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BASE CATALYSED REARRANGEMENT OF 2-METHYL-3,3-BISALKYLTHIOACRYLOPHENONES TO 2-ALKYLTHIOMETHYL-3-ALKYLTHIOACRYLOPHENONES VIA MOBILE KETO ALLYL INTERMEDIATES[1]

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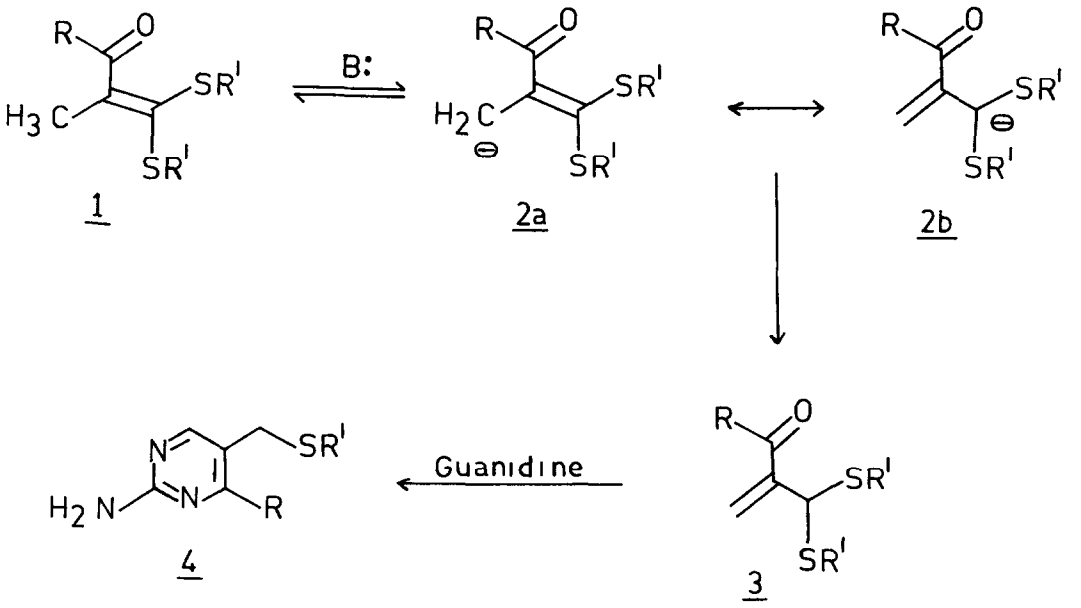
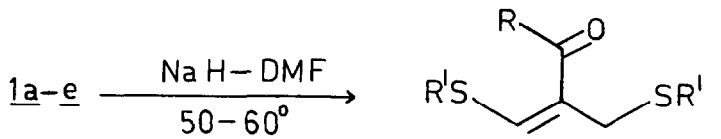
Abstract: The title compounds (1a-e) undergo facile base catalysed rearrangement to give 5a-e. A mechanism involving thioallylic rearrangement of intermediates, 2-bisalkylthiomethyl acrylophenones, (3a-e) has been proposed.

During the course of our studies on the synthetic utility of keto-ketene dithioacetals as three carbon fragments, we reported[2] the formation of pyrimidine 4 from 1 and guanidine in refluxing ethanolic sodium ethoxide (scheme 1). The proposed mechanism for the formation of 4 was rationalized to have involved the intermediate 3 via base induced 1,3-proton transfer from 1 through the anion 2b. The 1,3-proton transfer in these systems is not very unusual, since the 3d orbital participation of the adjacent sulfur atoms greatly stabilizes the negative charge on the carbon atom next to them. However, in our subsequent work it was intended to isolate 3 as discrete intermediates which are interesting mobile keto allyl systems of potential synthetic utility.



