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A CONVENIENT METHOD FOR THE SYNTHESIS OF 3,4-FURANDICARBOXYLIC ACID DERIVATIVES BY THE REACTIONS OF SULFONIUM YLIDES WITH DIMETHYL ACETYLENEDICARBOXYLATE

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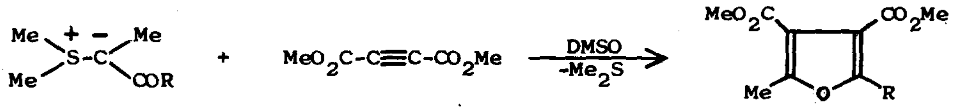
It has been found that the reactions of carbonyl stabilized sulfonium ylides with nucleophiles as ketene dimer and isocyanates afforded heterocyclic compounds, 3-hydroxyfurans (1) and hydantoins (2), respectively.

In the present experiment, a new method for the synthesis of furan derivatives by the reactions of sulfonium ylides (I) with dimethyl acetylenedicarboxylate (II) was investigated. When an equimolar mixture of dimethylsulfonium-α-methylacetonylide (Ia) and II was allowed to react in dimethyl sulfoxide (DMSO) with occasional ice cooling under an atmosphere of nitrogen, evolution of dimethyl sulfide was observed by its characteristic odor. The reaction mixture was poured into cold water and worked up with ether. The resultant needles were purified by sublimation to give dimethyl 2,5-dimethyl-3,4-furandicarboxylate (IIIa) in a 93% yield, mp 63.5-64.5°C. The structural assignment was made on the basis of elemental analyses (3) and NMR spectrum [$(CDCl_3)$: τ 7.57 (6H, s, $2CH_3$), 6.17 (6H, s, $2CH_3$-OCO)]. The melting point of IIIa was not depressed by admixture with an authentic sample (4). These data



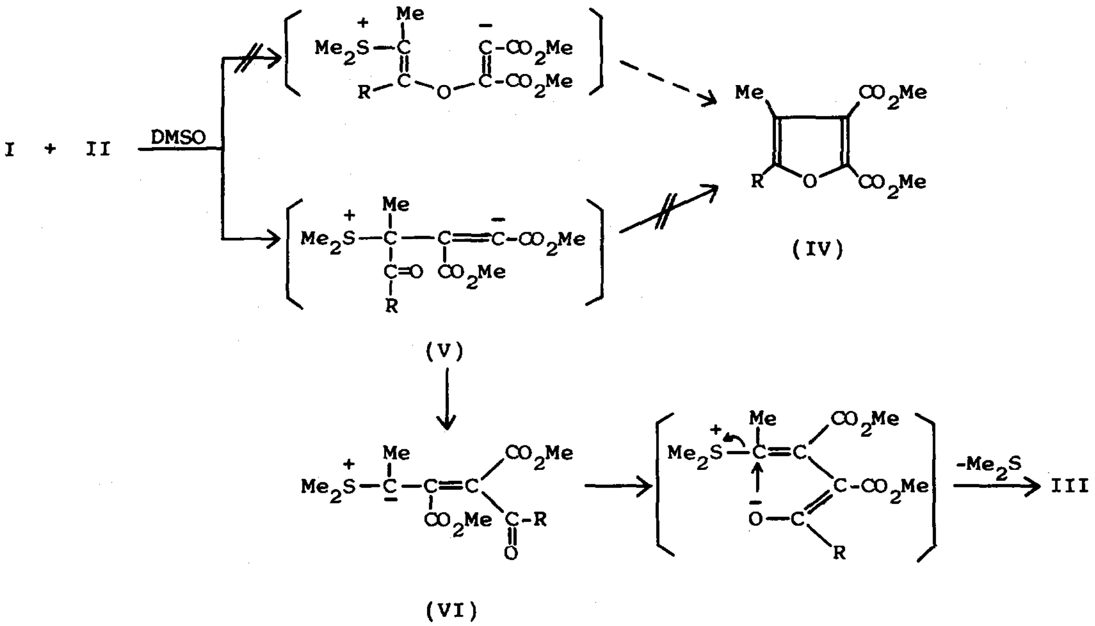
(I) a,R=Me
b,R=Ph

(II)

