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LETTERS TO THE EDITOR

SELECTIVE CYCLOPROPANATION OF CHROMENES WITH A PHENYLACRYLOYL SUBSTITUENT BY BROMINE-CONTAINING ZINC ENOLATES

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Halogen-containing metal enolates react with α,β-unsaturated carbonyl compounds to form a cyclopropane ring [1-4]. As the systems to be cyclopropanated, in this work we studied 3-(3-phenylacryloyl)chromen-2-ones and benzo[*f*]chromen-3-ones, which formally contain two C=C–C=O moieties in their molecules. Our studies have shown that nucleophilic bromine-containing zinc enolates **2a-c**, obtained from 1-aryl-2,2-dibromoalkanones **1a-c** and zinc, react exclusively with the double bond of the heterocycle, forming intermediate addition products **3a,b** and **4**, which in turn are converted to the cyclopropanation products: 1-alkyl-1-aroyl-1a-(3-phenylacryloyl)-1a,7b-dihydro-1H-cyclopropa[*c*]chromen-2-ones **4a,b** and 1-benzoyl-1-methyl-1a-(3-phenylacryloyl)-1a,9c-dihydro-1H-3-oxacyclopropa[*c*]phenanthren-2-one (**5**).

1-(4-Bromobenzoyl)-1-methyl-1a-(3-phenylacryloyl)-1a,7b-dihydro-1H-cyclopropa[*c*]chromen-2-one (4a). Yield 33%; mp 197-200°C. IR spectrum (vaseline oil), ν, cm^{-1}: 1590, 1685, 1740. ^1H NMR spectrum (300 MHz, DMSO-d_6), δ, ppm (*J*, Hz): 1.12 (3H, s, Me); 3.75 (1H, s, CH); 7.30, 7.55 (2H, d, *J* = 15, CH=CH); 7.17-7.80 (13H, m, C_6H_4, Ph, 4-BrC_6H_4). Found, %: C 66.90; H 4.03. $C_{27}H_{19}O_4Br$. Calculated, %: C 66.54; H 3.93.

1-Ethyl-1a-(3-phenylacryloyl)-1-(4-toluoyl)-1a,7b-dihydro-1H-cyclopropa[*c*]chromen-2-one (4b). Yield 29%; mp 144-145°C. IR spectrum (vaseline oil), ν, cm^{-1}: 1605, 1675, 1745. ^1H NMR spectrum (60 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 0.57 (3H, t, *J* = 7, $CH_2\underline{CH_3}$); 0.90-1.50, 1.60-2.20 (2H, two m, $\underline{CH_2}CH_3$); 2.26 (3H, s, $\underline{CH_3}C_6H_4$); 3.72 (1H, s, CH); 6.90-8.00 (15H, m, C_6H_4, Ph, 4-MeC_6H_4, CH=CH). Found, %: C 79.61; H 5.69, $C_{29}H_{24}O_4$. Calculated, %; C 79.80; H 5.54.

1-Benzoyl-1-methyl-1a-(3-phenylacryloyl)-1a,9c-dihydro-1H-3-oxacyclopropa[*c*]phenanthren-2-one (5). Yield 21%; mp 240-250°C. IR spectrum (vaseline oil), ν, cm^{-1}: 1600, 1675, 1745. ^1H NMR spectrum (60 MHz, DMSO-d_6 + $CDCl_3$, 1:1), δ, ppm: 1.17 (3H, s, CH_3); 4.13 (1H, s, CH); 6.90-8.00 (18H, m, $C_{10}H_6$, Ph, Ph, CH=CH). Found, %: C 81.00; H 5.01. $C_{31}H_{22}O_4$. Calculated, %: C 81.21; H 4.84.

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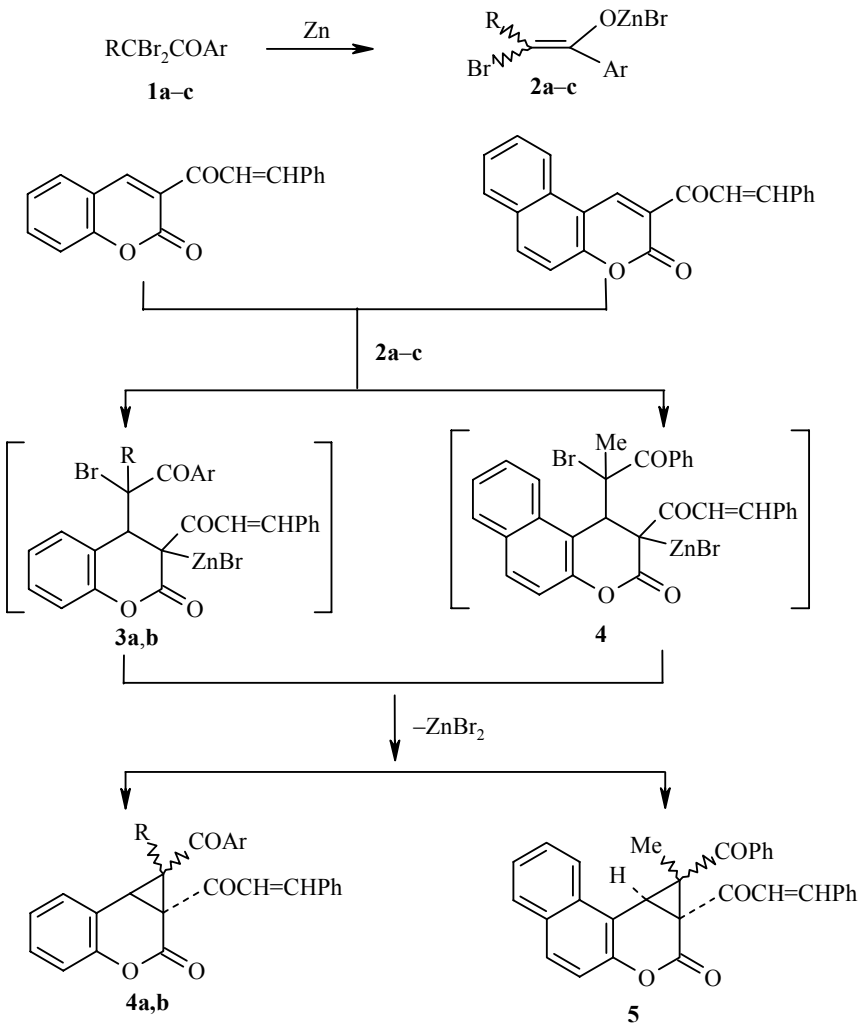

1-4 a R = Me, Ar = 4-BrC_6H_4, **b** R = Et, Ar = 4-MeC_6H_4; **1**, **2 c** R = Me, Ar = Ph

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