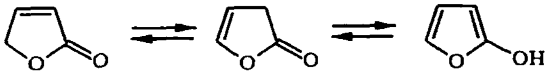
Chemistry of Heterocyclic Compounds, Vol.35, No. 1, 1999

2(5H)-FURANONE IN THE VILSMEIER—HAAK REACTION.* SYNTHESIS OF β-SUBSTITUTED FURANS. MOLECULAR STRUCTURES OF 3-DIMETHYLAMINOMETHYLENE-5-FORMYL-2(3H)-FURANONE AND DIMETHYLAMMONIUM 3,5-DI(2,2-DIMETHYL-4,6-DIOXO-1,3-DIOXAN-5-YLIDENEMETHYL)-2-FURANOLATE

G. D. Krapivin, N. D. Kozhina, L. A. Chernousenko, and V. E. Zavodnik

The reaction of 2(5H)-furanone with the Vilsmeier—Haak—Arnold reagent and subsequent addition of concentrated aqueous $HClO_4$ *to the reaction mixture give (3-dimethylaminomethylen-2-oxo-3H-5-furanyl)methylenimmonium perchlorate, whose hydrolysis under various conditions leads to 3-dimethylaminomethylene-5-formyl-2(3H)-furanone or to the potassium salt of 5-hydroxy-2,4-furandicarbaldehyde. The reaction of these products with CH-acids was studied. The structures of the key compounds of this work have been proved by the method of X-ray diffraction analysis.*

2(5H)-Furanone (I) is an ambident compound possessing properties of a weak CH-acid capable of giving products of condensation with aromatic aldehydes [2] and with an unsaturated ester, which adds electrophilic, nucleophilic, and radical agents at the double bond [3]. In addition, unsaturated lactone I by itself is capable, in principle, of prototropic tautomeric transformations with migration of the double bond and aromatization:



IA IB IC

Tautomeric form IC has been fixed as trimethylsilyl ester obtained by reaction with trimethylsilane [4].

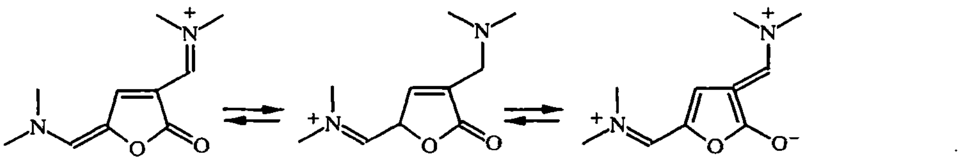
In the present work, we studied the reaction of I with Vilsmeier—Haak—Arnold (VHA) reagent obtained by mixing of DMF with $POCl_3$ [5]. The VHA reagent is capable of forming enamines with compounds containing activated methylene group and is also a very strong iminoalkylating agent relative to aromatic compounds [6] and multiple bonds [7]. Hence, we attempted to isolate and characterize the product of reaction of furanone I with VHA reagent and study its behavior upon hydrolysis and in reactions with CH-acids, (typical for the unaltered aldehyde group and the aldehyde group upon conversion to enamine).

The VHA reagent was obtained by the standard procedure. The DMF:$POCl_3$ mole ratio was 2:1. An equivalent of furanone was added to this reagent and the mixture was maintained at 60—70°C for 2 h. If the reaction mixture is then immediately neutralized by adding of aqueous potassium carbonate (the standard Vilsmeier reaction conditions), the reaction product yield is very low, possibly due to instability of the lactone ring in alkaline medium. Thus, the reaction mixture was cooled and diluted with ethanol. Then, a small excess of 70% $HClO_4$ was added. Yellow crystals of II ($C_{10}H_{15}ClN_2O_6$) separated out after a few minutes.

Kuban State Technological University. 350072 Krasnodar, Russia; e-mail: gemml8803@yahoo.com.
Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 24-34, January, 1999. Original article submitted December 15, 1997.