Scheme 1

We report in this communication our preliminary results on the base catalysed rearrangements of 1 using sodium hydride in dry dimethylformamide. The products thus isolated did not have the expected structural features as shown in 3 and on the basis of their spectral and analytical data, they were assigned the structures as shown in 5, apparently involving thioallylic rearrangement of 3. In a typical experiment, the ketene dithioacetal (1a) (0.01 mole) in dimethylformamide (10 ml) was added dropwise (30 min) to a well stirred suspension of sodium hydride (0.03 mole) and dry dimethylformamide (20 ml) and the reaction mixture was stirred at 50-60° for 4 hr. It was then quenched over crushed ice, and extracted with chloroform (2 X 100 ml), washed (H_2O), dried (Na_2SO_4) and the solvent was removed to give the crude residue, which on chromatography over silica gel column (hexane : EtOAc) gave first 1a (37%) and then 5a (R_f~0.5 in C_6H_6 on silica gel plate) in 35% yield (55% on the basis of recovered starting material).[3] Similarly the dithioacetals 1b-e were converted into the corresponding 5b-e in 35-45% yields.[4,5]



5a-e

		Yields(%)
1,5a,	R=C_6H_5; R'=CH_3	35(55)[a]
b,	R=C_6H_5; R'=C_2H_5	43(50)
c,	R=p-$MeOC_6H_4$; R'=CH_3	45(70)
d,	R=p-$MeOC_6H_4$; R'=C_2H_5	40(61)
e,	R=p-MeC_6H_4; R'=CH_3	35(60)

[a]yields indicated in parentheses are on the basis of recovered starting materials.

Scheme 2

The proposed mechanism for the formation of 5 from 1 is shown in the scheme 3. The allyl anions 2a and 2b generated under reversible conditions, compete with NaH in deprotonation of 1 to give either 1 or the rearranged acrylophenones 3. The conversion of 3 to 5 could either proceed through a concerted thioallylic rearrangement (1,3-sigmatropic shift) or a transient complex (6) involving sulfur assisted polar concerted mechanism. However, in view of the geometrical restrictions imposed on the thermally allowed 1,3-antarafacial sigmatropic shift and unfavourable orbital symmetry considerations to facile 1,3-suprafacial shift, we presume that the latter mechanism is

operative in these transformations. Similar mechanisms for thioallylic rearrangements have been proposed by Kwart and coworkers,[6] on the basis of their kinetic studies. Further, in the light of associative radical chain mechanism proposed by Warren and coworkers[7] for [1,3] PhS shift and the analogous rearrangements observed by Cromwell[8] et al, on β-ketoallylamines, experiments are in progress to understand more about these transformations.

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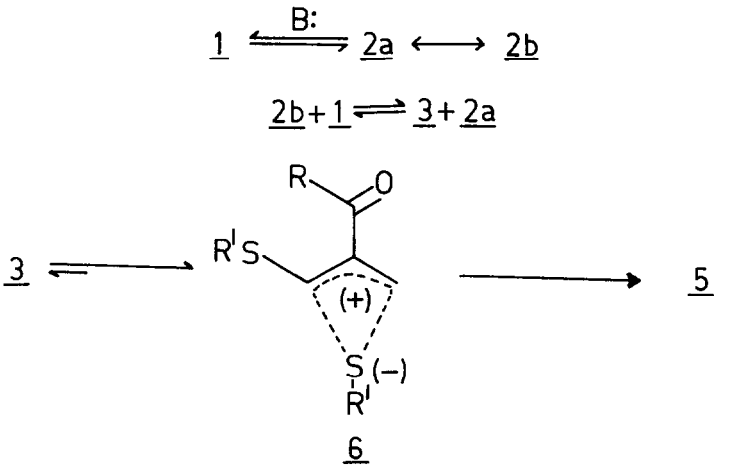

Scheme 3

References and Notes

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3. When the reaction was continued for longer time (12 hr), the yield of 5a was considerably reduced, although the starting material had completely disappeared. Attempts to increase the yield of 5a by carrying out reaction at lower temperatures, in the presence of a catalytic amount or an excess of sodium hydride, or under nitrogen were not successful. Attempted isomerisation of 1a in the presence of sodium ethoxide/ethanol gave only starting material at room temperature, while in refluxing sodium ethoxide/ethanol, only polymeric material was obtained.

