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SYNTHESIS OF 1-METHOXY-2-OXOALKYL PHENYL SULFIDES AND THEIR
SYNTHETIC APPLICATION TO 3-SUBSTITUTED FURANS
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1-Methoxy-2-oxoalky1 pheny1 sulfides were new1y synthesized from methoxy (phenylthio) methane and various N, N-dimethylalkanamides. Synthetic application of the compounds thus obtained to several 3-substituted furans also is reported.

In the previous paper, $^{(1)}$ we reported that methoxy(phenylthio)methane (1) and methoxy(phenylsulfonyl)methane (2) can serve as good one carbon homologation reagents and that the alkylation or hydroxy products obtained by treating the carbanions of 1 and 2 with alky1 halides, aldehydes, and epoxides can be successfully transformed to aldehydes, methylals, carboxylic acids, and enol ethers.

In connection with our study on synthetic utilization of 1 and 2, we have found that employment of N,N-dimethylalkanamides as an electrophile affords 1-methoxy-2-oxoalkyl phenyl sulfides 3 in good yields, which further proved to be novel intermediates for 3-substituted furans often encountered in natural products.

3-Substituted furans were prepared according to the following sequence of reactions (Scheme 1). A carbanion of 1 (generated by <u>n</u>-BuLi in THF at -78 °C for 1 h) was treated with N,N-dimethylalkanamides at -78 °C for 1 h and the reaction mixture was shaken with H_2O -benzene. Usual workup gave 3 in good yields. Condensation of 3 with a carbanion of methyl diethylphosphonoacetate (1.5 equiv.) in THF at room temperature for 12 h gave 4a, which then was subjected to reduction with DIBAL in ether at -30 °C for 1.5 h to yield allylic alcohols 4b. Furans 5 were successfully obtained by heating 4b in benzene under reflux for 1 h in the presence of a catalytic amount of p-toluenesulfonic acid. These procedures provide a new synthetic method for 3-substituted furans whose efficient preparation receives considerable recent attention²) and the results are summarized in Table 1. Scheme 1





i: n-BuLi, RCONMe₂, ii: (EtO)₂P(O)CH₂CO₂Me, NaH, ⁱBu₂A1H, iii: p-TsOH

		Yield/%			
Entry	R	<u>3</u> a)	$4a^{a,b}$	<u>4b</u> a,b)	<u>5</u> a)
1	Ph	81	86	68	87
2	C ₁₁ H ₂₃	82	75	83	75
3	to the second se	79	61	73	68
4	\checkmark	76	83	78	60
5	PhS(CH ₂) ₃	78	72	92	86

Table 1. Preparation of 3-substituted furans 5

a) Isolated yields after column chromatography (silica gel).

b) Yields of a mixture of (E)- and (Z)-isomers. The isomeric ratio can be determined approximately by ¹H NMR spectra (ca. 7/3 - 5/5).

According to the present method, we have achieved a synthesis of furanoterpenoids, dendrolasin^{2c)} and perillene,^{2d)} from readily available starting materials, geranyl and prenyl chlorides, respectively (Entries 3 and 4).

In the above reaction, we have obtained allylic alcohols $\underline{4b}$ as a mixture of (E)- and (Z)-isomers. It is apparent that on the basis of the yields of $\underline{5}$ the (E)-isomer as well as its (Z)-counterpart was consumed to give furans $\underline{5}$. Accordingly, we can deduce the following reaction mechanism which involves an isomerization step of the (E)-alcohol to the (Z)-form. Facile acid-prompted elimination of phenylthic group is due to the presence of α -methoxyl group as is evident from our previous observation that alkylation products of $\underline{1}$ were easily converted to methylals by a catalytic amount of \underline{p} -toluenesulfonic acid in methanol.



References

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(Received October 11, 1983)
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