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6-(1,3-DIOXOINDAN-2-YLIDENEMETHYL)-1,2,2,4-TETRAMETHYL-1,2-DIHYDRO-AND 1,2,3,4-TETRAHYDROQUINOLINES

M. Yu. Krysin, Kh. S. Shikhaliev, I. K. Anokhina, and Zh. V. Shmyreva

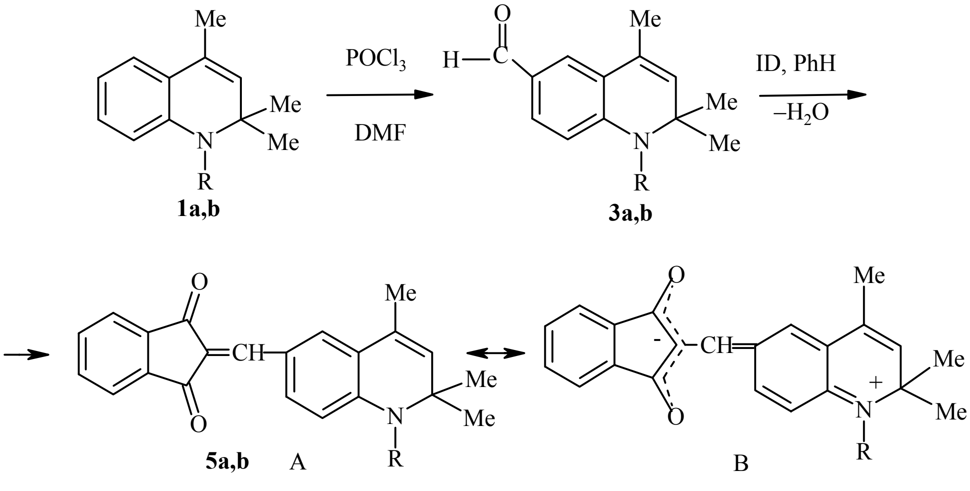
6-Formyl-1,2,2,4-tetraalkyldi- and -tetrahydroquinolines have been synthesized by the Vilsmeier reaction and they are readily condensed with 1,3-indanedione to give 2-hetarylidene-1,3-indanediones. The latter exist as complexes with charge transfer from the quinoid structure of the heterocyclic fragment.

Keywords: 6-formyl-1,2,2,4-tetraalkyldi- and -tetrahydroquinolines, condensation with 1,3-indanedione.

Charge-transfer (CT) complexes are chacterized by their specific electrophysical properties (photochromes, photosemiconductors). Aryl- and hetaryl- substituted 1,3-indanedione derivatives [1, 2] are of particular interest for their synthesis.

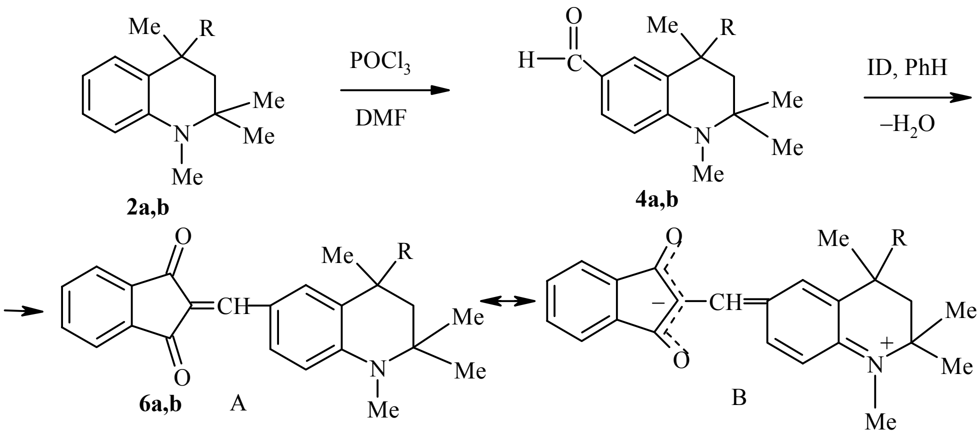
We have carried out the synthesis of 2-hetarylidene-1,3-indanediones which contain 1,2,2,4-tetraalkyldi- or -tetrahydroquinolines as the hetaryl fragment (see Scheme 1).