TABLE 1. Physicochemical Characteristics of Synthesized Compounds

Compound	Empirical formula	Found, % / Calculated, %				IR spectrum, ν, cm^{-1}	UV spectrum (ethanol), λ_{max}, nm (lg ε)	mp, °C	*Rf*	Yield, %
		C	H	N	Hal					
II	$C_{10}H_{15}ClN_2O_6$	$\frac{40,62}{40,76}$	$\frac{5,22}{5,13}$	$\frac{9,45}{9,51}$	$\frac{12,10}{12,03}$	1725; 1740		245		93
III	$C_8H_9NO_5$	$\frac{57,42}{57,46}$	$\frac{5,56}{5,43}$	$\frac{8,33}{8,38}$		1650; 1720	290 (3,84) 384 (4,53)	193...194	0,17	70
IV	$C_6H_3O_4K$	$\frac{40,41}{40,44}$	$\frac{1,39}{1,10}$			1720; 1655		235...240		73
Va	$C_{15}H_{19}NO_6$	$\frac{58,50}{58,23}$	$\frac{6,24}{6,19}$	$\frac{4,35}{4,43}$		1713; 1725; 1738	413 (4,68)	172...173	0,49	13
Vb	$C_{14}H_{17}NO_5$	$\frac{60,35}{60,19}$	$\frac{6,06}{6,14}$	$\frac{4,88}{5,02}$		1713; 1725; 1750	430 (4,53)	170...171	0,38	35
Vc	$C_{13}H_{15}NO_4$	$\frac{62,55}{62,63}$	$\frac{5,92}{6,07}$	$\frac{5,37}{5,62}$		1710	228 (4,63) 427 (4,23)	216...217	0,61	16
Vd	$C_9H_{10}N_2O_4$	$\frac{51,22}{51,41}$	$\frac{5,03}{4,80}$	$\frac{13,40}{13,33}$		1715	291 (3,51) 380 (3,96)	203...204	0,51	32
Ve	$C_{12}H_{11}NO_4$	$\frac{61,55}{61,78}$	$\frac{4,96}{4,76}$	$\frac{5,83}{6,01}$		1720; 1760; 1780	457 (3,73)	250...251	0,77	30
Vf	$C_{16}H_{16}N_2O_4$	$\frac{64,12}{63,98}$	$\frac{5,23}{5,37}$	$\frac{9,17}{9,33}$		1725; 1745; 1762; 2225	509 (4,34)	305...306	0,51	84
Vg	$C_{13}H_{14}N_2O_4$	$\frac{59,44}{59,52}$	$\frac{5,18}{5,38}$	$\frac{10,56}{10,69}$		1680; 1715; 2200	461 (4,62)	232...233	0,35	38
VIa	$C_{20}H_{23}NO_{10}$	$\frac{54,61}{54,90}$	$\frac{5,57}{5,30}$	$\frac{3,00}{3,20}$		1680; 1720	558 (4,64)	191...192	0,12	68
VIb	$C_{18}H_{21}N_5O_6$	$\frac{57,76}{57,58}$	$\frac{5,37}{5,64}$	$\frac{11,28}{11,20}$		1700; 1990; 2015	539 (4,72)	186...187	0,28	57



Perchlorate II thus obtained is a typical salt with good solubility in water and may be stored by preventing access to moisture. The elemental analysis and spectral data given in Tables 1 and 2 indicate that this product is a monoperchlorate, whose cation may be represented as a set of canonical structures IIA—IIC.

The PMR spectrum of salt II (Table 2) displays three singlet olefin proton signals of equal intensity (1H) and signals for 12 protons of the two dimethylamino groups as four singlets, each with intensity of 3H. The occurrence of strong infrared absorption band at 1740 cm^{-1} (Table 2) characteristic for stretching vibrations of lactone carbonyl group indicates that the contribution of structure IIC to the overall resonance is slight.

