

SHORT
COMMUNICATIONSChemistry of 1,5-Diketones. A New Synthetic Approach
to Unsaturated 1,5-Diketones

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It is known that substituted pent-2-ene-1,5-diones **IIa** and **IIb** and their fused analogs **IIc** and **Ile** can be obtained by base hydrolysis of pyrylium and dihydrobenzochromenium salts [1, 2]. Opening of the pyrylium ring by the action of sodium acetate smoothly afforded aryl-substituted pent-2-ene-1,5-diones **IIa** and **IIb** in 92–96% yield [3]. The hydrolysis of 4-(3-nitrophenyl)-2,6-diphenylpyrylium and 2,4-diphenyl- and 4-(4-methoxyphenyl)-2-phenyldihydrobenzochromenium tetrafluoroborates **Ic–Ie** in aqueous alcohol in the presence of sodium acetate gave the corresponding unsaturated 1,5-diketones **IIc–Ile** in 31–52% yield [4]. Opening of the labile heteroring in alkyl/aryl-substituted pyrylium salts with formation of unsaturated 1,5-diketones also occurred during thin-layer chromatography (TLC) on aluminum oxide or weakly basic sorbents [5].

We were the first to accomplish hydrolysis of pyrylium salts **Ia–Ic** and dihydrobenzochromenium salts **Id** and **Ie** in aqueous ethanol in the presence of 5 equiv of sodium acetate and 6 equiv of powdered aluminum oxide as catalyst. The yields of unsaturated diketones **IIa–Ile** were 75–98%. Pentenedione **IIc** was isolated as *cis-s-cis* isomer; diketone **Ile** was a mixture of *cis* and *trans* isomers (according to the GC–MS data). Presumably, aluminum oxide promotes polarization of

the C–O bond in the heteroring, thus favoring its opening with formation of unsaturated diketone.

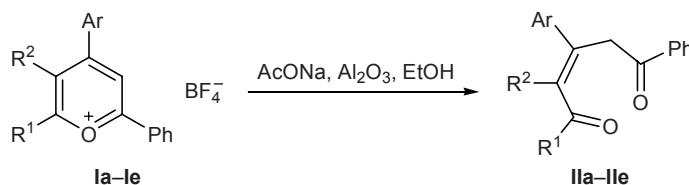
Initial pyrylium tetrafluoroborates **Ia–Ic** were synthesized according to the procedure reported in [6], and salts **Id** and **Ie** were prepared as described in [7].

General procedure for the hydrolysis of pyrylium and dihydrobenzochromenium salts. A suspension of 11 mmol of tetrafluoroborate **Ia–Ie** and 55 mmol of Al₂O₃ in 40 ml of ethanol was heated to 70–80°C under stirring, a solution of 66 mmol of sodium acetate in 15 ml of water was added, and the mixture was kept for 24 h. The precipitate was filtered off and washed with chloroform, the filtrate was evaporated, and the crystalline product was separated and dried.

1,3,5-Triphenylpent-2-ene-1,5-dione (IIa). Yield 98%, mp 118–119°C [1].

3-(4-Methoxyphenyl)-1,5-diphenylpent-2-ene-1,5-dione (IIb). Yield 97%, mp 121–122°C (from ethanol) [7].

3-(3-Nitrophenyl)-1,5-diphenylpent-2-ene-1,5-dione (IIc). Yield 81%, yellow crystals, mp 126–127°C (from ethanol). IR spectrum, ν , cm⁻¹: 1686 (C¹=O), 1664 (C⁵=O), 1580 (C=C). ¹H NMR spectrum, δ , ppm:



R¹ = Ar = Ph, R² = H (**a**); R¹ = Ph, R² = H, Ar = 4-MeOC₆H₄ (**b**); R¹ = Ph, R² = H, Ar = 3-O₂NC₆H₄ (**c**); R¹R² = *o*-(CH₂)₂C₆H₄, Ar = Ph (**d**); R¹R² = *o*-(CH₂)₂C₆H₄, Ar = 4-MeOC₆H₄ (**e**).

8.16–7.12 m (14H, H_{arom}), 6.86 s (1H, CH=), 4.72 s (2H, CH₂). ¹³C NMR spectrum, δ_C, ppm: 190.2 (C¹), 124.0 (C²), 150.9 (C³), 42.0 (C⁴), 195.8 (C⁵). Found, %: C 74.10; H 4.73; N 3.52. C₂₃H₁₇NO₄. Calculated, %: C 74.29; H 4.61; N 3.89.

2-(3-Oxo-1,3-diphenylpropylidene)-1,2,3,4-tetrahydronaphthalen-1-one (II_d). Yield 76%, mp 138–139°C (from ethanol) [2].

2-[1-(4-Methoxyphenyl)-3-oxo-3-phenylpropylidene]-1,2,3,4-tetrahydronaphthalen-1-one (II_e). Yield 75%, mp 108–109°C (from propan-2-ol). IR spectrum, ν, cm⁻¹: 1726, 1681 (C=O); 1654 (C=C). Mass spectrum, *m/z*: 382 [M]⁺, 381 [M – 1]⁺. Found, %: C 81.51; H 5.77. C₂₆H₂₂O₃. Calculated, %: C 81.75; H 5.76.

The IR spectra were recorded on a Specord M-80 spectrophotometer from samples dispersed in mineral oil or hexachlorobutadiene. The ¹H and ¹³C NMR spectra were measured on a Bruker MSL-400 instrument from solutions in chloroform-*d* or DMSO-*d*₆ using hexamethyldisiloxane as internal reference.

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