Scheme 1



Voronezh State University, Voronezh 394693, Russia; e-mail: root@chem.vsu.ru. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 253-255, February, 2001. Original article submitted April 29, 1999.

Scheme 1 (continued)



1–**5** **a** R = Me, **b** R = CH$_2$Ph; **2**, **4**, **6** **a** R = H, **b** R = Ph, ID = 1,3-indanedione

Formylation of 1-R-2,2,4-trimethyl-1,2-dihydroquinolines **1a,b** and 4-R-1,2,2,4-tetramethyl-1,2,3,4-tetrahydroquinolines **2a,b** using the Vilsmeier complex gave the corresponding 6-formyl derivatives **3a,b** and **4a,b**. Condensation of these 6-formyl derivatives **3a,b** and **4a,b** with 1,3-indanedione was carried out in benzene

TABLE 1. Spectral Characteristics of the Compounds Synthesized

Compound	UV spectrum		IR spectrum, ν, cm^{-1}	^{1}H NMR spectrum, δ, ppm, spin-spin coupling* (J), Hz
	λ_{max}	log ε		
3a	255	3.14	1640 (C=C), 1665 (HC=O)	1.35 (6H, s, 2,2-$(CH_3)_2$); 2.01 (3H, s, 4-CH_3); 3.44 (3H, s, NCH_3); 5.25 (1H, s, 3-H); 6.31-7.40 (3H, m, H arom.); 9.52 (1H, s, CHO)
3b	260	3.27	1645 (C=C), 1668 (HC=O)	1.38 (6H, s, 2,2-$(CH_3)_2$); 2.05 (3H, s, 4-CH_3); 4.46 (2H, s, CH_2); 5.21 (1H, s, 3-H); 6.25-7.40 (8H, m, H arom.); 9.57 (1H, s, CHO)
4a	250	3.02	1665 (HC=O)	1.66 (6H, s, 2,2-$(CH_3)_2$); 1.73 (3H, d, J_{Me4} = 7.5, 4-CH_3); 2.21 (1H, dd, $^2J_{3a3b}$ = 12.0, J_{3b4} = 4.5, 3-H_b); 2.29 (1H, dd, $^2J_{3a3e}$ = 12.0, J_{3e4} = 5.0, 3-H_a); 2.38 (1H, qd, J_{Me4} = 7.5, J_{3a4} = 5.0, J_{3b4} = 4.5, 4-H); 3.33 (3H, s, NCH_3); 6.28-7.40 (3H, m, H arom.); 9.50 (1H, s, CHO)
4b	255	3.09	1665 (HC=O)	1.64 (6H, s, 2,2-$(CH_3)_2$); 1.70 (3H, s, 4-CH_3); 2.31 (1H, d, $^2J_{ab}$ = 12.2, 3-H_a); 2.69 (1H, d, $^2J_{3a3b}$ = 12.2, 3-H_b); 3.46 (3H, s, NCH_3); 6.35-7.45 (8H, m, H arom.); 9.55 (1H, s, CHO)
5a	525	5.09	1630 (C=C), 1660 (C=O)	1.38 (6H, s, 2,2-$(CH_3)_2$); 2.04 (3H, s, 4-CH_3); 3.53 (3H, s, NCH_3); 5.30 (1H, s, 3-H); 6.30-7.60 (7H, m, H arom.); 7.89 (1H, s, CH)
5b	520	5.14	1630 (C=C), 1670 (C=O)	1.41 (6H, s, 2,2-$(CH_3)_2$); 2.11 (3H, s, 4-CH_3); 4.49 (2H, s, CH_2); 5.27 (1H, s, 3-H); 6.25-7.65 (12H, m, H arom.); 7.92 (1H, s, 6-CH)
6a	495	5.16	1670 (C=O)	1.68 (6H, s, 2,2-$(CH_3)_2$); 1.78 (3H, d, J_{Me4} = 7.2, 4-CH_3); 2.25 (1H, dd, $^2J_{3a3b}$ = 12.1, J_{3b4} = 4.5, 3-H_b); 2.30 (1H, dd, $^2J_{3a3b}$ = 12.1, J_{3b4} = 5.1, 3-H_a); 3.32 (1H, qd, J_{Me4} = 7.2, J_{3a4} = 5.1, J_{3b4} = 4.5, 4-H); 3.54 (3H, s, NCH_3); 6.30-7.65 (7H, m, H arom.); 7.88 (1H, s, 6-CH)
6b	495	5.13	1670 (C=O)	1.66 (6H, s, 2,2-$(CH_3)_2$); 1.74 (3H, s, 4-CH_3); 2.36 (1H, d, $^2J_{3a3b}$ = 12.2, 3-H_a); 2.69 (1H, $^2J_{3a3b}$ = 12.2, 3-H_b); 3.54 (3H, s, NCH_3); 6.35-7.65 (12H, m, H arom.); 7.90 (1H, s, 6-CH)

