SYNTHESIS AND PROPERTIES OF N,N′-BIS(1,3-INDANEDION-2-YL)IMIDAZOLIUM BETAINE

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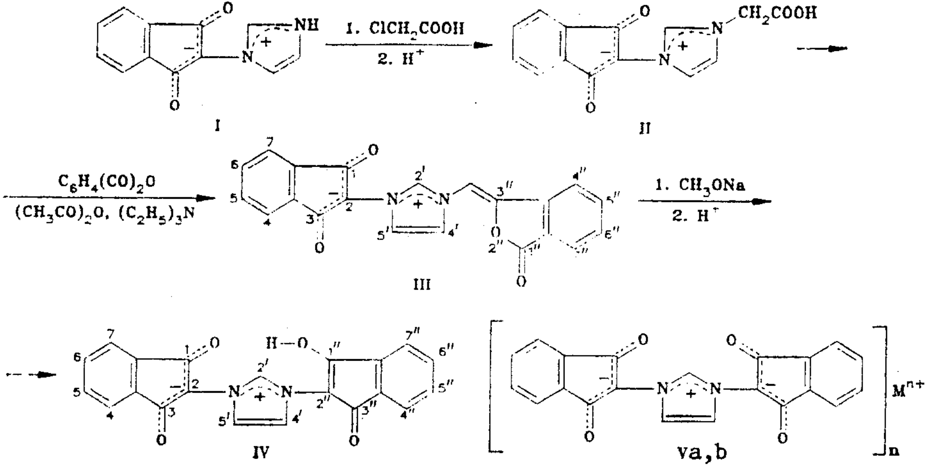
UDC 547.665'785.1:543.422

A method for the synthesis of a new type of onium derivative of 1,3-indanedione — N,N′-bis(1,3-indanedion-2-yl)imidazolium betaine — by anhydride condensation of N-(1,3-indanedion-2-yl)-N′-carboxymethylimidazolium betaine with phthalic anhydride was developed. The new substance is an acid and forms stable salts.

N-(1,3-Indanedion-2-yl)imidazolium betaine (I) is formed in up to 60% yield as a result of the reaction of 2-dicyanomethylene-1,3-indanedione oxide with imidazole in dioxane [1, 2]. However, in addition to major product I, yet another substance in the form of orange-red crystals is formed in a yield of no greater than 15%. N,N′-Bis(1,3-indanedion-2-yl)imidazolium betaine structure IV was assigned to this compound on the basis of PMR spectral data [3]. The present paper is devoted to obtaining this compound and studying its properties.

Compound IV cannot be obtained by the reaction of betaine I with 2-dicyanomethylene-1,3-indanedione oxide, evidently because of the very low solubility of betaine I in dioxane. In this connection we selected the method of anhydride condensation [4, 5]. As the methylene component in the condensation with phthalic anhydride we used N-(1,3-indanedion-2-yl)-N′-carboxymethylimidazolium betaine (II), which is readily obtained by the reaction of betaine I with chloroacetic acid. By condensation of betaine II with phthalic anhydride in the presence of acetic anhydride and triethylamine we were able to obtain a yellow crystalline substance — N-(1,3-indanedion-2-yl)-N′-(3″-phthalidylenemethyl)imidazolium betaine (III).

Compound III is evidently a mixture of two stereoisomers (*cis—trans* isomerism with respect to the double bond at the $C_{3''}$ atom). This is apparent in the PMR spectra, in which a complex multiplet of signals appears at 7.65-7.85 ppm for the =CH proton (see Table 1).



I, II, III, IV, Va,b

V a M=K, n=1; b M=Cu, n=2

In the presence of sodium methoxide III undergoes rearrangement to give the sodium salt of betaine IV in high yields; acidification of a solution of this sodium salt gives betaine IV [6, 7].

Betaine IV is only slightly soluble in organic solvents; its salts are somewhat more soluble. Orange potassium salt Va and brown copper salt Vb were obtained. Betaine IV is evidently an extremely strong acid. The electronic absorption spectrum of betaine IV in a saturated methanol solution (c ≈ $5 \cdot 10^{-5}$ mole/liter) is identical to the spectrum of the potassium salt (see Fig. 1), which provides evidence for its complete dissociation.

