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Acid-Catalyzed Condensation of 1,3,5-Triphenylpentane-1,5-dione with Benzaldehyde—A New Domino Reaction

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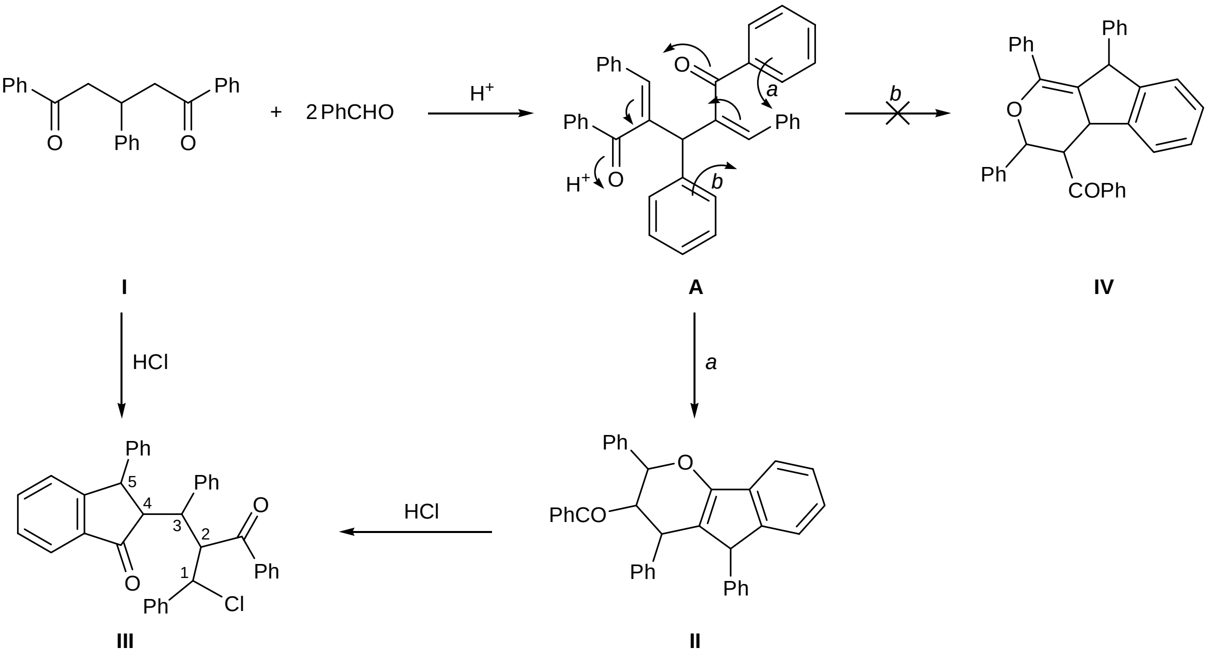
Abstract—Aldol-like condensation of 1,3,5-diphenyl-1,5-pentanedione with benzaldehyde in the presence of acids is accompanied by the Nazarov cyclization with formation of substituted indanone or indeno[1,2-*b*]pyran in a one-pot process.

An actual problem of organic synthesis is search for new domino reactions [1] which make it possible to create complex structures in a one-pot process. While studying the reaction of 1,5-diketone **I** with benzaldehyde in the presence of sulfuric acid, we isolated compound **II**. Compound **II** was formed as a result of a new domino reaction which involves closure of three new carbon–carbon bonds via crotonization and Nazarov cyclization. When the reaction was initiated by gaseous hydrogen chloride, we obtained 2-(2-benzoyl-3-chloro-1,3-diphenylpropyl)-3-phenylindan-1-one (**III**) which was also synthesized by treatment of **II** with hydrogen chloride. The structure of product **III** was proved by X-ray analysis [2] (see figure), thus confirming reaction path *a* and excluding alternative path *b* which would lead to structure **IV** (Scheme 1).

A product structurally related to **II**, 3-benzoyl-4-phenyl-2,3,4,5-tetrahydroindeno[1,2-*b*]pyran, was obtained previously by cyclization of 2,4-dibenzoyl-3-phenyl-1,4-pentadiene [3].

Scheme 1.



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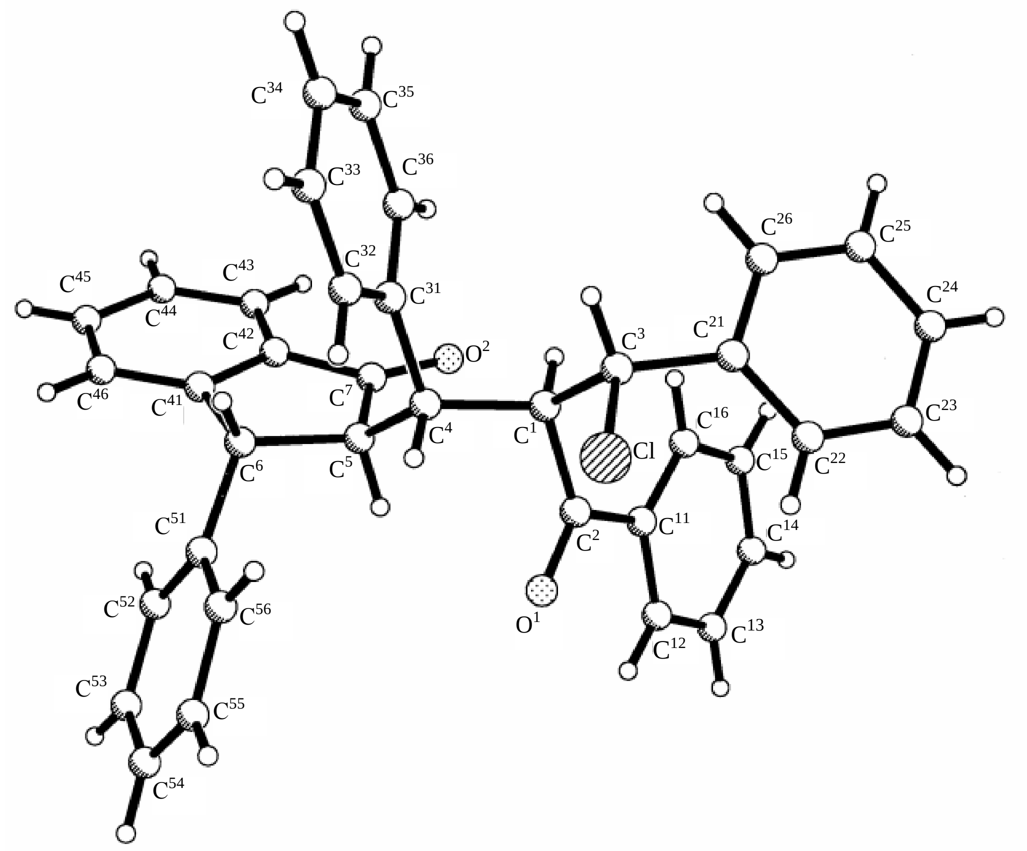