TABLE 2. PMR Spectral Characteristics of Synthesized Compounds

Compound	Solvent	Chemical shift of protons, δ, ppm
II	CF_3COOD	3.43 (3H, s, N-CH_3); 3,47 (3H, s, N-CH_3); 3,53 (3H, s, N-CH_3); 3,57 (3H, s, N-CH_3); 7,50 (1H, s, α-H); 7,85 (1H, s, β-H); 8,02 (1H, s, 4-H)
III	$CDCl_3$	3,26 (3H, s, N-CH_3); 3,46 (3H, s, N-CH_3); 6,46 (1H, s, β-H); 7,66 (1H, s, 4-H); 9,56 (1H, s, CHO)
IV	DMSO-d_6	7,30 (1H, s, 4-H); 8,73 (1H, s, CHαO); 9,27 (1H, s, CHβO)
Va	$CDCl_3$	1,25 (3H, t, $CH_2\underline{CH_3}$); 1,30 (3H, t, $CH_2\underline{CH_3}$); 3,17 (3H, s, N-CH_3); 3,25 (3H, s, N-CH_3); 4,20 (2H, q, $\underline{CH_2}CH_3$); 4,30 (2H, q, $\underline{CH_2}CH_3$); 6,57 (1H, s, β-H); 6,93 (1H, s, 4-H); 7,23 (1H, s, α-H)
Vb	$CDCl_3$	E-isomer: 1,40 (3H, t, $CH_2\underline{CH_3}$); 2,23 (3H, s, $COCH_3$); 3,20 (3H, s, NCH_3); 3,26 (3H, s, N-CH_3); 4,30 (2H, q, $CH_2\underline{CH_3}$); 6,73 (1H, s, β-H); 6,83 (1H, s, 4-H); 7,30 (1H, s, α-H); Z-isomer: 1,25 (3H, t, $CH_2\underline{CH_3}$); 2,40 (3H, s, $COCH_3$); 3,20 (3H, s, N-CH_3); 3,26 (3H, s, N-CH_3); 4,21 (2H, q, $\underline{CH_2}CH_3$); 6,63 (1H, s, β-H); 6,90 (1H, s, 4-H); 7,20 (1H, s, α-H); E/Z isomer ratio = 2 : 3
Vc	$CDCl_3$	2,23 (3H, s. $COCH_3$); 2,40 (3H, s, $COCH_3$); 3,20 (3H, s, N-CH_3); 3,25 (3H, s, N-CH_3); 6,73 (1H, s, β-H); 6,80 (1H, s, 4-H); 7,36 (1H, s, α-H)
Vd	$CDCl_3$	E-isomer: 3.30 (3H, s, N-CH,); 3,35 (3H, s, N-CH,); 6,70 (1H, s, α-H); 7,32 (1H, d, β-H); 7,40 (1H, d, γ-H); 7,45 (1H, s, 4-H)
Ve	$CDCl_3$	3.18 (3H, s, N-CH_3); 3,22 (3H, s, N-CH_3); 7,45 (1H, s, α-H); 7,46 (1H, d, H_B); 7,53 (1H, s, 4-H) 7,58 (1H, d, β-H); 7,62 (1H, dd, H_A, J_{AB} = 4,0, $J_{A\beta}$ = 0,6)
Vf	$CDCl_3$	1,46 (6H, s, 2 × CH_3); 3,23 (3H, s, N-CH_3); 3,30 (3H, s, N-CH3); 6,31(1H, d, γ-H); 6,73 (1H, s, α-H); 7,36 (1H, s, 4-H); 7,38 (1H, d, β-H, $J_{\beta,\gamma}$ = 16,0)
Vg	$CDCl_3$	1,36 (3H, t, $CH_2\underline{CH_3}$); 3,34 (3H, s, N-CH_3); 3,40 (3H, s, N-CH_3); 4,32 (2H, q, $\underline{CH_2}CH_3$); 7,42 (1H, s, α-H); 7,59 (1H, s, 4-H); 7,64 (1H, s, β-H)
VIa	$(CD_3)_2CO$	1,69 (12H, s, 4 × CH_3); 3,00 (6H, s, $N(CH_3)_2$); 7,60 (1H, s, α-H); 8,18 (1H, s, β-H); 9,56 (1H, br. s., 4-H)
VIb	$CDCl_3$	1,36 (6H, t, 2 × $CH_2\underline{CH_3}$); 2,89 (6H, s, $N(CH_3)_2$); 4,28 (4H, q, 2 × $\underline{CH_2}CH_3$); 7,41 (1H, s, α-H); 7,95 (1H, s, 4-H); 7,97 (1H, s, β-H)
VIc	DMSO-d_6	2,50 (6H, s, $N(CH_3)_2$); 7,35 (1H, s, α-H); 7,45 (1H, s, β-H); 7,70 (1H, s, 4-H);