4. 5a, M^+ 238; $C_{12}H_{14}OS_2$; Yellow viscous oil, (TLC single spot); IR(Neat), 1635 cm^{-1}, (ν C=O), NMR($CDCl_3$): δ 2.05 (s,3H,$-CH_2-S-CH_3$); 2.25 (s,3H, $\diagup\!\!=\!\!\diagdown SCH_3$); 3.50 (s,2H,$-CH_2-S-CH_3$); 7.04 (s,1H, $\diagup\!\!=\!\!\diagdown H$); 7.25-7.53 (m,5H,arom).

4. 5b, M^+ 266; $C_{14}H_{18}OS_2$; Orange viscous oil; (TLC single spot); IR(Neat), 1638 cm^{-1} (νC=O); NMR(CCl_4): δ 1.25 [two t,6H,($-SCH_2\underline{CH_3}$)$_2$]; 2.50 (q,2H,$-S\underline{CH_2}CH_3$); 2.75 (q,2H,$-S\underline{CH_2}CH_3$); 3.50 (s,2H,$-\underline{CH_2}-S-CH_2CH_3$); 6.92 (s,1H,); 7.25-7.80 (m,5H,arom).

   5c, M^+ 268; $C_{13}H_{16}O_2S_2$; Orange solid, m.p. 57-58°C (Hexane); IR(Nujol), 1630 cm^{-1}(νC=O); NMR(CCl_4): δ 2.00 (s,3H,$-CH_2-S-\underline{CH_3}$); 2.30 (s,3H, ); 3.45 (s,2H,$\underline{CH_2}-S-CH_3$); 3.75 (s,3H,$-O\underline{CH_3}$); 6.76 (d,3H, $2H_{arom}$* ); 7.52 (d,2H,arom).

   5d, M^+ 296, $C_{15}H_{20}O_2S_2$; Orange viscous oil; (TLC single spot); IR (Neat), 1630 cm^{-1}(νC=O); NMR(CCl_4): δ 1.30 [two t,6H,($SCH_2\underline{CH_3}$)$_2$]; 2.50 (q,2H,$-S\underline{CH_2}CH_3$); 2.70 (q,2H,$-S\underline{CH_2}CH_3$); 3.50 (s,2H,$-\underline{CH_2}SCH_2CH_3$);3.80 (s,3H,$-O\underline{CH_3}$); 6.80 (d,3H,$2H_{arom}$* ); 7.55 (d,2H,arom).

   5e, M^+ 252; $C_{13}H_{16}OS_2$; Red viscous oil; (TLC single spot); IR(Neat), 1635 cm^{-1} (νC=O); NMR(CCl_4): δ 2.05 (s,3H,p-$\underline{CH_3}$); 2.30 (s,3H,$-CH_2-S-\underline{CH_3}$); 2.35 (s,3H, ); 3.45 (s,2H,$-\underline{CH_2}-S-CH_3$); 6.85 (s,1H, ); 7.05-7.55 (dd, 4H,arom).

   5a-e gave satisfactory microanalysis.

5. The rearrangement exhibits high stereoselectivity and only E-5 isomers are formed. The configuration was assigned on the basis of chemical shift values of vinyl protons in similar type of compounds [ArCOC(R)=C<u>H</u>SMe; R = alkyl] prepared in our laboratory; δ_H = 7.6 - 7.9 (cis to ArCO); δ_H = 6.0 - 7.1 (trans to ArCO) (B. Myrboh, H. Ila, H. Junjappa, Synthesis, in press). No equilibriation of E-5a to Z-5a was observed, when the former was treated separately with NaH under identical conditions.

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