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LETTERS TO THE EDITOR

CHARACTERISTIC FEATURES OF A HETERO DIELS–ALDER REACTION: THE REACTION OF AROYLKETENE WITH ALLOBETULONE AS AN EXAMPLE

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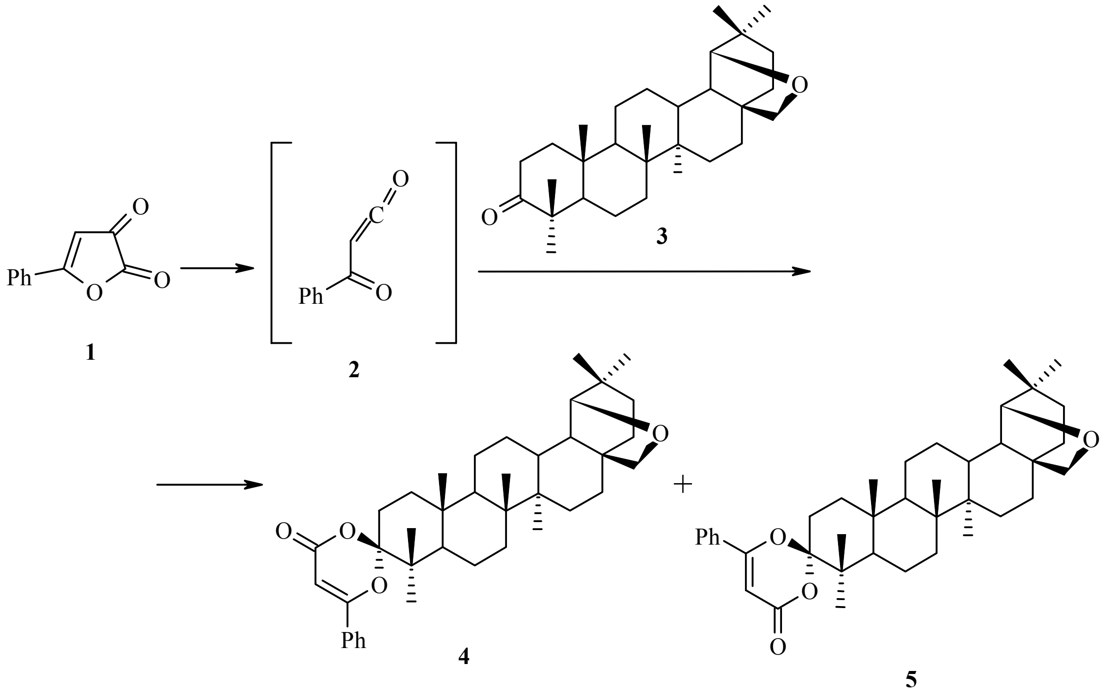
5-Phenyl-2,3-dihydrofuran-2,3-dione (**1**) is a convenient synthon for generation of benzoylketene [1]. In reactions with ketones, benzoylketene (**2**) forms 2,2-disubstituted 6-phenyl-1,3-dioxin-4-ones [2]. In the reaction of benzoylketene **2** (obtained *in situ* from furandione **1**) with allobetulone (3-oxo-19,28-epoxyoleane) (**3**) [3], two stereoisomeric spiro adducts **4, 5** were unexpectedly isolated.



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Based on the integrated intensity of the singlet for the CH group of the dioxinone ring in the ^{1}H NMR spectrum of the reaction mixture, the optical isomers are formed in 1:2 ratio.

The studied conversion occurs according to a hetero Diels–Alder reaction with reversed electronic effects in the addends, where benzoylketene **2** acts as the heterodiene while the keto group of allobetulone **3** acts as the heterodienophile. The optical isomers were separated by column chromatography. We obtained colorless crystalline compounds with R_f 0.55 and 0.50, which have similar spectral characteristics.

In the ^{1}H NMR spectrum of compounds **4,5**, there is a set of signals from the aromatic protons with center at 7.45 ppm, a singlet from the methine proton of the dioxinone ring in the 5.78 ppm and 5.82 ppm region, and also a set of protons from the condensed oleane system.

Spiro[(6-phenyl-3,4-dihydro-2H-1,3-dioxin)-2R(S),3'-(19',28'-epoxyolean)]-4-ones (4, 5). A solution of compound **1** (0.01 mol) and compound **3** (0.01 mol) in anhydrous benzene (50 ml) was refluxed for 5 h. The solvent was removed, the tarry residue was chromatographed on a column (Silicagel L 100/250), and eluted with a 1:5 ethyl acetate–hexane mixture. It was recrystallized from hexane.

Compound 4, R_f 0.55 (Silufol UV-254, 1:5 ethyl acetate–hexane), mp 200-202°C (hexane), $[\alpha]_D^{18} = 17.5°$ (chloroform). IR spectrum, ν, cm^{-1}, 1715 (C=O), 1615 (C=C). ^{1}H NMR spectrum, δ, ppm: 7.45 (5H, m, Ph); 5.78 (1H, s, =CH–); 3.71 (1H, d, 28-H); 3.71 (1H, s, 19-H); 3.38 (1H, d, 28-H); 2.48 (1H, t, 2-H); 2.44 (1H, t, 2-H); 1.84 (2H, td, 1-H); 0-1.8 (42H, set of signals from aliphatic protons). Found: *m*/*z* 586 [M]$^+$. $C_{39}H_{54}O_4$. Calculated: M = 586.86.

Compound 5, R_f 0.50 (Silufol UV-254, 1:5 ethyl acetate–hexane), mp 149-151°C (hexane), $[\alpha]_D^{18} = 52.2°$ (chloroform). IR spectrum, ν, cm^{-1}: 1725 (C=O), 1615 (C=C). ^{1}H NMR spectrum, δ, ppm: 7.45 (5H, m, Ph); 5.81 (1H, s, =CH–); 3.72 (1H, d, 28-H); 3.46 (1H, s, 19-H); 3.39 (1H, d, 28-H); 2.48 (1H, t, 2-H); 2.43 (1H, 5, 2-H); 1.90 (2H, td, 1-H); 0-1.8 (42H, set of signals from aliphatic protons). Found: *m*/*z* 587 [M]$^+$. $C_{39}H_{54}O_4$. Calculated: M = 585.86

The IR spectra were recorded on a UR-20 in vaseline oil; the ^{1}H NMR spectra were recorded on a MERCURYplus 300 (300 MHz) in $CDCl_3$, internal standard HMDS. The mass spectra were obtained on an MKh-1310 with emission current 1000 mA, electron ionizing energy 70 eV, vaporizer temperature 120°C, source temperature 200°C. The angle of rotation was determined on a Perkin–Elmer 341 polarimeter (c1 $CHCl_3$).

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