Salt II is smoothly hydrolyzed in aqueous solution to the dienaminoaldehyde III. Optimal results are achieved by heating for 1 h at 60-70°C. This product is a yellow crystalline compound with a sharp melting point (Table 1). The carbonyl absorption band of the aldehyde group is shifted to the higher frequencies (to 1650 cm^{-1}) due to strong conjugation similar to the lactone carbonyl group (1720 cm^{-1}). The PMR spectrum of this compound (Table 2) has a characteristic aldehyde proton signal, two olefin proton singlets (these three protons have identical intensity 1H) and two dimethylamino group singlets. A special feature of this aldehyde is that it fails to give typical reactions with the Fehling and Tollens reagents and does not form semicarbazones or thiosemicarbazones.

TABLE 3. Bond Lengths and Angles in III

Bond	d, Å	Angle	φ, deg
$O_{(1)}$—$C_{(1)}$	1,392 (4)	$C_{(6)}$—N—$C_{(7)}$	122,4 (3)
$O_{(1)}$—$C_{(4)}$	1,391 (4)	$C_{(6)}$—N—$C_{(8)}$	121,3 (3)
$O_{(2)}$—$C_{(1)}$	1,220 (4)	$C_{(1)}$—$O_{(1)}$—$C_{(4)}$	106,6 (2)
$C_{(3)}$—$C_{(5)}$	1,213 (5)	$O_{(1)}$—$C_{(1)}$—$O_{(2)}$	119,6 (3)
N—$C_{(6)}$	1,306 (4)	$C_{(1)}$—$C_{(2)}$—$C_{(3)}$	105,2 (3)
N—$C_{(7)}$	1,471 (6)	$C_{(2)}$—$C_{(3)}$—$O_{(4)}$	108,5 (3)
N—$C_{(8)}$	1,466 (5)	$C_{(3)}$—$C_{(4)}$—$O_{(1)}$	111,4 (3)
$C_{(1)}$—$C_{(2)}$	1,446 (5)	$O_{(1)}$—$C_{(4)}$—$C_{(5)}$	120,3 (3)
$C_{(2)}$—$C_{(3)}$	1,422 (5)	$C_{(4)}$—$C_{(5)}$—$O_{(3)}$	126,5 (4)
$C_{(2)}$—$C_{(6)}$	1,380 (5)		
$C_{(3)}$—$C_{(4)}$	1,343 (5)		
$C_{(4)}$—$C_{(5)}$	1,430 (5)		

TABLE 4. Atomic Coordinates* (Å×10^4) and Temperature Factors (Å^2×10^3) in the molecule of compound III

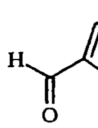
Atom	x	y	z	U^{*2}
$O_{(1)}$	5129 (4)	6163 (2)	7457 (2)	41 (1)
$O_{(2)}$	1829 (4)	5436 (2)	6801 (3)	55 (1)
$O_{(3)}$	9048 (4)	7052 (2)	8805 (3)	66 (1)
N	3606 (4)	5992 (2)	2173 (3)	38 (1)
$C_{(1)}$	3560 (6)	5854 (3)	8379 (4)	39 (1)
$C_{(2)}$	4422 (5)	6104 (2)	4879 (4)	32 (1)
$C_{(3)}$	6557 (6)	6552 (3)	5134 (4)	38 (1)
$C_{(4)}$	6921 (6)	6580 (3)	6643 (4)	39 (1)
$C_{(5)}$	8813 (7)	6993 (3)	7434 (5)	49 (2)
$C_{(6)}$	3154 (6)	5861 (2)	3618 (4)	36 (1)
$C_{(7)}$	5722 (7)	6442 (4)	1640 (5)	49 (2)
$C_{(8)}$	2056 (8)	5636 (4)	987 (5)	56 (2)
$H_{(3)}$	754 (6)	680 (2)	442 (4)	5 (1)
$H_{(5)}$	993 (6)	726 (3)	673 (4)	5 (1)
$H_{(6)}$	17,1 (6)	556 (3)	383 (4)	5 (1)

---

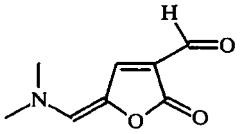
*The coordinates of hydrogen atoms are not reported (data available from the authors).

