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REACTIONS OF SULFONIUM PHENACYLIDE WITH ACTIVE METHYLENE COMPOUNDS

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The reaction of dimethylsulfonium phenacylide **1** with malononitrile gave C-phenacylated compound. The reaction of **1** with acetylacetone or ethyl acetoacetate led to dihydrofuran derivatives via O-phenacylation followed by cyclization.

Recently, we have described the reactions of S-N ylide with active methylene compounds to give stable S-C ylides via the nucleophilic substitution on S-atom.1) In this paper, for comparison of S-N with S-C ylide, the reactions of dimethylsulfonium phenacylide **1**2) with several active methylene compounds have been described, and the results obtained were compared with the reactions of phenacyl bromide **4**.

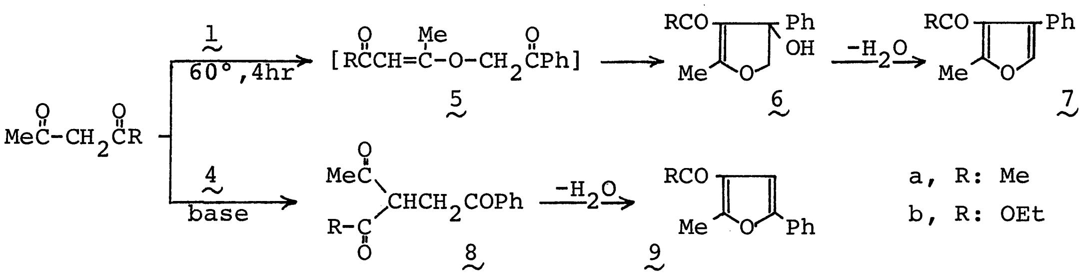
The reaction of **1** with an equimolar amount of malononitrile in THF at 40°C for 4 hr gave phenacylmalononitrile **3**3) quantitatively. **3** was identified by comparison with the compound which was given by treatment of malononitrile with **4** in the presence of triethylamine in dichloromethane.

$$(NC)_2CH_2 + \underset{\mathbf{1}}{Me_2\overset{+}{S}\text{-}\overset{-}{C}HCOPh} \longrightarrow [(NC)_2\overset{-}{C}H + \underset{\mathbf{2}}{Me_2\overset{+}{S}\text{-}CH_2COPh}] \xrightarrow{-Me_2S} \underset{\mathbf{3}}{(NC)_2CH\text{-}CH_2COPh} \quad (100\%)$$

$$(NC)_2CH_2 + \underset{\mathbf{4}}{BrCH_2COPh} \longrightarrow \mathbf{3}\ (74\%)$$

The reaction of 5.0 mmol of **1** with 2.0 ml of acetylacetone did not afford phenacylacetylacetone **8a**, but dihydrofuran **6a** quantitatively. In order to elucidate the structure of **6a**, the attempted dehydration by heating(130°C, 1 hr) was performed to result in the formation of an expected furan **7a**(87%). The reaction of **4**, in turn, with acetylacetone in the presence of NEt_3 in CH_2Cl_2 gave **8a**(67%) which was a phenacylated compound on the C-atom and cyclized to furan **9a** in 98% yield in 20% sulfuric acid at 100°C.

Next, **1** was allowed to react with ethyl acetoacetate under similar conditions to afford dihydrofuran **6b** in quantitative yield,$^{4)}$ and the dehydration of **6b** in 20% H_2SO_4 at 100°C produced an expected furan **7b**. The reaction of ethyl acetoacetate with **4** in the presence of NaOEt or NEt_3 gave ethyl α-phenacylacetoacetate **8b** in 94% or 69% yield, respectively, which cyclized to furan **9b** in 20% H_2SO_4 at 100°C.



In the above reactions, the phenacylide may behave as a base to accept a proton from an active methylene compound and the sulfonium ion **2** formed is subject to nucleophilic attack by the deprotonated methylene, which acts as an ambident nucleophile ($RC(=O)\bar{C}HX \rightleftharpoons RC(-O^-)=CHX$). Thus, it seems reasonable that the methylene incapable of enolization gives only a C-phenacylated compound(**3**), and the enolizable methylene affords only an O-phenacylated compound(**6**). The reason for the remarkable difference between the reaction of **1** and **4** with enolizable methylene will be discussed elswhere.

In addition, these results may present a new synthetic route to substituted furan derivatives via the O-phenacylation of acetylacetone and ethyl acetoacetate.

References and notes

1) T.Yamamoto, Y.Harigaya, and M.Okawara, Chem. Lett., 1009 (1972).

2) K.W.Ratt and A.N.Yao , J. Org. Chem., 31, 1185, 1689 (1966).

3) All new compounds reported here gave satisfactory elemental analysis and consistent IR and NMR.

4) Y.Hayashi, T.Ohashi, T.Takemura, and R.Oda, The 24th Annual Meeting of the Chemical Society of Japan (1971). Although they reported the reaction of **1** with ethyl acetoacetate in benzene at room temperature to give **7b**(41%), **8b**(5%) and **9b**(3%), the details are not clarified.

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