Riga Technical University, Riga 226048. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 771-774, June, 1991. Original article submitted December 26, 1989.

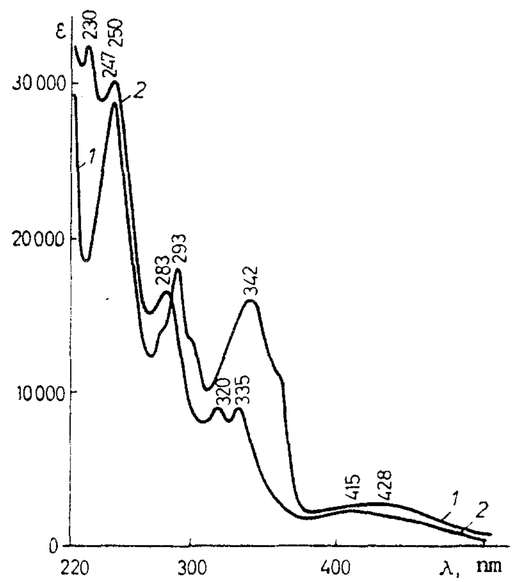


Fig. 1. Electronic absorption spectra in solutions in methanol (c = $5 \cdot 10^{-5}$ mole/liter) of N,N′-bis(1,3-indanedion-2-yl)imidazolium betaine potassium salt (Va) and betaine IV (1) and of the same solutions acidified with concentrated HCl (2).

TABLE 1. Spectral Characteristics of N-Substituted N′-(1,3-Indanedion-2-yl)imidazolium Betaines and Some N,N′-Bis(1,3-indanedion-2-yl)imidazolium Betaine Salts

Compound	IR spectrum, ν, cm^{-1} (absorption, %)*	PMR spectrum (d_6-DMSO), δ, ppm
БИМ**	1658 (20), 1620 (62), 1585 (75), 1555 (77)	3,89 (3H, s, CH_3); 7,24...7,40 (4H, m, phythaloyl); 7,69 (1H, t, 4′-H); 8,30 (1H, t, 5′-H); 9,57 (1H, s, 2′-H)
II	1698 (62) (carboxy C=O 1652 (73), 1616 (62), 1602 (68), 1580, (52), 1566 (68)	5,11 (2H, s, CH_2); 7,2...7,3 (4H, m, phthaloyl); 7,71 (1H, t, 4′-H); 8,33 (1H, t, 5′-H); 9,63 (1H, t, 2′-H)
III	1780 (55) (C=O фталида), 1674 (18), 1610 (50), 1572 (52), 1558 (62), 1523 (40)	7,27...7,38 (4H, m, phthaloyl); 7,65...7,85 (1H, m, =CH); 7,88...8,09 (5H, m, phthalidyle 4′-H); 8,68 (1H, t, 5′-H); 9,99 (1H, t, 2′-H)
IV	1689 (35), (keto-enol C=O), 1618 (30), 1577 (35), 1558 (35), 1509 (28)	7,2...7,3 (8H, m, phthaloyl 8,37 (2H, br.s., 4′-H 5′-H); 10,1 (1H, br.s., 2′-H)
Va	1664 (28), 1625 (73), 1588 (82), 1548 (82)	7,22...7,38 (8H, m, phthaloyl); 8,43 (2H, d, 4′-H and 5′-H); 10,22 (1H, t, 2′-H)
V6	1658 (10), 1618 (9), 1570 (22), 1534 (19)	

*The IR spectra were recorded in mineral oil.

**IMB stands for N-(1,3-indanedion-2-yl)-N′-methylimidazolium betaine.

Strong intermolecular hydrogen bonds are probably realized in crystals of betaine IV, as evidenced by the low solubility of the substance and the IR spectra (see Table 1). Thus in the IR spectrum of betaine IV one observes a relatively intense absorption band at 1689 cm^{-1}, which can be assigned to the carbonyl group of the keto—enol system of 1,3-indanedione, which forms an intramolecular hydrogen bond. This sort of band is not present in the spectrum of potassium salt Va; here one observes a relatively low-intensity band at 1664 cm^{-1}, which, together with other more intense absorption bands at 1510-1610 cm^{-1}, gives the characteristic absorption pattern of 1,3-indanedione Nheterocyclic onium betaines [1, 2, 8]. The IR spectra of N-(1,3-indanedion-2-yl)-N′-methylimidazolium betaine (IMB) and II are presented in Table 1 for comparison.