*2The equivalent isotropic factors were determined as one third of the projection of the orthogonalized $U_{(i,j)}$ tensor.

Analysis of the spectral data does not provide an unequivocal conclusion concerning the structure of dienaminoaldehyde obtained since the same set of signals may correspond to alternative structures IIIA and IIIB:



IIIA



IIIB

An X-ray diffraction structural analysis was carried out on a monocrystal of III grown from solution in ethanol for precise determination of the structure and for study of peculiarities of conjugation in this molecule. A projection of a molecule of III is given in Fig. 1, the major bond lengths and angles are given in Table 3, while the atomic coordinates in the unit cell are given in Table 4.

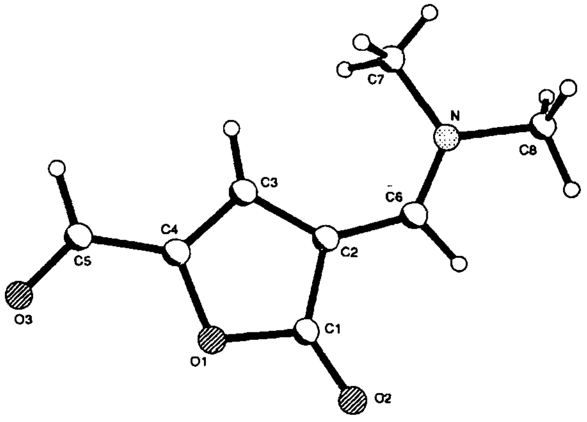
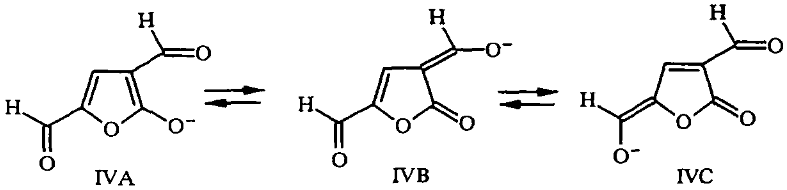


Fig. 1. Projection of three-dimensional model of molecule of aldehyde III.

Figure 1 shows that the hydrolysis product is 3-dimethylaminomethylene-5-formyl-2(3H)-furanone. In the crystal, molecule of III is almost planar, excluding the hydrogen atoms of the methyl groups (the mean extrusion does not exceed 0.027 Å). The oxygen atoms of the aldehyde group and lactone ring are in *cis* arrangement.

Conjugation in the bond system between the aldehyde and dimethylamino groups distorts the interatomic distances. Thus, the $C_{(6)}$—N formal single bond is considerably shortened (to 1.306 Å) and the length of this bond is even less than the C=N bond length in conjugated systems (1.340 Å [8]), The $C_{(2)}$—$C_{(3)}$ single bond is shortened by 0.04 Å relative to the standard value. On the other hand, the $C_{(2)}$—$C_{(6)}$ and $C_{(4)}$—$C_{(5)}$ formal double bonds are much longer than standard ones (by 0.03 and 0.015 Å, respectively). We note that both the C—O bond lengths in the lactone ring are much larger than in the furan ring (by about 0.02 Å), which may be related to the lack of aromaticity in the latter.

Hydrolysis of salt II by aqueous methanol in the presence of KOH (or potassium methylate) proceeds more extensively to give 5-hydroxy-2,4-furandicarbaldehyde, which was isolated as potassium salt IV (Table 1). The anion of salt IV may be represented by the following set of resonance structures:



IVA IVB IVC

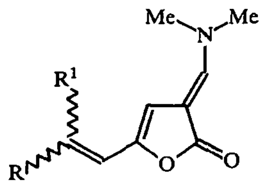
Structures IVB and IVC apparently make a very small contribution to the total resonance of the anion since the lactone ring carbonyl group absorption band is lacking in the IR spectrum (Table 2) and the aldehyde group absorption bands coalescence into a single signal at 1716 cm^{-1}. The PMR signals of the nonequivalent aldehyde protons are shifted upfield (Table 2), indicating significant transfer of electron density from ionized oxygen to the highly polarized C=O double bonds and, as a consequence, increased shielding of the adjacent protons.

