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LETTERS TO THE EDITOR

SYNTHESIS OF METHYLAMMONIUM 4-ACETYL-2,1',3'-TRIOXOSPIRO[2,5-DIHYDRO-FURAN-5,2'-INDAN]-3-OLATE

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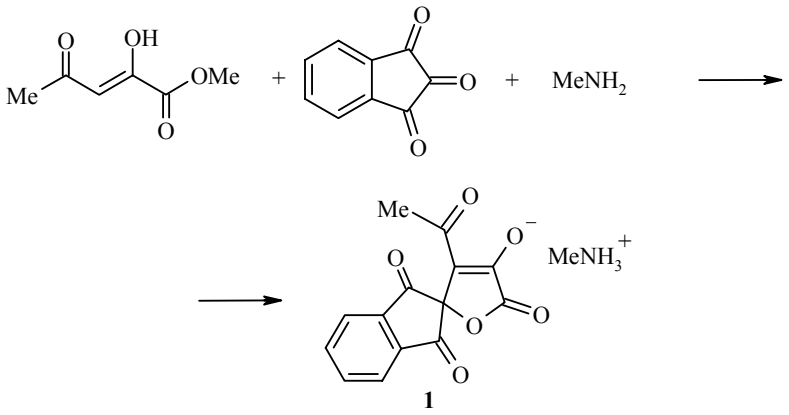
We know that the reaction of acetylpyruvic acid methyl ester with a mixture of an aromatic aldehyde and methylamine leads to formation of 4-acetyl-5-aryl-3-hydroxy-1-methyl-3-pyrrolin-2-ones [1]. We have observed that when equivalent amounts of acetylpyruvic acid methyl ester, ninhydrin, and methylamine are mixed in dioxane with brief heating, methylammonium 4-acetyl-1,1',3'-trioxospiro[2,5-dihydrofuran-5,2'-indan]-3-olate (**1**) is formed.



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The compound **1** obtained is a pale-yellow substance that is soluble in the usual organic solvents. Its ^{1}H NMR spectrum contains a multiplet for the four aromatic protons at 8.06 ppm, a signal from two protons of the NH group and one proton from the OH group as a broadened singlet at 7.67 ppm, a singlet for the three protons of the methyl group of the acetyl residue at 2.13 ppm, and a signal from the methyl group of the methylamine at 2.41 ppm.

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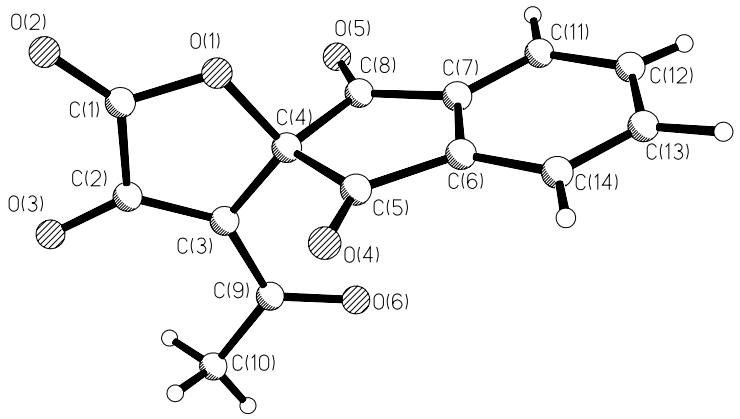

Fig. 1. Structure of the anion of **1**.

In the IR spectrum of compound **1**, there are bands for the stretching vibrations of the carbonyl groups in the 5 and 10 positions (1720 cm^{-1}), the lactone carbonyl group (1760 cm^{-1}), the carbonyl group of the side chain (1630 cm^{-1}), the enol hydroxyl group (3110 cm^{-1}), and the NH bonds at 3210 cm^{-1} and 3500 cm^{-1}.

In the mass spectrum, there is a molecular ion peak $[M]^+$ with *m/z* (I_{rel}, %): 272 (4.80).

The IR spectra were obtained on a UR-20 in vaseline oil; the ^1H NMR spectra were obtained on a Bruker DRX 500 spectrometer (500.13 MHz) in DMSO-d_6. The mass spectra were obtained on an MKh-1320, electron ionizing energy 70 eV.

