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HETEROCYCLIZATION OF α,α'-DIBROMO 1,5-DIKETONES

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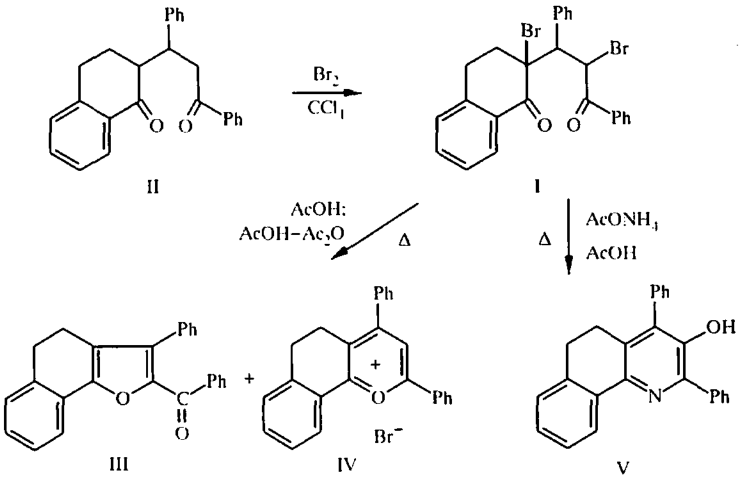
1,5-Diaryl- and 1,3,5-triaryl-2,4-dichloropentane-1,5-diones when treated with ammonia in protonic (acetic acid) or aprotonic (ether, dioxane) solvents form 3-chloropyridines and 2-aroylpyrroles [1,2]. Their unsaturated analogs (1,3,5-triaryl-2,4-dichloro-2-pentene-1,5-diones) under Chichibabin reaction conditions yield 3,5-dichloropyridines, and when heated in acetic acid they yield 2-aroyl-3,5-diaryl-4-chlorofurans [3].

Study of the behavior under similar conditions of α,α'-dibromo 1,5-diketones for the case of 2-bromo-2-(2'-bromo-3'-oxo-1',3'-diphenylprop-1'-yl)-1,2,3,4-tetrahydronaphthalen-1-one (I), obtained by bromination of the semicyclic 1,5-diketone II in tetrachloromethane, showed that when 1,5-diketone I is boiled in acetic acid, two competing processes occur connected with conversion of the latter initially probably to the unsaturated monobromodiketone followed by its heterocyclization to 2-benzoyl-3-phenyl-4,5-dihydronaphtho[1,2-*b*]furan (III) and cyclization of the substrate I to the hydronaphthopyrylium bromide IV. The yield of benzoylfuran III may be increased from 21% to 39% by using a mixture of acetic anhydride and acetic acid (3:1).



Under Chichibabin reaction conditions, the dibromoketone I, in contrast to noncyclic dichloro-1,5-dioxo compounds [1,2], owing to the presence of mobile bromine atoms is converted to the previously unknown 3-hydroxy-2,4-diphenyl-5,6-dihydrobenzo[*h*]quinoline (V).

2-Bromo-2-(2'-bromo-3'-oxo-1',3'-diphenylprop-1'-yl)-1,2,3,4-tetrahydronaphthalen-1-one (I). Bromine (4.1 g, 25.6 mmol) was added dropwise with stirring to a solution of diketone II (3 g, 8.5 mmol) in CCl_4 (40 ml). The precipitated crystals were washed with ethanol and acetone. Yield 3.2 g (74%); mp 149-151°C (decomp., acetone). IR spectrum: 1688, 1668 (C=O). Found, %: C 57.18; H 3.87; Br 31.70. $C_{25}H_{20}Br_2O_2$. Calculated, %: C 57.62; H 3.94; Br 31.20.

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2-Benzoyl-3-phenyl-4,5-dihydronaphtho[1,2-*b*]furan(III) and **2,4-Diphenyl-5,6-dihydronaphtho[1,2-*b*]-pyrylium Bromide (IV).** Dibromo diketone I (1.5 g, 2.9 mmol) was boiled for 3 h in acetic acid (50 ml). The reaction mixture was poured into ether (200 ml), then after 48 h the crystals of salt IV were separated. Yield 0.9 g (74%); mp 267-269°C (ethanol) [4]. The filtrate was neutralized with a saturated soda solution to pH 7. The ether layer was removed, then it was dried with $MgSO_4$ and the solvent was evaporated. Yield of dihydronaphthofuran III 0.21 g (21%); mp 143-144°C (2-propanol). IR spectrum: 1630 (C=O). ^1H NMR spectrum ($CDCl_3$): 2.78-3.03 (4H, m, CH_2–CH_2); 7.24-8.40 (14H, m, Ar). Found, %: C 85.25; H 5.16. $C_{25}H_{18}O_2$. Calculated, %: C 85.69; H 5.18.

We obtained 0.4 g (39%) benzoylfuran III and 0.05 g (4%) bromide IV similarly, by heating diketone I in 40 ml of an acetic anhydride–acetic acid mixture (3:1 by volume).

3-Hydroxy-2,4-diphenyl-5,6-dihydrobenzo[*h*]quinoline (V). Dibromo diketone I (1.56 g, 2.9 mmol), ammonium acetate (0.89 g, 1.2 mmol), and acetic acid (40 ml) were boiled for 10 h. The reaction mixture was extracted with ether (2×40 ml). The ether layer was washed with water, dried with $MgSO_4$, and the solvent was evaporated. Tarry substances were removed from the oil formed by column chromatography (silica gel, *l* = 10 cm, *d* = 2 cm, eluent hexane–ether). The yield of hydroxyhydrobenzoquinoline V 0.32 g (31%); mp 148-150°C (2-propanol). IR spectrum: 3532 (OH). ^1H NMR spectrum ($CDCl_3$): 2.74-2.90 (4H, m, CH_2–CH_2); 5.12 (1H, s, OH); 7.19-8.32 (14H, m, Ar). Found, %: C 85.53; H 5.55; N 4.11. $C_{25}H_{19}NO$. Calculated, %: C 85.93; H 5.48; N 4.01.

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