Dialdehyde IV itself is a very unstable, hygroscopic compound. Thus, its reactions have been somewhat less extensively studied. Dialdehyde IV reacts with CH-acids similarly to starting salt II and monoaldehyde III. However, similar to III, dialdehyde IV does not give reactions with the Fehling and Tollens reagents typical for aldehydes.

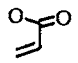
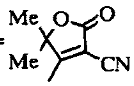
Salt II and aldehyde III react rather readily with CH-acids under conditions of the Knoevenagel reaction (ethanol as the solvent and several drops of triethylamine as the catalyst or even without catalyst in the case of strong CH-acids) to give the same Knoevenagel reaction products. Weak CH-acids such as diethyl malonate, acetylacetone, and nitromethane form only products V even when these CH-acids are present in excess.

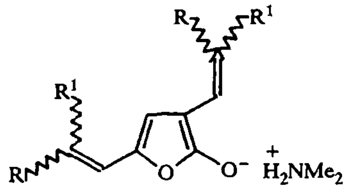
The structures of Va-Vg were confirmed by elemental analysis and spectral data (Tables 1 and 2).

Stronger CH-acids such as Meldrum's acid and malonodinitrile mainly give condensation products VI (1:2 addition). Rigorous control of the reagent proportions and reaction time is required to obtain products V and even

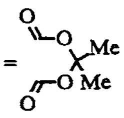


Va–g

a R = R^1 = COOEt; b R = COOEt, R^1 = COMe;
c R = R^1 = COMe; d R = H, R^1 = NO_2;
e R + R^1 =  f R = H, R^1 = 
g R = COOEt, R^1 = CN



VIa–c

a R + R^1 = 
b R = COOEt, R^1 = CN; c R = R^1 = CN

when these conditions are maintained, products V must be purified repeatedly to remove products of more extensive condensation such as by column chromatography on silica gel. Pure products VI are always obtained when a two-fold or larger excess of strong CH-acid is used.

The structure of VI holds interest since the elemental analysis and spectral data given in Tables 1 and 2 indicate that these compounds are dimethylammonium salts of 3,5-disubstituted 2-hydroxyfuran, just as how dialdehyde IV described above is the potassium salt of disubstituted 2-hydroxyfuran.

Attempts were made to grow monocrystals of III and VI for an X-ray diffraction crystallographic study to obtain more information on the structure of the hydroxyfuran anion. We were able to grow monocrystals of VIa containing crystallization water and ethanol ($VIa \cdot 2H_2O \cdot 0.5C_2H_5OH$) from 50% aqueous ethanol. Water and ethanol in the crystal may account for its low stability under conditions of the X-ray diffraction measurements (the crystal rather rapidly decomposes upon irradiation, leading to imprecise data). Nevertheless, in light of the unusual nature of products VI, we submit these results.

A projection of three-dimensional model of VIa is given in Fig. 2. Hydrogen atoms of the ammonium ion methyl groups are not shown. The major bond lengths are given in Table 5, while the coordinates of one of the independent molecules are given in Table 6. Figure 2 shows that VIa is indeed dimethylammonium salt of substituted hydroxyfuran. The dimethylammonium cation in the crystal is situated in immediate vicinity of the ionized oxygen atom $O_{(2)}$ and is bound to it by a linear hydrogen bond $O_{(2)} \cdots H_{(1)}—N$ such that $H_{n(1)}$ and N are within the plane of the pyran ring.

The ionized oxygen atom, $O_{(2)}$ acts as a strong electron donor, causing significant changes in the bond lengths in the $O_{(2)}—C_{(1)}—C_{(2)}—C_{(3)}—C_{(4)}—C_{(5)}—C_{(6)}$ conjugated system and then in the dioxanedione ring carbonyl groups. The transfer of electron density is so great that it leads to realternation of the bonds in the conjugation system: the $C_{(1)}—C_{(2)}$, $C_{(3)}—C_{(4)}$, and $C_{(5)}—C_{(6)}$ formal double bonds are longer than the $C_{(2)}—C_{(3)}$ and $C_{(4)}—C_{(5)}$ formal single bonds. (We have observed a similar effect in a nonionized molecule of N-[5-(2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)methyl-2-furyl]iminotriphenylphosphorane [9], where the iminophosphorane group nitrogen atom acts as a strong electron donor). The $O_{(2)}—C_{(1)}$ bond length is intermediate between the standard values for the C—O single bond (1.37 Å [10]) and C=O double bond (1.20 Å [9]).

