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POLYNUCLEAR HETEROCYCLIC COMPOUNDS

XXI. Cyclization of Halogenophenyldiindanedionylmethanes*

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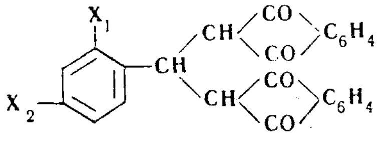
The cyclization of halogenophenyldiindanedionylmethanes to the corresponding halogenophenyldibenzoylenepyrans and dibenzoylenedihydropyridines is investigated. The latter are readily oxidized to dibenzoylenepyridines.

Compounds with two gem-indanedione groups in the molecule, prepared by condensing indane-1,3-dione with aldehydes and quinones, can be cyclized to dibenzoylenepyrans and dibenzoylenedihydropyridines [1-3]. The former are readily obtained from diindanediones in acetic anhydride plus concentrated sulfuric acid. They are yellow crystalline compounds, insoluble in alkalies. Halogenophenyldiindanedionylmethanes (Ia-d) [4] are cyclized by the ordinary method to the corresponding dibenzoylenepyrans (IIa-d).



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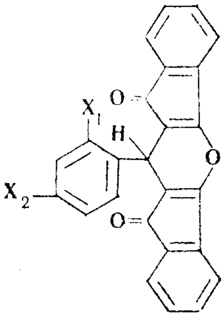

II

a $X_1=H$, $X_2=Cl$; b $X_1=H$, $X_2=Br$; c $X_1=H$, $X_2=I$ d $X_1=Cl$, $X_2=Cl$

Generally dibenzoylenedihydropyridines are obtained from the corresponding pyrans by boiling with ammonia or amines in ethanol or acetic acid solution [2, 5], but if reaction proceeds with difficulty, heating in sealed tubes or even use of liquid ammonia must be resorted to [1, 2, 6].

The halogenophenyldibenzoylenepyrans IIa-d undergo reaction with ethanolic ammonia with great difficulty. They can be more effectively prepared by boiling the diindanedionyl compounds with ammonium acetate in glacial acetic acid [7]. Those conditions readily cyclize compounds Ia-d to the corresponding dihydropyridines; it is enough to boil them well for 1-3 minutes with ammonium acetate in glacial acetic acid, for the red crystals of the dihydropyridines (IIIa-d) to be formed. Dibenzoylenedihydropyridines with an unsubstituted hydrogen atom at $C_{(4)}$ are readily oxidized to the corresponding pyridines either in air or under the conditions of the reaction [5, 8]. In the present work, prolonged boiling also led to formation of halogenophenyldibenzoylenepyridines (IVa-d), and to obtain IIIa-d pure the condensation products had to be purified by treatment with alkali. The dihydropyridines III form greenish-blue solutions in ethanolic alkali or ammonia [5, 7], whereas the pyridines IV formed by oxidation of III remain undissolved, so that they can easily be separated. Since in alkali solution the dihydropyridines oxidize particularly readily to pyridines, losses of dihydropyridines in alkali purification are considerable.

Prolonged condensation also leads to splitting off of halogen from IIIa-d, and the amount of it in the condensation product drops. The most unstable of these compounds is the iodine one IIIc. One minute cyclization of Ic gives IIIc as red quadrilateral plates, along with pale yellow IVc, and an amorphous brown substance. If the cyclization is prolonged to 30 minutes, the latter is the main product, and the alkali-purified dihydropyridine has a diminished content of halogen.

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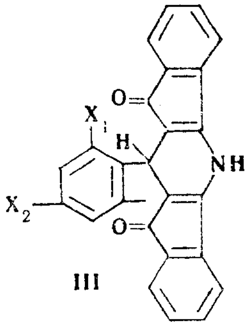
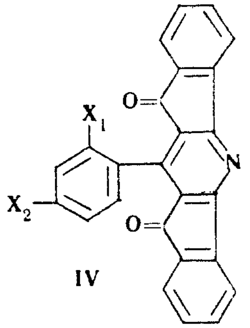
* For Part XX see [15].



III



IV

a $X_1=H$, $H_2=Cl$; b $X_1=H$, $X_2=Br$; c $X_1=H$, $X_2=I$ d $X_1=Cl$, $X_2=Cl$

Due to its low solubility, the dibenzoylenepyridine IV is virtually unreduced to the dihydropyridine III by bisulfite in ethanol solution [9-11].

Characteristic of all the dibenzoylenedihydropyridines is formation of a green solution in concentrated sulfuric acid.

Later papers will deal with a spectroscopic study of the compounds of the present paper.

p-Halogenophenyldibenzoylenepyrans (II)

Compound number	mp, °C	Formula	Found, %			Calculated, %			Yield, %
			C	H	halogen	C	H	halogen	
IIa	296	$C_{25}H_{13}ClO_3$	75.73	3.31	Cl 9.04	75.60	3.28	Cl 8.94	86.6
IIb	294	$C_{25}H_{13}BrO_3$	67.94	2.99	Br 18.07	68.02	2.95	Br 18.14	92.0
IIc	291	$C_{25}H_3IO_3$	61.58	2.68	I 25.97	61.49	2.61	I 26.09	81.0
IId	258	$C_{25}H_{12}Cl_2O_3$	69.79	3.12	Cl 16.08	69.58	2.78	Cl 16.46	93.7

Experimental

Halogenophenyldibenzoylenepyrans (IIa-d). 1.0 g halogenophenyldiindanedionylmethane (Ia-d), 5 ml Ac_2O, and 1 drop concentrated H_2SO_4 were heated together for 30 min. Yellow crystals of IIa-d separated, yields 80-90%. Compounds II did not dissolve in alkali, and the solubility in organic solvents was slight. The physical properties of the II compounds are given in the table.