Structure of 2-(2-benzoyl-3-chloro-1,3-diphenylpropyl)-3-phenylindan-1-one according to the X-ray diffraction data.

EXPERIMENTAL

The IR spectrum was recorded on a Perkin–Elmer Spectrum BX FT-IR System spectrometer. The mass spectrum (chemical ionization) was obtained on an Agilent Series 1100 LC/MSD instrument. The ^{1}H and ^{13}C NMR spectra were measured on an Avance 500 spectrometer (500 MHz for ^{1}H). X-Ray diffraction data were obtained with the aid of a SMART-1000 CCD diffractometer (MoK_α radiation, graphite monochromator)..

3-Benzoyl-2,4,5-triphenyl-2,3,4,5-tetrahydroindeno[1,2-*b*]pyran (II). Concentrated sulfuric acid, 35 g, was added over a period of 2.5 h under vigorous stirring to a mixture of 6.56 g (0.02 mol) of diketone **I** and 6.5 g (0.06 mol) of benzaldehyde, maintained at –15°C. The mixture was kept for 2 days at –4 to 0°C, and the crystalline product was separated, washed with water, and recrystallized from benzene. Yield 4.03 g (40%), mp 191–193°C. IR spectrum (CH_2Cl_2), ν, cm^{-1}: 1681 (C=O), 1652 (C=C–O). ^{1}H NMR spectrum ($CDCl_3$) δ, ppm: 3.85 d (1H, 4-H, *J* = 5.8 Hz), 4.32 s (1H, 5-H), 4.52 d.d (1H, 3-H, *J* = 5.8, 10.6 Hz), 5.67 d (1H, 2-H, *J* = 10.6 Hz); signals from aromatic protons are omitted. ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 41.8 (C^4), 52.1 (C^5), 52.3 (C^3), 76.8 (C^2), 197.7 (C=O); signals from aromatic carbon nuclei are omitted. Mass spectrum, *m/z* (I_{rel}, %): 505.2 [*M* + 1] (100), 297.1 [*M* + 1 – $C_6H_5CH{=}CHCOC_6H_5$] (37), 209.1 [$C_6H_5CH{=}CHCOC_6H_5$ + 1] (10). Found, %: C 87.90; H 5.90. $C_{37}H_{28}O_2$. Calculated, %: C 88.06; H 5.59.

2-(2-Benzoyl-3-chloro-1,3-diphenylpropyl)-3-phenylindan-1-one (III). *a*. Dry hydrogen chloride was passed over a period of 3 h through a suspension of 4.9 g (0.015 mol) of diketone **I** in 7.2 g (0.07 mol) of benzaldehyde, maintained at –7°C, and the mixture was kept for 3 days at –4 to 0°C. The crystalline product was filtered off, washed with diethyl ether, and recrystallized from ethyl acetate. Yield 2.73 g (38%), mp 199–200°C.

b. Dry hydrogen chloride was passed over a period of 6 h through a solution of 0.54 g (1 mmol) of compound **II** in 2 ml of a 1 : 10 (by volume) mixture of anhydrous ethanol and dioxane, maintained at –5°C. The mixture was evaporated, and the residue was recrystallized from ethyl acetate. Yield 0.34 g (64%), mp 199–200°C. IR spectrum, ν, cm^{-1}: 1702, 1675 (C=O). ^1H NMR spectrum, δ, ppm: 3.07 t (1H, 4-H, *J* = 5.0, 5.0 Hz), 4.03 d.d (1H, 3-H, *J* = 5.1, 11.1 Hz), 4.05 d (1H, 5-H, *J* = 5.1 Hz), 4.84 d (1H, 1-H, *J* = 3.2 Hz), 5.72 d.d (1H, 2-H, *J* = 3.2, 11.1 Hz). ^{13}C NMR spectrum, δ_C, ppm: 46.4 (C^3), 49.6 (C^5), 54.5 (C^2), 56.6 (C^4), 63.4 (C^1), 199.5 (C=O), 208.0 (C=O). Mass spectrum, *m/z* (I_{rel}, %): 541.5 [*M* + 1] (100), 505 [M + 1 – Cl] (78.5), 297.1 [*M* + 1 – $C_6H_5CH=CHCOC_6H_5$] (29.7), 209.1 [$C_6H_5CH=CHCOC_6H_5$ + 1] (5). Found, %: Cl 6.59. $C_{37}H_{29}ClO_2$. Calculated, %: Cl 6.56.

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