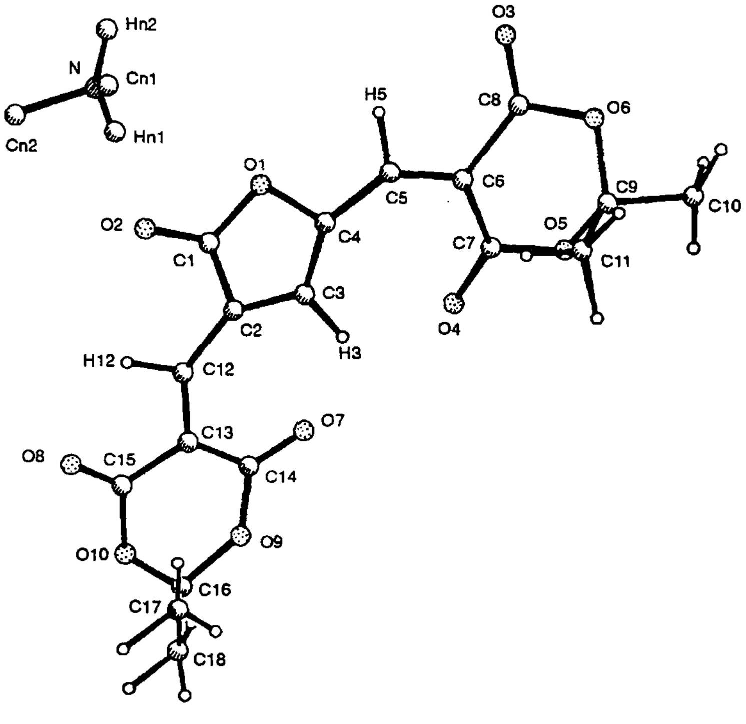


Fig. 2. Projection of three-dimensional model of dimethylammonium salt VIa.

The second dioxane fragment (in the β-position of the furan ring) is excluded from conjugation with the furan ring. The $C_{(2)}$—$C_{(12)}$ and $C_{(12)}$—$C_{(13)}$ bonds have normal alternation. The slight extrusion of the $C_{(12)}$—$C_{(13)}\cdots C_{(15)}$ dioxanedione fragment plane from the furan ring plane and folding at the $C_{(2)}$—$C_{(12)}$ bond, which is a classical type of deformation in sterically strained conjugated systems [11], may be seen as a result of exclusion from conjugation.

A nonclassical type of deformation of conjugated systems is observed in exocycles $H_{(3)}$—$C_{(3)}$—$C_{(4)}$—$C_{(5)}$—$C_{(6)}$—$C_{(7)}$—$O_{(4)}$ and $H_{(3)}$—$C_{(3)}$—$C_{(2)}$—$C_{(12)}$—$C_{(13)}$—$C_{(14)}$—$O_{(7)}$, namely, distortion of the bond anges at the sp^2-hybridized $C_{(5)}$ and $C_{(12)}$ atoms to 135°. The plane of the dioxanedione fragment traversing $O_{(6)}$, $C_{(8)}$, $C_{(6)}$, $C_{(7)}$, and $O_{(5)}$ virtually coincides with the furan ring plane, i.e., there is virtually no folding at the exocyclic $C_{(5)}$—$C_{(6)}$ and $C_{(6)}$—$C_{(7)}$ bonds. Such nonclassical bond angle deformations have been observed in sterically strained furfurylidenedioxanedione molecules [9, 12, 13].

