UNUSUAL REACTION OF ALKENYLFURANS WITH DIAZOACETIC ESTER IN THE PRESENCE OF COPPER SULFATE

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The addition of many carbenes to aromatic double bonds is known [1]. However, carbenes add to the exocyclic double bond in the case of alkenylaromatic compounds, without involving the aromatic ring [2].

We found that the reaction of 0.12 mole of 1-(α-furyl)-1-propene (I) with 0.02 mole of ethyl diazoacetate (II) in the presence of 0.1 g of $CuSO_4$ at 130-135° leads to $CH_3CH=CHCOCH=CHCH=CHCOOC_2H_5$ (III), yield 43%, mp 83° (from hexane). Infrared spectrum (ν, cm^{-1}): 1645 and 1660 (C = C), 1705 (C = O), 1250 (COOR). Ultraviolet spectrum (in heptane): λ_{max} 286 nm (ε 30000). Found: C 68.45; H 7.62%; mol.wt. 194 (mass spectrum). $C_{11}H_{14}O_3$. Calculated: C 68.02; H 7.26%; mol.wt. 194.2. 2,4-DNPH, mp 136° (from ethanol). Found: N 15.38%. $C_{17}H_{18}N_4O_6$. Calculated: N 14.96%. The hydrogenation of (III) over Raney Ni in ethanol at 20° (1 abs. atm) until saturation gave the ethyl ester of ε-ketopelargonic acid with bp 102° (2 mm); n_D^{20} 1.4344, identical with the standard specimen.

The formation of (III) must be explained by the addition of the carbethoxycarbene to the unsubstituted multiple bond of the furan ring of (I), with subsequent rearrangement of the adduct. Such a reaction course is evidently associated with the greater complexing ability of the furan ring when compared with the exocyclic double bond of (I), which should be manifested in the formation of the complex: carbene–catalyst –acceptor, which precedes the addition product of the carbene to (I).

Under the same conditions, (II) reacts in a similar manner with some other 2-alkenylfurans, and also with 2,5-dimethylfuran (the yield of $CH_3COCH=CHC(CH_3)=CHCOO-C_2H_5$ 45%, mp 53°), and according to [3], also with sylvan. In contrast, the photolysis of (II) in excess (I) does not lead to the formation of (III).

The reaction of (I) and other alkenylfurans with dichlorocarbene (from $CCl_3COOC_2H_5$ and CH_3ONa) at ~0° leads to the corresponding furyl-gem-dichlorocyclopropanes in 35-55% yields.

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