SYNTHESIS OF 2-ARYL-4-AZAINDAN-1,3-DIONES
AND 2-ARYL-4-AZA-5,6-BENZINDAN-1,3-DIONES

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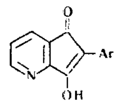
Condensation of 2-hydroxymethylnicotinic and 2-hydroxymethylquinoline-3-carboxylic acid lactones with aromatic aldehydes in the presence of sodium methoxide gives, respectively, 2-aryl-4-azaindan-1,3-diones and 2-aryl-4-aza-5,6-benzindan-1,3-diones. Alkylation of 2-aryl-4-azaindan-1,3-diones with diazomethane gives the N-methylbetaines. According to the IR spectra, in the solid state the 4-azaindan-1,3-diones seem to have a strongly polarized enol structure.

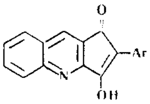
The interesting electrophysical properties [1] possessed by the previously obtained 2-(4'-dimethylaminophenyl)-4-azaindan-1,3-diones [2] and 2-(4'-dimethylaminophenyl)-4-aza-5,6-benzindan-1,3-diones [3] have prompted us to synthesize some new 2-aryl-4-azaindan-1,3-diones, having electron-donating methoxy groups in the phenyl moiety, and also a compound with a longer conjugated chain, having a β-naphthyl residue in the 2-position.

The synthesis of methoxyphenyl- and 2-naphthyl-4-azaindan-1,3-diones (I and II, Table 1) was carried out via the corresponding 4-azanaphthalides (the lactones of 2-hydroxymethylnicotinic and 2-hydroxymethylquinoline-3-carboxylic acids) by a modification of the Dieckmann condensation [4, 5]. Compounds I and II are high-melting solids which do not have sharp melting points. They are almost black in color, and are sparingly soluble in water and in organic solvents. They can be recrystallized only from dimethylformamide. Compound IId differs from this general description in being less dark (deep brown powder) and in being insoluble even in dimethylformamide and dimethyl sulfoxide.

Methylation of I with diazomethane results in an attack on the nitrogen atom with the formation of the internal salt, the N-methylbetaine III (table 2). Compound III differs little in its outward appearance from the starting azaindan-diones. Methyl ethers of the enol form are not produced in this reaction, as

TABLE 1


I


II

Compound	Ar	mp (decomp) °C	Molecular formula	Found, %			Calculated, %			Yield, %
				C	H	N	C	H	N	
Ia	$4\text{-}CH_3OC_6H_4$	250—260	$C_{15}H_{11}NO_3$	70.90	4.48	5.60	71.14	4.38	5.54	54
Ib	$3,4\text{-}(CH_3O)_2C_6H_3$	250—255	$C_{16}H_{13}NO_4$	68.06	4.85	5.00	67.84	4,63	4.95	64
Ic	$3,4,5\text{-}(CH_3O)_3C_6H_2$	245—255	$C_{17}H_{15}NO_5$	65.39	5.00	4.47	65.14	4,82	4.47	63
Id	2-Naphthyl	260—275	$C_{18}H_{11}NO_2$	78.79	4.33	5.06	79.11	4.06	5.14	60
IIa	$4\text{-}CH_3OC_6H_4$	335—345	$C_{19}H_{13}NO_3$	75.43	4.17	4.64	75.27	4.32	4.62	36
IIb	$3,4\text{-}(CH_3O)_2C_6H_3$	310—320	$C_{20}H_{15}NO_4$	72,13	4.58	4.29	72.06	4.54	4,20	38
IIc	$3,4,5\text{-}(CH_3O)_3C_6H_2$	295—305	$C_{21}H_{17}NO_5$	69.41	4.72	3.85	69.26	4.75	3,84	43
IId	2-Naphthyl	360—370	$C_{22}H_{13}NO_2$	82.04	4.01	4.57	81.72	4.06	4.34	36

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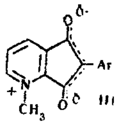
TABLE 2