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* Spin-spin coupling was determined using a double resonance method.

TABLE 2. Characteristics of Compounds Synthesized

Compound	Empirical formula	Found, % Calculated, %				mp, °C	Yield, %
		M*	C	H	N		
3a	$C_{14}H_{17}NO$	215 215.30	78.35 78.03	7.97 7.90	6.16 6.51	44-45	51
3b	$C_{20}H_{21}NO$	291 291.40	82.18 82.47	7.40 7.21	4.66 4.81	116-118	80
4a	$C_{14}H_{19}NO$	217 217.31	77.55 77.42	8.89 8.75	6.70 6.45	66-65	92
4b	$C_{20}H_{23}NO$	293 293.41	81.78 81.91	7.98 7.85	4.59 4.77	117-118	76
5a	$C_{23}H_{21}NO_2$	343 343.44	80.59 80.47	6.38 6.12	3.97 4.08	169-170	54
5b	$C_{29}H_{25}NO_2$	419 419.53	83.28 83.05	5.75 5.97	3.15 3.34	167-168	66
6a	$C_{23}H_{23}NO_2$	345 345.45	80.22 80.00	6.48 6.66	4.13 4.06	178-179	71
6b	$C_{29}H_{27}NO_2$	421 421.54	82.39 82.66	6.48 6.41	3.15 3.32	198-200	82

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* Determined by mass spectrometry.

with azeotropic distillation of water. The 2-hetarylidene-1,3-indanediones **5a,b** and **6a,b** evidently exist in the B form as the intramolecular CT complex involving the quinoid structure of the hydroquinoline fragment. This isapparent from the deep violet coloration and the UV spectra, in which characteristic, high intensity absorption bands are observed in the region 495-520 nm (Table 1). The shift of the absorption bands to long wavelength in the case of the 1,2-dihydroquinoline derivatives **5a,b** is evidently associated with the participation of the multiple bonds of the dihydroquinoline fragment in the conjugation.

Yields and characteristics for the compounds synthesized are given in Tables 1 and 2.

EXPERIMENTAL

Monitoring of the reaction course and the purity of the compounds obtained was carried out by TLC on Silufol UV-254 plates with chloroform eluent. UV spectra were measured on a Specord instrument with chloroform solvent and IR spectra on a UR-20 instrument. ^{1}H NMR spectra were taken on a Bruker AC-300 spectrometer (300 MHz) using DMSO-d$_6$ solvent and TMS reference and mass spectra were recorded on an LKB 9000 instrument with electron ionization energy 70 eV.

The starting compounds **1a,b**, **2a,b** were obtained as reported in [3].

6-Formyl-1,2,2,4-tetraalkyldi- and -tetrahydroquinolines (3a,b, 4a,b). $POCl_3$ (9.2 ml, 0.1 mol) was added dropwise with stirring to a solution of the tetraalkyldihydroquinoline (0.1 mol) in dry DMF (25 ml) at 15-20°C. The reaction mixture was held at 35-40°C for 4-6 h and then cooled, ice (50 g) was added, and then 5 N NaOH to pH 6, and the product was extracted with ether. The extract was washed with $NaHCO_3$ solution and then water and dried. Ether was distilled off and the residue was recrystallized from hexane.

2-Hetarylidene-1,3-indanediones (5a,b, 6a,b). Piperidine (0.2 ml) was added to a mixture of aldehyde **3** or **4** (0.01 mol) and 1,3-indanedione (1.46 g, 0.01 mol) and refluxed for 4-5 h with a Dean–Stark apparatus. After cooling, the precipitated solid was filtered off and purified by TLC on Brockmann neutral alumina using chloroform as eluent.

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