The IR spectrum of copper salt Vb differs from the spectrum of potassium salt Va with respect to the increased intensity of the absorption at 1660 cm^{-1} as compared with the intensity of the absorption at 1620 cm^{-1}. It might be assumed that the copper ion is more localized on one of the two possible indanedionyl residues of the two betaine IV anions. The formation of an intramolecular chelate bond is less likely because of steric factors.

The PMR spectrum of betaine IV in DMSO also provides evidence for the symmetrical structure of the anion formed as a consequence of dissociation (the 4′-H and 5′-H signals merge; see Table 1). In the PMR spectra of II and III we assign the signals at weaker field to the 5′-H protons rather than to the 4′-H protons due to the influence of the field effect of the oxygen atom of the indanedionyl anion [9]. The signal of the 2′-H protons is found at even weaker field — 9.99 ppm (see Table 1).

EXPERIMENTAL

The IR spectra of suspensions of the compounds in mineral oil were recorded with IKS-14A and Specord IR-75 spectrometers. The electronic spectra were obtained with a Specord UV-vis spectrophotometer. The PMR spectra of solutions of the compounds in d_6-DMSO were recorded with a WH 90/DS spectrometer with hexamethyldisiloxane (HMDS) as the internal standard.

N-(1,3-Indanedion-2-yl)-N′-carboxymethylimidazolium Betaine (II, $C_{14}H_{10}N_2O_4$). A 1.12-g (20 mmole) sample of potassium hydroxide and 0.95 g (10 mmole) of chloroacetic acid were added to a solution of 2.12 g (10 mmole) of betaine I in 30 ml of water, and the mixture was refluxed for 1 h. It was then cooled and acidified to pH 3 by the addition of 2 N HCl to give 2.27 g (84%) of orange II with mp 238-240°C (dec.) [from acetic acid—water (1:1)].

N-(1,3-Indanedion-2-yl)-N′-(3″-phthalidylenemethyl)imidazolium Betaine (III, $C_{21}H_{12}N_2O_4$). A mixture of 0.54 g (2 mmole) of betaine II, 0.37 g (2.5 mmole) of phthalic anhydride, 6 ml of acetic anhydride, and 2 ml of triethylamine was refluxed until precipitation of III ceased (10-12 min). The precipitate was removed by filtration and washed on the filter with ethanol (8-10 ml) to give yellow III with mp 282-285°C (dec.) (from acetic acid). The yield was 0.5 g (70%).

N,N-Bis(1,3-indanedion-2-yl)imidazolium Betaine (IV, $C_{21}H_{12}N_2O_4$). A 7-ml sample of a 6% solution of sodium methoxide obtained from 0.18 g of Na and 6.5 ml of methanol was added to 0.36 g (1 mmole) of betaine III, and the mixture was stirred vigorously at 20°C, during which the color of the mixture changed from yellow to orange red. The mixture was then acidified to pH 2-3 by the addition of 2 N HCl and stirred for another 5 min, after which it was filtered to give orange-red betaine IV with mp 265-270°C (dec.) (from DMF). The yield was 0.33 g (92%).

N,N′-Bis(1,3-indanedion-2-yl)imidazolium Betaine Potassium Salt (Va, $C_{21}H_{11}KN_2O_4$). A solution of 0.03 g (0.5 mmole) of potassium hydroxide in 5 ml of ethanol was added to a suspension of 0.17 g (0.5 mmole) of betaine IV in 10 ml of ethanol, the mixture was stirred for 5 min, 20 ml of water was added, and orange salt Va, with mp > 300°C (dec.) (from ethanol), was removed by filtration. The yield was 0.18 g (90%).

N,N′-Bis(1,3-indanedion-2-yl)imidazolium Betaine Copper Salt (Vb, $C_{42}H_{22}CuN_4O_8$). A solution of 0.05 g (0.25 mmole) of copper acetate in 10 ml of ethanol was added to a solution of 0.17 g (0.5 mmole) of betaine IV in 60 ml of ethanol, and the mixture was worked up to give brown salt Vb with mp > 300°C (dec.) [from DMF—ethanol (1:1)]. The yield was 0.15 g (83%).

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