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LETTERS TO THE EDITOR

SIMPLE SYNTHESIS OF 1a,7b-DIHYDROCYCLOPROPA-[*c*]CHROMENE DERIVATIVES

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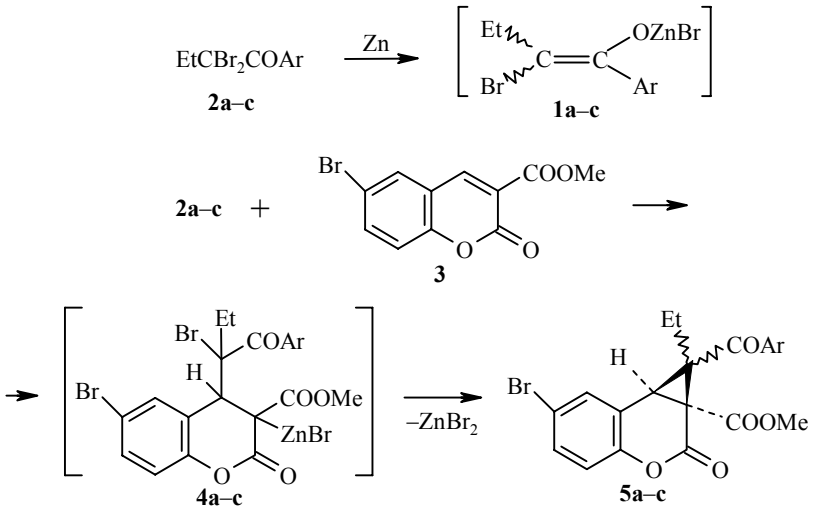
Keywords: bromine-containing butanones, methyl ester of 6-bromo-2-oxo-3-chromenecarboxylic acid, methyl esters of 1-aroyl-1-ethyl-2-oxo-1a,7b-dihydrocyclopropa[*c*]chromene-1a-carboxylic acid, zinc.

In a continuation of a study of the reaction of bromine-containing zinc enolates at the activated electron-withdrawing groups at the double bond [1], we investigated the reaction of zinc enolates **1a-c**, obtained from 1-aryl-2,2-dibromobutanones **2a-c**, with the methyl ester of 6-bromo-2-oxo-3-chromenecarboxylic acid (**3**).

The reaction proceeds in ether–ethyl acetate, probably through the intermediate formation of **4a-c**, which then cyclize to give the methyl esters of 1-aroyl-6-bromo-1-ethyl-2-oxo-1a,7b-dihydrocyclopropa-[*c*]chromene-1a-carboxylic acids **5a-c** according to the following scheme:



1, 2, 4, 5 a Ar = 4-MeC_6H_4, **b** Ar = 4-FC_6H_4, **c** Ar = 4-ClC_6H_4

The ^{1}H NMR spectra of **5a-5c** indicate that these products are formed as a single geometric isomer with the least strained structure and overlapping of the hydrogen atom at C(7b) and the methoxycarbonyl group at C(1a).

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6-Bromo-1-ethyl-1-(4-methylbenzoyl)-2-oxo-1a,7b-dihydrocyclopropa[*c*]chromene-1a-carboxylic Acid (5a) was obtained in 54% yield; mp 196-197°C. IR spectrum (vaseline mull), ν, cm^{-1}: 1620, 1690, 1730, 1770. ^1H NMR spectrum at 60 MHz ($CDCl_3$), δ, ppm: 0.53 (3H, t, $CH_2\underline{CH_3}$); 0.80-1.60, 1.60-2.40 (2H, m, $\underline{CH_2}CH_3$); 2.35 (3H, s, $\underline{CH_3}C_6H_4$); 3.48 (3H, s, OCH_3); 3.58 (1H, s, CH); 6.70-8.10 (7H, m, 4-$CH_3C_6H_4$, BrC_6H_3). Found, %: C 59.50; H 4.23. $C_{22}H_{19}BrO_5$. Calculated, %: C 59.61; H 4.32.

6-Bromo-1-ethyl-1-(4-fluorobenzoyl)-2-oxo-1a,7b-dihydrocyclopropa[*c*]chromene-1a-carboxylic Acid (5b) was obtained in 60% yield; mp 197-198°C. IR spectrum (vaseline mull), ν, cm^{-1}: 1600, 1685, 1730, 1770. ^1H NMR spectrum at 60 MHz ($CDCl_3$), δ, ppm: 0.53 (3H, t, $CH_2\underline{CH_3}$); 0.80-1.60, 1.60-2.40 (2H, m, $\underline{CH_2}CH_3$); 3.47 (3H, s, OCH_3); 3.54 (1H, s, CH); 6.70-8.10 (7H, m, FC_6H_4, BrC_6H_3). Found, %: C 56.28; H 3.46. $C_{21}H_{16}FBrO_5$. Calculated, %: C 56.40; H 3.61.

6-Bromo-1-(4-chlorobenzoyl)-1-ethyl-2-oxo-1a,7b-dihydrocyclopropa[*c*]chromene-1a-carboxylic Acid (5c) was formed in 65% yield; mp 228-230°C. IR spectrum (vaseline mull), ν, cm^{-1}: 1595, 1695, 1730, 1770. ^1H NMR spectrum at 60 MHz ($CDCl_3$), δ, ppm: 0.47 (3H, t, $CH_2\underline{CH_3}$); 0.70-1.50, 1.50-2.30 (2H, m, $\underline{CH_2}CH_3$); 3.40 (3H, s, OCH_3); 3.63 (1H, s, CH); 7.10-7.90 (7H, m, ClC_6H_4, BrC_6H_3). Found, %: C 53.80; H 3.38. $C_{21}H_{16}ClBrO_5$. Calculated, %: C 53.93; H 3.45.

REFERENCES

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