III

Compound	Ar	mp (decomp), ° C (recrystallization solvent)	Molecular formula	N, %		Yield, %
				Found	Calculated	
IIIa	4-$CH_3OC_6H_4$	270—280 (30% ethanol)	$C_{16}H_{13}NO_3$	5.38	5.25	56
IIIb	3,4-$(CH_3O)_2C_6H_3$	220—230 (50% ethanol)	$C_{17}H_{15}NO_4$	4.83	4.71	73
IIIc	3,4,5-$(CH_3O)_3C_6H_2$	230—240 (30% ethanol)	$C_{18}H_{17}NO_5$	4.39	4.28	76
IIId	2-Naphthyl	280—290 (75% ethanol)	$C_{19}H_{13}NO_2$	4.93	4.87	73

TABLE 3. IR spectra of the Compounds Prepared

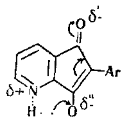
Compound	Absorption, cm^{-1} (intensity, %)	
	1800—1480-cm^{-1} region	3600—2300-cm^{-1} region
I a	1660(26), 1621(23), 1600(22), 1540(54), 1509(53)	3058, 2963, 2908, 2837, 2702—2484
I b	1658(36), 1617(32), 1572(37), 1532(70), 1507(66)	3090, 3050, 2950, 2917, 2831, 2763—2584
I c	1665(25), 1639(23), 1618(28), 1571(40), 1538(47), 1511(49)	3053, 3022, 2976, 2930, 2875, 2828, 2715—2570
I d	1657(32), 1621(31), 1545(67), 1513(48)	3018, 2857, 2660—2465
II a	1661(22), 1641(18), 1618(22), 1600(21), 1548(47)	3081, 3030, 3013, 2945, 2875, 2838, 2800—2755
II b	1668(58), 1635(53), 1612(53), 1568(60), 1530(68), 1507(70)	3090, 3030, 2945, 2880, 2830—2750
II c	1657(34), 1640(29), 1615(28), 1547(55), 1530(50),	3140, 3100, 3010, 2945, 2895, 2836, 2764
II d	1660(35), 1639(34), 1619(30), 1559(86), 1538(66), 1504(63)	3140, 3030, 3004, 2945, 2918, 2875, 2820, 2757
IIIa	1653(14), 1628(22), 1604(32), 1543(38), 1509(35)	3060, 2967, 2830
IIIb	1658(42), 1616(69), 1547(89), 1514(85)	3085, 3050, 2993, 2940, 2830
IIIc	1657(11), 1614(66), 1570(52), 1547(64), 1512(59)	3035, 2985, 2925, 2828
IIId	1658(39), 1612(64), 1593(54), 1549(74), 1501(60)	3048

has been observed in other azaindan-diones [2,3]. This is in agreement with the electronic spectra of the azaindan-diones [6], which indicate that the readily protonated nitrogen atom is the most nucleophilic center in the molecule. The IR spectra (Table 3) of the methylation products also exclude the enol-ether structure [7].

The 4-azaindan-diones I and II show characteristic IR spectra in the crystalline state, which are different from those of both the enol and diketone forms of β-dicarbonyl compounds [8]. In the 1750-1705-cm^{-1} region, no band is found in the region characteristic of the carbonyl groups of the diketo forms, and the usual strong bands due to the slightly polarized enol form, $\nu_{C=O}$ 1700-1680 cm^{-1} and $\nu_{C=C}$ 1600-1570 cm^{-1}, are also absent. In all the 4-azaindole-1,3-diones the most intense bands are found in the 1560-1530 cm^{-1} region, and the bands with the highest frequencies at 1668-1657 cm^{-1} are weak and apparently correspond to the stretching of the carbonyl group with reduced electron density.

The N-methylbetaines III were used as model compounds with an ionized structure. In the spectra of these compounds, also, the strongest absorption occurred at 1549-1543 cm^{-1}, and the bands at 1668-1653 cm^{-1} were of low intensity. The similar spectra of I, II, and III show that the structure of the 2-arylazaindandiones I and II is close to that of the betaines III, i.e., I and II exist in the strongly polarized enol form, which closely approaches the ionic structure.

Compounds I and II in the enol form can form intramolecular hydrogen bonds:



The formation of intramolecular hydrogen bonds of the $-OH \cdots O=C$ or $-OH \cdots N \lessgtr$ is not excluded.

