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REACTION OF CARBANION FROM DIMETHYL N-ETHOXYCARBONYLMETHYLIMINODITHIOCARBONATE WITH BENZALDEHYDE[1]

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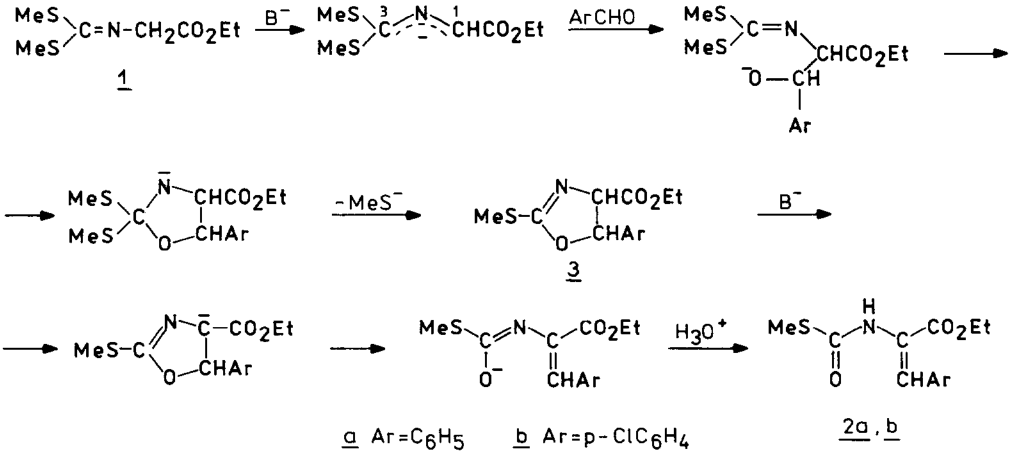
Summary. The title reaction gave ethyl 1-(methylthio)carbonylamino-2-phenylacrylate rather than 5-phenyl-2-ethoxycarbonyl-4-methylthio-2,3-dihydrooxazole as was reported recently.

Recent paper by Ibarra[2] on the reaction of carbanion from dimethyl N-ethoxycarbonylmethyliminodithiocarbonate 1 with aromatic aldehydes prompts us to present this communication on our results concerning reactions of this carbanion.

Our interest in this ambident, azaallylic carbanion was due to an expection that it could react with electrophiles at C-1 and C-3 positions and the reaction at C-3 with nitroarenes would result in the vicarious nucleophilic substitution of hydrogen[3]. In order to learn more about reactivity of the carbanion from 1 we have also studied its reaction with other electrophiles.

The reaction of 1 with benzaldehyde (NaH/DMSO or t-BuOK/THF at room temp.) gave a product m.p. 115-116°C identified as ethyl 1-(methylthio)carbonylamino-2-phenylacrylate 2a[4] contrary to the reported[2] formation of 5-phenyl-2-ethoxycarbonyl-4-methylthio-2,3-dihydrooxazole m.p. 99-100°C. Due to this discrepancy we have repeated Ibarra's procedure (t-BuOK/THF at -78 to -20°C) but the compound 2a m.p. 115-116°C was obtained again. The reaction of 1 with p-chlorobenzaldehyde gave in our hands product m.p. 98-100°C identical to the reported, but again special characteristics suggests the arylacrylate structure 2b.

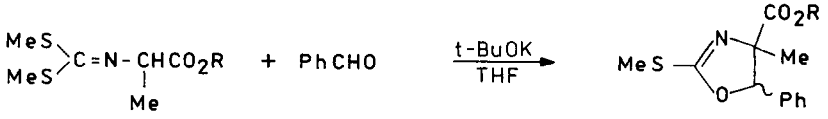
The formation of 2a and 2b can be rationalized as shown on scheme.



The crucial difference between Ibarra's results and ours is that he has claimed that addition of arylaldehydes to the carbanion from 1 takes place at C-3 carbon whereas we have observed addition at C-1 carbon. The carbanion from 1 is known to undergo alkylation also at C-1[6]. In our hands methylation of 1 with methyl iodide (t-BuOK/THF, -70°C) also proceeded at C-1 giving 4.

Intermediate oxazoline 3 is known to undergo rearrangement in basic condition (t-BuOK/THF) producing 2[7].

More sterically demanding carbanion of 4 reacts with benzaldehyde also at C-1 to give oxazoline 5[8] which has no acidic proton and therefore does not undergo the rearrangement.



4

5

R=CH_3, C_2H_5

Thus it seems that the products reported in Ibarra's paper as 5-aryl-2-ethoxycarbonyl-4-methylthio-2,3-dihydrooxazoles are actually 1-(methylthio)carbonylamino-2-arylacrylates.

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References and Notes.

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3. M. Mąkosza in "Current Trends in Organic Synthesis" H. Nozaki Ed., Pergamon Press, Oxford, p. 401 (1983). M.Mąkosza, J.Goliński and J.Baran, J.Org.Chem., 49, 1488 (1984).
4. 2a, ^{1}H NMR($CDCl_3$)δ: 1.35(t,3H); 2.36(s,3H); 4.35(q,2H); 7.1(broad s,1H); 7.34-7.8(m,6H). This spectra is in excellent agreement with ^{1}H NMR spectra of Z isomer of 2a reported by Hoppe[7]. ^{13}C NMR ($CDCl_3$) δ: 12.59(S-CH_3); 14.25($CH_2\underline{C}H_3$); 61.85($\underline{C}H_2CH_3$); 124.22(=$\underline{C}$<) 128.65; 129.90 130.0; 133.38(C_6H_5); 133.50(Ph$\underline{C}$H=); 165.01(COS); 165.16(COO), signal assignment based on proton coupled and noice-band decoupled spectrum with Cr(acac)$_3$ added.
5. 2b, ^{1}H NMR ($CDCl_3$) δ: 1.36(t,3H); 2.35(s,3H), 4.35(q,2H); 7.2-7.6(m,6H). ^{13}C NMR ($CDCl_3$) δ: 12.59; 14.23; 62.09; 124.10; 128.91; 131.10; 132.15; 135.51; 164.93; 167.73 (assignment as for 2a).
6. D.Hoppe, Angew.Chem., 87, 450 (1975).
7. D.Hoppe, Liebigs Ann.Chem., 1843 (1976).
8. 5 R=CH_3, ^{1}H NMR ($CDCl_3$) δ: 0.98(s,3H); 2.52(s,3H); 3.80(s,3H); 5.95(s,1H); 7.2-7.4(m,5H). ^{13}C NMR ($CDCl_3$) δ: 14.39; 20.02; 52.90; 77.50; 87.50; 126.08; 128.39; 135.66; 167.22;174.12.

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