Syntheses of Heterocyclic Compounds by the Use of Ylides Stabilized by Diketovinyl Groups

Yasumitsu Tamura, Yoshio Sumida, Yasuyoshi Miki, Tomohisa Miyamoto, Hiroshi Taniguchi, Masayoshi Tsunekawa, Shin-ichi Haruki, and Masazumi Ikeda

Faculty of Pharmaceutical Sciences, Osaka University, Toneyama, Toyonaka, Osaka 560

A variety of ylides stabilized by diketovinyl groups, $X^{+}-Y^{-}-CH=C(COR)_2$ (X= pyridine, $Me_2S\rightarrow O$, Me_2S; Y=C or N; R=OEt or Me), were prepared and their chemical properties were examined.

The syntheses of the ylides were readily accomplished by treatment of ylides ($X^{+}-Y^{-}H$) with diethyl ethoxymethylenemalonate or 3-ethoxymethylene-2,4-pentanedione

The ylides thus obtained were found to be useful to the syntheses of various heterocyclic compounds. For examples, heating pyridinium 3,3-diacyl-1-benzoyl- (or ethoxycarbonyl)allylides in refluxing xylene or mesitylene gave indolizine derivatives. Similar treatment of N-(2,2-diethoxycarbonylvinyl)iminopyridinium betaines gave ethyl pyrazolo[1,5-a]pyridine-3-carboxylates, while N-(2,2-diacetylvinyl)iminopyridinium betaines underwent N-N bond cleavage to give 4-acetyl-5-methylisoxazole. Treatment of dimethylsulfoxonium 1-ethoxycarbonyl-3,3-diacetylallylide with sodium hydride gave 4-acetyl-1,3-dimethyl-6-ethoxycarbonylthiabenzene-1-oxide, while heating of the ylide in refluxing xylene resulted in the formation of ethyl 3-acetyl-2-methylfuran-5-carboxylate. The same furan was also obtained by heating dimethylsulfonium 1-ethoxycarbonyl-3,3-diacetylallylide in refluxing mesitylene.