In the 3-nm region, I and II show diffuse bands which appear to be due to stretching of the strongly polarized O—H or $\overset{+}{N}$—H bonds. In I these bands are found at 2700-2460 cm^{-1}, but in II they are shifted towards shorter wavelengths, and appear at 2950-2750 cm^{-1}. This difference probably arises from the different stabilities of the hydrogen bonds. Fusion with a benzene ring as in II reduces the proton-acceptor properties of the nitrogen atom, and hinders the formation of hydrogen bonds.

It is, however, impossible to explain all the properties of I and II solely on the basis of intramolecular hydrogen bonding, or even by the association due to intermolecular hydrogen bonds, since the strong color and poor solubility of I and II is shared by the N-methylbetaines III, for which association by intermolecular hydrogen bonding is not possible. We therefore have to assume that the association in I, II, and III is of the donor-acceptor type, with the formation of autocomplexes. This assumption, however, still requires confirmation with the help of the electronic spectra.

Graduate É. Shifer participated in this work.

EXPERIMENTAL

2-(4'-Methoxyphenyl)-4-azaindan-1,3-dione (Ia). A 0.81-g (0.06 mole) quantity of 2-hydroxymethylnicotinic acid lactone [9] and 0.72 ml (0.06 mole) of freshly distilled 4-methoxybenzaldehyde were dissolved with heating in 12 ml of dry ethyl acetate, and a solution of sodium methoxide [from 0.35 g (0.015 g-atom) of sodium and 10 ml of dry methanol] was added. The mixture turned blood-red in color. About 1-2 ml of liquid was distilled off, and the mixture was heated under reflux for an additional 30 min. Most of the solvent was removed by distillation, and the residue dissolved in 5 ml of water. The solution was heated to boiling, treated with activated charcoal, and filtered. The filtrate was treated with 3 ml of 50% acetic acid, the mixture was kept for 24 hr, and the violet-black crystals were filtered off to give 0.82 g (54%) of Ia. The compound was sparingly soluble in water and ethanol, but somewhat more soluble in dioxane. It was recrystallized from dimethylformamide and dried in vacuo at 120-150°C.

Compounds Ib-d and IIa-c were prepared in a similar manner.

2-(2'-Naphthyl)-4-aza-5,6-benzindan-1,3-dione (IId). To a suspension of 0.37 g (0.002 mole) of 2-hydroxymethylquinoline-3-carboxylic acid lactone [3] and 0.31 g (0.002 mole) of 2-naphthaldehyde in 10 ml of dry ethyl acetate was added a solution of sodium methoxide [prepared from 0.14 g (0.006 g-atom) of sodium and 6 ml of absolute methanol]. A 2-ml sample of the liquid was distilled from the reaction mixture, and the latter was boiled under reflux for 2 hr. The orange salt of IId separated during the reaction. Most of the solvent was distilled off, and the residue was treated with 50% acetic acid. The reaction mixture acquired a brownish-red color. After 24 hr, IId was filtered off to give 0.23 g (36%) yield. The compound was almost insoluble in organic solvents, and it was purified by conversion to its potassium salt using methanolic KOH. The salt was recrystallized from dimethylformamide, and IId was regenerated from its salt by treatment of a solution of the latter in dimethylformamide with 50% acetic acid.

N-Methylbetaine (IIIa). A 0.25-g (0.001 mole) quantity of Ia was suspended in 4 ml of ether and 0.2 ml of dimethylformamide. A solution of diazomethane (prepared from 1 g of N-nitrosomethylurea) was added to the solution with ice cooling. After 24 hr, the solid was filtered off, washed on the filter with a solution of sodium carbonate, water, and ether. Yield 0.15 g (56%) of IIIa, sparingly soluble in water and ethanol, but somewhat more soluble in a mixture of the two.

The N-methylbetaines IIIb-d were obtained in a similar manner.

The IR spectra were taken on an IKS-14 spectrophotometer, between 1800-1480 cm^{-1} in Vaseline oil suspension, and between 3600-2300 cm^{-1} in hexachlorobutadiene.

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