REACTIONS OF PERFLUOROCARBONYL COMPOUNDS WITH 1,3,3-TRIMETHYL-2-METHYLENEINDOLINE

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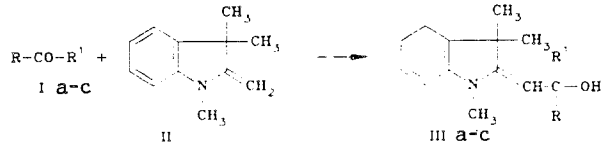
Reaction of perfluorinated carbonyl compounds with enamines are limited mainly to examples of reaction with nitrogen-containing aromatic heterocycles [1].

We have found that hexafluoroacetone (Ia), methyl trifluoropyroracemate (Ib), and perfluorovaleraldehyde (Ic) in a solution of hexane at 0°C react exothermically with Fischer's base (II) and form, in high yield, the corresponding products of vinyl substitution at the methylene group IIIa-c.



I,III a R=R'=CF_3; b R=CF_3, R'=$COOCH_3$; c R=H, R'=C_4F_9

According to data of NMR and IR spectra, compounds IIIa-c are formed as a mixture of Z and E isomers (1:2 ratio). In compound IIIb, the methyl groups in the 3 position of the indoline fragment of one of the isomers are magnetically nonequivalent, probably because of hindered rotation about the $C_{(1)}$–$C_{(2)}$ bond in the trifluoropropylidene radical.

Compounds IIIa and IIIb are colorless crystalline substances, and IIIc is a viscous oil, rapidly becoming red during storage.

1,3,3-Trimethyl-2-[2-hydroxy-2-(trifluoromethyl)-3,3,3-trifluoropropylidene] indoline (IIIa). The yield was 96%, with mp 98-100°C. IR spectrum (CH_2Cl_2): 3520 (OH); 1630, 1590 cm^{-1} (N–C=C). PMR spectrum [$(CD_3)_2CO$]: 1.24; 1.54 [singlet, 2(CH_3)]; 3.45; 3.02 (singlet, N–CH_3); 4.02; 4.11 (singlet, OH); 7.2-6.6 ppm (multiplet, C_6H_4, CH). Fluorine-19 NMR spectrum [$(CH_3)_2CO$]: −76.84; −77.39 ppm (singlet, CF_3).

1,3,3-Trimethyl-2-[2-hydroxy-2-(methoxycarbonyl)-3,3,3-trifluoropropylidene] indoline (IIIb). The yield was 71%, with mp 87-89°C. IR spectrum (CH_2Cl_2): 3500 (OH); 1725 (C=O); 1645, 1595 cm^{-1} (N–C=C). PMR spectrum [$(CD_3)_2CO$]: 1.52; 1.43; 1.23 [singlet, 2(CH_3)]; 3.30; 2.48 (singlet, N–CH_3); 3.79; 3.77 (singlet, OCH_3); 4.42 (singlet, OH); 5.73; 5.71 (singlet, CH); 7.11-6.56 ppm (multiplet, C_6H_4). Fluorine-19 NMR spectrum [$(CD_3)_2CO$]: −78.92; −78.90 ppm (singlet, CF_3).

1,3,3-Trimethyl-2-(2-hydroxy-2-hydrononafluorohexylidene) indoline (IIIc). The yield of the oil was 67%. IR spectrum (CH_2Cl_2): 3575 (OH); 1645, 1595 cm^{-1} (N–C=C).

The data of elemental analysis of compounds IIIa-c corresponded to the calculated values.

LITERATURE CITED

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