J = 8$)
(*E*)-2e′	1620, 1465	0.9 (t, 3H, CH_3, $J = 5$); 1.32 (m, 20H, CH_2); 2.2 (m, 4H, $=CCH_2$); 2.45 (t, 2H, SCH_2, $J = 6$); 5.65 (t, 1H, $=CH$, $J = 8$)
(*Z*)-2e′	1620, 1465	0.9 (t, 1H, CH_3, $J = 5$); 1.32 (m, 20H, CH_2); 2.2 (m, 4H, $=CCH_2$); 2.45 (t, 2H, SCH_2, $J = 6$); 5.15 (t, 1H, $=CH$, $J = 8$)
4	1650, 1590	1.7 (m, 4H, CH_2); 1.9 (s, 3H, CH_3); 2.2 (m, 4H, $=CCH_2$); 7.2 (m, 5H, Ph)
5	1650, 1590	1.4 (s, 3H, CH_3); 1.7 (m, 2H, CH_2); 2.2 (m, 4H, $=CCH_2$); 5.9 (m, 1H, $=CH$); 7.2 (m, 5H, Ph)
7	1615, 1590	2.1–3.2 (m, 2H, $=CH_2$); 5.1 (s, 1H, $=CH$); 7.2 (m, 5H, Ph)
9	1640, 1585	0.65–0.9 (s, 15H, CH_3); 1.1–2.0 (m, 29H, CH_2, CH); 5.9 (s, 1H, $=CH$); 7.1–7.3 (m, 5H, Ph)
11	1620, 1580	0.6–1.1 (s, 15H, CH_3); 1.2–2.4 (m, 26H, CH_2, CH); 5.6 (m, 1H, $=CH$); 6.5 (s, 1H, $=CH$); 7.3–7.5 (m, 5H, Ph)
13	1610, 1590	5.2 (s, 1H, $=CH$); 6.2 (s, 1H, $=CH$); 7.1–7.3 (m, 5H, Ph)

[a] Recorded on Perkin-Elmer 684 and 1420 IR spectrophotometers.

[b] Recorded on a Varian EM 360 spectrometer.

product is purified by Kugelrohr distillation or flash chromatography (Table 1). All the products reported are characterized by their IR and ^{1}H-NMR spectra (Table 2).

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(11) Montmorillonite KSF is commercially available from Fluka and Aldrich.