(III) a,R=Me
b,R=Ph

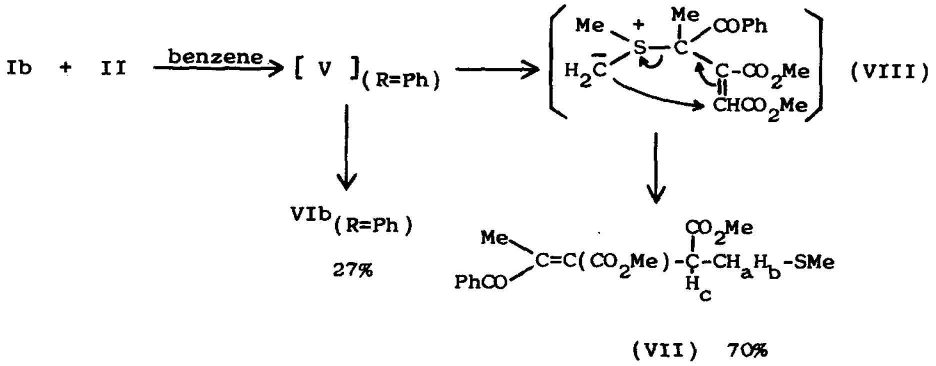
show that the isomeric furan (IV, R=Me) is excluded (5).

In a similar manner, the reaction of dimethylsulfonium-α-methylphenacylide (Ib) with II in DMSO afforded dimethyl 2-methyl-5-phenyl-3,4-furandicarboxylate (IIIb) (3) in an 88% yield, mp 62.7-63.7°C, NMR [(CDCl$_3$) : τ 7.41 (3H, s, CH$_3$), 6.17 (3H, s, CH$_3$-OCO), 6.12 (3H, s, CH$_3$-OCO), 2.2-2.75 (5H, m, C$_6$H$_5$)].



It seems reasonable to consider that the reaction proceeds through an initial formation of a 1,4-betaine (V) (6), which is subsequently transformed into an ylide (VI) by means of 1,3-migration of the acyl group (7). The ylide VI is in turn changed to III <u>via</u> its tautomeric betaine by intramolecular nucleophilic displacement (1).

The reaction mechanism was firmly supported by the isolation of the intermediate ylide VI. Thus, the reaction of Ib with II was carried out in benzene in place of DMSO to give yellow crystals and an oily substance. The crystals were identified as dimethylsulfonium-α-methyl-β,γ-dicarbomethoxy-γ-benzoylallylide (VIb, R=Ph) from spectral data [IR (KBr) : 1728, 1665, 1596 cm^{-1}. NMR (DMSO-d_6) : τ 7.93 (3H, s, CH_3-C), 7.13 (6H, s, $(CH_3)_2\overset{+}{S}$-), 6.85 (3H, s, CH_3-OCO), 6.36 (3H, s, CH_3-OCO), 2.4-2.9 (5H, m, C_6H_5)], 27% yield, mp 124-5°C (dec). The configuration about the carbon-carbon double bond is still not determined. However, the structure in which the carbanion and the benzoyl group have trans relationship would probably be favorable. An attempt to recrystallize VIb from hot ethanol gave IIIb in a quantitative yield along with evolution of dimethyl sulfide. In addition, it was found that IIIb was also obtained by stirring VIb in DMSO at room temperature. On the other hand, no detectable change was observed when VIb was stirred in benzene for 5 days at room temperature, and VIb was recovered.



The oily substance, obtained from the reaction of Ib with II in benzene, was distilled <u>in vacuo</u> to give 2-benzoyl-3,4-dicarbomethoxy-5-methylthio-2-pentene (VII) (3) in a 70% yield, bp 150-152°C/0.026 mmHg, IR [(neat) : 1738, 1722, 1675, 1637 cm^{-1}], NMR [($CDCl_3$) : τ 7.85 and 7.82 (6H, a pair of singlets, CH_3-S and CH_3-C=), 6.99 (1H, dd, H_a), 6.62 (1H, dd, H_b), 6.58 (3H, s, CH_3-OCO), 6.24 (3H, s, CH_3-OCO), 6.08 (1H, dd, H_c), 1.9-2.7 (5H, m, C_6H_5). J_{ab}=14Hz, J_{ac}=9Hz, J_{bc}=5Hz.]. The pentene VII would be formed by a rearrangement of the intermediate allylsulfoniummethylide (VIII) (8) initially formed from V by a proton transfer.

These results indicate that, in benzene, the formation of VII from V *via* VIII predominates over that of VI being stable in the solvent, and that, in DMSO, the acyl rearrangement (V→VI) followed by the displacement reaction (VI→III) takes place exclusively.

In conclusion, it is noted that the reactions of I with II in DMSO gave III in high yields under mild conditions accompanied with the acyl rearrangement.

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