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SHORT COMMUNICATIONS

Transformation of 9-Aryl-3,3,6,6-tetramethyl-1,2,3,4,5,6,7,8,9,10-decahydroacridine-1,8-diones in Mineral Acids

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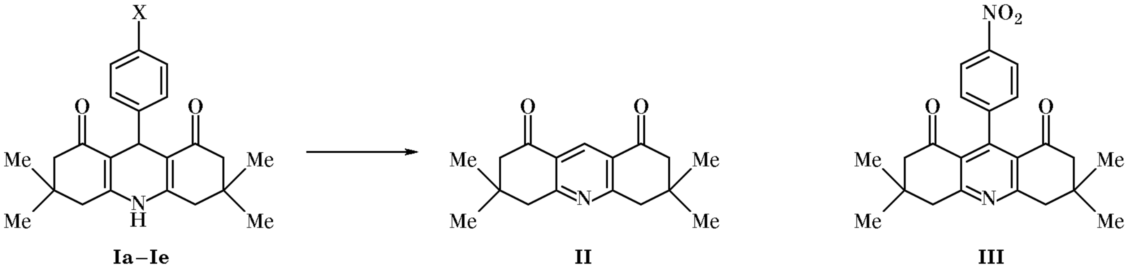
It is known [1] that heating of 9-(4-dimethylaminophenyl)decahydroacridinedione **Ia** in acetic acid leads to elimination of *N*,*N*-dimethylaniline molecule and formation of octahydroacridinedione **II** (Scheme 1). We made an attempt to involve other derivatives of the same series in an analogous transformation. In particular, as substrates we selected compounds **Ib**–**Ie** having various substituents in the *para*-position of the benzene ring. However, 9-arylacridinediones **Ib**–**Ie** turned out to be stable, and they did not change on heating in boiling acetic acid for 6 h. Elimination of the 9-aryl group with formation of octahydroacridinedione **II** occurred when compounds **Ib**–**Ie** were heated in polyphosphoric (PPA), phosphoric, and sulfuric acids. By condensation of volatile products formed in the reaction of **Id** with phosphoric acid we isolated phenol. These data indicate that the mechanism of this reaction is analogous to that reported in [1]. Heating of 9-(*p*-nitrophenyl)decahydroacridinedione **Ie** in PPA resulted in aromatization of the heteroring with formation of 9-(*p*-nitrophenyl)octahydroacridinedione **III** (Scheme 1).

Thus heating of compounds **Ia**–**Ie** in mineral acids is accompanied by elimination of the 9-aryl substituent if the latter contains a donor group in the *para*-position. No elimination occurs when the *para*-position of the 9-aryl group is occupied by an electron-acceptor substituent. We failed to effect an analogous transformation of 9-isobutyl-3,3,6,6-tetramethyl-1,2,3,4,5,6,7,8,9,10-decahydroacridine-1,8-dione under similar conditions: the compound remained intact on heating in phosphoric acid for 4 h at 155°C.

3,3,6,6-Tetramethyl-1,2,3,4,5,6,7,8-octahydroacridine-1,8-dione (II) (see table). A mixture of 1.5 mmol of compound **Ib**–**Id** and 20 g of sulfuric, phosphoric, or polyphosphoric acid was stirred under conditions specified in table. The mixture was cooled to room temperature and was then either poured into 200 ml of water (in the reactions with H_3PO_4 and H_2SO_4) or carefully diluted with water (200 ml; in the reactions with PPA). The mixture was left to stand for 15 h and filtered, and the filtrate was neutralized to pH 7–8 by adding solid sodium hydroxide. The precipitate was filtered off, washed with water, dried in air, and recrystallized from ethyl acetate–hexane (1 : 1). The product was identical to a sample prepared by the procedure described in [2].

3,3,6,6-Tetramethyl-9-(*p*-nitrophenyl)-1,2,3,4,5,6,7,8-octahydroacridine-1,8-dione (III). A mixture of 0.59 g (1.5 mmol) of compound **Ie** and 20 g of

Scheme 1.



X = NMe_2 (**a**), H (**b**), OMe (**c**), OH (**d**), NO_2 (**e**).

Reaction of 9-aryldecahydroacridines **Ib**–**Id** with mineral acids

Comp. no.	Reaction conditions			Yield of **II**, %
	acid	time, h	temperature, °C	
Ib	PPA	3	130	84
	H_3PO_4	0.5	290	71
	H_2SO_4	2.5	130	42
Ic	PPA	2	85	84
	H_3PO_4	2	100	86
Id	PPA	2	85	83
	H_3PO_4	2.5	100	86
	H_2SO_4	2	100	81

85% phosphoric acid was stirred for 1.5 h at 100°C. It was then cooled to room temperature and poured into 200 ml of water. After 15 h, the mixture was filtered, and the filtrate was neutralized to pH 7 with solid NaOH. The precipitate was filtered off, washed with 200 ml of water, and dried in air. The product was purified by passing it through a 1–2-cm layer of silica gel (40–100 μm) using ethyl acetate–hexane (1 : 1) as eluent. Yield 0.28 g (48%), mp 251–253°C; published data [3]: mp 250–252°C. UV spectrum (EtOH), λ_{max}, nm (ε): 223.1 (21 990), 293.5 (10 015). ^{1}H NMR spectrum (CD_2Cl_2), δ, ppm: 1.08 s (12H, 3-Me, 6-Me), 2.43 s (4H, 2-H, 7-H), 3.11 s (4H, 4-H, 5-H), 7.15 d (2H, J = 8 Hz, 2′-H, 6′-H), 8.18 d (2H, J = 8 Hz, 3′-H, 5′-H). ^{13}C NMR spectrum (CD_2Cl_2), δ_C, ppm: 28.28 (Me), 32.58 (C^3, C^6), 48.25 (C^4, C^5), 54.07 (C^2, C^7), 122.05 ($C^{1'}$), 123.15 ($C^{3'}$, $C^{5'}$), 125.04 (C^{8a}, C^{9a}), 128.09 ($C^{2'}$, $C^{6'}$), 147.16 and 147.70 (C^9, $C^{4'}$), 166.99 (C^{4a}, C^{10a}), 197.22 (C^1, C^8).

Decahydroacridinediones Ib–**Ie** were synthesized by reactions of dimedone with ammonium acetate and appropriate aldehyde according to the procedures described in [1, 3]. The reactions of compounds **Ib**–**Ie** were carried out with concentrated sulfuric acid and 85% phosphoric acid. Polyphosphoric acid was prepared by mixing 140 g P_2O_5 with 60 ml of 85% phosphoric acid.

The electron absorption spectrum was recorded on a Specord M-400 spectrophotometer. The ^{1}H and ^{13}C NMR spectra were obtained on a Bruker AC-200 spectrometer at 200 and 50 MHz, respectively, using tetramethylsilane as internal reference. The progress of reactions and the purity of compounds **II** and **III** were monitored by TLC on Silufol UV-254 plates using ethyl acetate–hexane (1 : 1) as eluent; spots were visualized with UV light or iodine vapor with subsequent heating at 250–350°C. The melting points were determined on a Boetius device.

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