SYNTHESIS OF 3-ETHOXYALKYL CYCLOPROPYL KETONES BY THE REACTION OF 1-TRIMETHYLSILYLOXY-1-CYCLOPROPYLETHYLENE WITH ACETALS AND THEIR ANALOGS

A. Kh. Khusid and O. M. Nefedov

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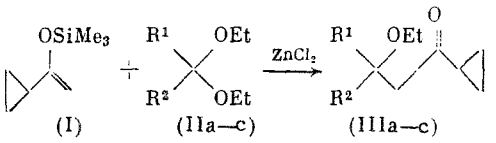
Cyclopropyl ketones are convenient starting blocks in the formation of trans double bonds by the Julia–Johnson reaction with 95-97% steric selectivity. However, no convenient general methods have been reported for the synthesis of functionally substituted cyclopropyl ketones.

We have developed a preparative synthesis of 3-ethoxyalkyl cyclopropyl ketones based on readily available 1-trimethylsilyloxy-1-cyclopropylethylene [1] and acetals of various carbonyl compounds. 1-Trimethylsilyloxy-1-cyclopropylethylene (I) reacts with the diethyl acetal of acetaldehyde (IIa), the diethyl ketal of cyclohexanone (IIb) and triethyl orthoformate (IIc) in the presence of $ZnCl_2$ to give 3-ethoxyalkyl cyclopropyl ketones (IIIa)-(IIIc) in 70-75% yields.



(I) (IIa–c) (IIIa–c)

R^1 = H, R^2 = Me (a), $R^1 + R^2$ = cyclo-C_6H_4 (b), R^1 = H, R^2 = OEt (c).

A sample of 0.2 mole acetal (IIa)-(IIc) was added to 150 ml 10% $ZnCl_2$ in ethyl acetate and, then, 0.2 mole ether (I) was added dropwise at 20°C. The mixture was stirred for 10-15 h, poured into 150 ml saturated aqueous $NaHCO_3$, and extracted with ether. The ethereal layer was separated, dried over Na_2SO_4, and distilled to give (IIIa) with bp 95-97°C (20 mm), n_D^{20} 1.4360, (IIIb) with bp 95-97°C (0.2 mm), n_D^{20} 1.4760, and (IIIc) with bp 68-70°C (0.4 mm), n_D^{20} 1.4405 [2]. The structures of (IIIa)-(IIIc) were proved by elemental analysis and ^1H and ^{13}C NMR spectral data.

This method for the synthesis of 3-ethoxyalkyl cyclopropyl ketones permits expansion of the scope of the Julia–Johnson reaction in the synthesis of compounds containing a trans double bond.

LITERATURE CITED

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N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow.
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