USUAL BEHAVIOR OF METHYL ESTER OF 3-PHENYL-3-CHLORO-2-KETOPROPIONIC ACID IN ITS REACTION WITH SODIUM METHYLATE

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 α -Haloketones undergo the Favorskii rearrangement by the action of a base with alteration of the carbon skeleton [1].

We have discovered that the methyl ester of 3-phenyl-3-chloro-2-ketopropionic acid (I) reacts with MeONa in methanol to give products, which differ from those of the Favorskii rearrangement. Substitution product (II) is formed in quantitative yield at 0°C. Heating the reaction mixture in methanol at reflux for 1 h gave product (III) in 47% yield, mp 158.5-160°C:



The structure and composition of the methyl ester of 3-phenyl-3-methoxy-2-ketopropionic acid (II) were supported by elemental analysis and IR and PMR spectroscopy. The dimethyl ester of 2,5-diketo-3,4-diphenyl-3-methoxyhexanedioic acid (III) was identified by elemental analysis, IR, ¹H and ¹³C NMR spectroscopy, and mass spectrometry. The chemical ionization mass spectrum of (III) has peaks with m/z 385 and 353, corresponding to $[MH]^+$ and $[MH-CH_3OH]^+$. Found: $[MH]^+$, 385.1289, $C_{21}H_{21}O_7$; $[MH-CH_3OH]^+$, 353.1015, $C_{20}H_{17}O_6$. Calculated: $[MH]^+$, 385.1287; $[MH-CH_3OH]^+$, 353.10215.

LITERATURE CITED

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