Methylammonium 4-Acetyl-2,1',3'-trioxospiro[2,5-dihydrofuran-5,2'-indan]-3-olate (1). A mixture of acetylpyruvic acid methyl ester (1.44 g, 0.01 mol) and ninhydrin (1.96 g, 0.01 mol) in dioxane (10 ml) was heated until dissolved. Then an aqueous solution of methylamine (1.3 ml) was added to the solution obtained after cooling down to room temperature. The reaction mixture was held for 5-6 h at ~20°C. The precipitate formed was filtered out and recrystallized from ethanol. Yield 1.7 g (56%); mp 162-164°C. Found, %: C 59.60; H 4.25; N 4.51. $C_{15}H_{13}NO_6$. Calculated, %: C 59.41; H 4.32; N 4.62.

X-ray Diffraction Study. The $C_{14}H_8O_5 \cdot CH_3NH_2$ crystals belong to monoclinic syngony: a = 14.969(3), b = 12.192(2), c = 7.746(2) Å; β = 92.91(3)°; V = 1411.8(5) $Å^3$; M = 303.26; d_{calc} = 1.427 g/cm^3, Z = 4, space group $P2_1/c$. The set of experimental reflections was obtained on a KM-4 (KUMA DIFFRACTION) automatic 4-circle diffractometer with χ geometry by the ω/2θ scanning method in monochromatic MoKα radiation ($2\theta \leq 50.8°$). We measured a total of 2629 reflections, of which 2446 reflections were independent [R(int) = 0.0176, R(σ) = 0.0497]. We did not correct for absorption (μ = 0.112 mm^{-1}). The structure was determined by the direct method using the program SIR92 [2] followed by a series of calculations of the electron density maps. The hydrogen atoms were determined from a difference electron density synthesis and only their positional parameters were least-squares refined. In the full-matrix anisotropic least-squares refinement using the SHELXL-97 program [3], the final R values were $R1$ = 0.0331, $wR2$ = 0.1058 using 1336 reflections with $I \geq 2\sigma(I)$ and $R1$ = 0.0904, $wR2$ = 0.1064 using all 2446 reflections.

The X-ray diffraction study established that crystals of **1** are built up from 4-acetyl-2,1',3'-trioxospiro[2,5-dihydrofuran-5,2'-indan]-3-olate anions and methylamine cations. The structure of anion **1** is shown in Fig. 1. The plane of the lactone ring is orthogonal to the plane of the bicyclic moiety. The plane of the acetyl group is coplanar with the plane of the lactone ring. The $C_{(2)}C_{(3)}C_{(9)}O_{(6)}$ torsional angle is equal to 178.5°. All the bond lengths in the molecule, including the $C_{(2)}=C_{(3)}$ double bond 1.368(3) Å, mainly agree well with literature data [4]. The distances between the $O_{(3)}$ and $C_{(2)}$ atoms, 1.268(2) Å, is appreciably shortened, which

probably is evidence for proton transfer from the hydroxyl group to the nitrogen atom of the methylamine with formation of an N–H···O hydrogen bond. The type and parameters of the hydrogen bonds in the crystal are given below.

D–H···A	d(D–H), Å	d(H···A), Å	<DHA, degrees	d(D···A) A, Å
N–(H-1)C···$O_{(3)}$*	0.954	1.850	166.03	2.786
N–(H-1)A···$O_{(3)}$*[2]	0.924	1.800	168.16	2.711
N–(H-1)B···$O_{(5)}$*[3]	0.907	2.051	146.04	2.849

* $x, y + 1, z$.
*[2] $x, -y + 1/2, z + 1/2$.
*[3] $-x + 1, -y + 1, -z$.

The crystal consists of alternating anionic and cationic layers parallel to the *bc* plane of the unit cell. The anions and cations, connected *via* N–H···$O_{(3)}$ hydrogen bonds, form an infinite chain which is connected with the analogous chain related by a center of symmetry via an N–(H–1)B···$O_{(5)}$.

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