Dibenzoylenedihydropyridine.* 2.0 g diindanedionylmethane [12,13], 6 g NH_4OAc, and 20 ml glacial AcOH were refluxed together for 15 min. The dark red crystals formed were filtered off and washed with EtOH. Yield of dibenzoylenedihydropyridine, 0.8 g. After purification by boiling with AcOH it had mp 276°. It was only slightly soluble in organic solvents, and dissolved in ethanolic alkali to give a green solution. Found: C 79.97; H 4.00; N 5.19%. Calculated for $C_{19}H_{11}NO_2$: C 80.00; H 3.86; N 4.91%.

p-Chlorophenyldibenzoylenedihydropyridine (IIIa) and p-chlorophenyldibenzoylenepyridine (IVa). 1.0 g p-chlorophenyldiindanedionylmethane, 3 g NH_4OAc, and 10 ml glacial AcOH were refluxed together for 5 min. Dark red crystals (0.6 g) formed. When treated with ethanolic ammonia or ethanolic alkali, with boiling, there was partial solution, and an insoluble yellow residue IVa was obtained. The blue solution was filtered into dilute HCl, when a red precipitate of IIIa, mass 0.2-0.35 g, was obtained. For analysis, purification of IIIa with ammonia was repeated, mp 317°. It was soluble in acetone, dioxane, AcOH, EtOH, slightly soluble in $CHCl_3$, and solutions in ethanolic alkali were blue. Found: C 76.10; H 3.90; Cl 8.50; N 3.62%. Calculated for $C_{25}H_{14}ClNO_2$: C 75.85; H 3.54; Cl 8.97; N 3.54%.

The yellow solid insoluble in ethanolic ammonia was again treated with the latter to remove the remainder of IIIa. Yield of IVa, 0.2-0.35 g, mp 346°, soluble in $CHCl_3$, AcOH, and dioxane. Found: C 76.02; H 3.12; Cl 9.19; N 3.22%. Calculated for $C_{25}H_{12}ClNO_2$: C 76.25; H 3.04; Cl 9.02; N 3.55%.

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*The substance obtained by boiling dibenzoylenepyran with ethanolic ammonia [14] is not dibenzoylenedihydropyridine, but has a different and so far undetermined structure.

p-Bromophenyldibenzoylenedihydropyridine (IIIb) and p-bromophenyldibenzoylenepyridine (IVb). 1.0 g Ib, 3g NH_4OAc, and 10 ml glacial AcOH were refluxed together for 3 min. Dark red crystals (0.7 g) were formed. These were worked up as described for IIIa, to give 0.3–0.4 g red IIIb, mp 314°, slightly soluble in $CHCl_3$, glacial AcOH, and EtOH. Found:C 68.14; H 3.40; Br 18.08; N 3.18%. Calculated for $C_{25}H_{14}BrNO_2$: C 68.18; H 3.18; Br 18.18; N 3.18%.

The yellow solid (0.2 g) IVb insoluble in alkali, melted at 328°, was insoluble in $CHCl_3$, dioxane, sparingly in acetone and glacial acetic acid. Found C 68.42; H 3.00; Br 18.79; N 3.16%. Calculated for: $C_{25}H_{12}BrNO_2$: C 68.49; H 2.74; Br 18.26; N 3.17%.

p-Iodophenyldibenzoylenedihydropyridine (IIIc) and p-iodophenyldibenzoylenepyridine (IVc). 10 ml hot glacial AcOH was added to 1.0 g Ic and 3 g NH_4OAc, and the mixture brought to the boil. A mixture of red and yellow crystals, along with amorphous material was formed, yield 0.5 g. The AcOH filtrate was diluted with water when a further 0.5 g amorphous material was obtained. The mixture of amorphous material plus crystals was worked up as described above, to give 0.35 g of reddish-brown IIIc, mp 312°, slightly soluble in EtOH, $CHCl_3$, and glacial AcOH. Found: C 61.46; H 2.85. I 26.55; N 2.43%. Calculated for $C_{25}H_{14}INO_2$: C 61.60; H 2.88; I 26.08; N 2.88%. Yield of yellow IVc, 0.25 g, mp 319° (ex AcOH), soluble in $CHCl_3$ and dioxane, slightly soluble in AcOH. Found: C 62.20; H 2.82; I 25.90; N 2.99%. Calculated for $C_{25}H_{12}Cl_2NO_2$: C 61.85; H 2.47; I 26.18; N 2.88%.

2, 4-Dichlorophenyldibenzoylenedihydropyridine (IIId) and 2, 4-dichlorophenyldibenzoylenepyridine (IVd). 1.0 g Id, 3 g NH_4OAc, and 10 ml glacial AcOH were refluxed together for 6 min. Large red crystals were formed, yield 0.7 g. They were worked up in the way described above, to give 0.4 g red IIId, mp 311°, readily soluble in acetone, dioxane, glacial AcOH, slightly soluble in $CHCl_3$ and EtOH. Found: C 69.69; H 3.25; Cl 16.26; N 3.51%. Calculated for $C_{25}H_{13}Cl_2NO_2$: C 69.82; H 3.02; Cl 16.48; N 3.26%.

Yield of yellow IVd, 0.3 g, mp 344°, slightly soluble in dioxane, $CHCl_3$, and AcOH. Found: C 69.81; H 2.84; Cl 16.47; N 3.52%. Calculated for $C_{25}H_{12}INO_2$: C 61.85; H 2.47; I 26.18; N 2.88%.

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