The $H_{(3)}$ sphere is so distorted due to the $H_{(3)}\cdots O_{(4)}$ and $H_{(3)}\cdots O_{(7)}$ contacts (the $H_{(3)}\cdots O_{(4)}$ and $H_{(3)}\cdots O_{(7)}$ interatomic distances are 2.55 and 2.79 Å, respectively) that the chemical shift of this proton in the PMR spectrum is shifted downfield to 9.56 ppm (Table 2).

Products V and VI differ strongly not only in their color intensity but also in the shape of the absorption band in their electron spectrum. Nonionized products V have broad, smooth, and symmetrical bands in the visible range, while salts VI have narrow and asymmetric bands. The bands of salts VI at longest wavelength are shifted more towards the red region of spectrum. The position of the long-wavelength absorption bands of salts VI probably results from the occurrence of cross-conjugation systems in their anions, which, according to Kipriyanov [14],

TABLE 5. Bond Lengths and Angles in the molecule of compound VIa

Bond	d, Å	Bond angle	φ, deg
$O_{(1)}$—$C_{(1)}$	1,34 (2)	$Cn_{(1)}$—N—$Cn_{(2)}$	111,2 (11)
$O_{(1)}$—$C_{(4)}$	1,47 (1)	$O_{(2)}$—$Hn_{(1)}$—N	179,9 (10)
$O_{(2)}$—$C_{(1)}$	1,25 (2)	$C_{(1)}$—$O_{(1)}$—$C_{(4)}$	101,4 (10)
$C_{(1)}$—$C_{(2)}$	1,42 (2)	$O_{(1)}$—$C_{(1)}$—$O_{(2)}$	128,8 (15)
$C_{(2)}$—$C_{(3)}$	1,38 (2)	$O_{(1)}$—$C_{(1)}$—$C_{(2)}$	115,0 (11)
$C_{(3)}$—$C_{(4)}$	1,38 (2)	$C_{(1)}$—$C_{(2)}$—$C_{(3)}$	104,7 (13)
$C_{(4)}$—$C_{(5)}$	1,42 (2)	$C_{(2)}$—$C_{(3)}$—$C_{(4)}$	108,6 (11)
$C_{(5)}$—$C_{(6)}$	1,36 (2)	$C_{(3)}$—$C_{(4)}$—$O_{(1)}$	110,2 (11)
$C_{(6)}$—$C_{(7)}$	1,47 (2)	$C_{(3)}$—$C_{(4)}$—$C_{(5)}$	138,1 (11)
$C_{(7)}$—$O_{(4)}$	1,22 (2)	$C_{(4)}$—$C_{(5)}$—$C_{(6)}$	135,2 (13)
$C_{(6)}$—$C_{(8)}$	1,46 (2)	$C_{(5)}$—$C_{(6)}$—$C_{(7)}$	124,6 (13)
$O_{(3)}$—$C_{(8)}$	1,18 (2)	$C_{(5)}$—$C_{(6)}$—$C_{(8)}$	115,5 (11)
$O_{(5)}$—$C_{(7)}$	1,37 (1)	$C_{(7)}$—$C_{(6)}$—$C_{(8)}$	119,8 (11)
$O_{(6)}$—$C_{(8)}$	1,39 (1)	$O_{(3)}$—$C_{(8)}$—$C_{(6)}$	126,9 (11)
$O_{(5)}$—$C_{(9)}$	1,43 (2)	$O_{(3)}$—$C_{(8)}$—$O_{(6)}$	118,5 (12)
$O_{(6)}$—$C_{(9)}$	1,41 (1)	$O_{(4)}$—$C_{(7)}$—$C_{(6)}$	126,0 (11)
$C_{(9)}$—$C_{(10)}$	1,51 (2)	$O_{(3)}$—$C_{(8)}$—$O_{(6)}$	117,5 (10)
$C_{(9)}$—$C_{(11)}$	1,50 (2)	$O_{(5)}$—$C_{(9)}$—$O_{(6)}$	109,8 (9)
$C_{(2)}$—$C_{(12)}$	1,42 (2)	$C_{(10)}$—$C_{(9)}$—$C_{(11)}$	112,3 (11)
$C_{(12)}$—$C_{(13)}$	1,37 (2)	$C_{(2)}$—$C_{(12)}$—$C_{(13)}$	133,6 (12)
$C_{(13)}$—$C_{(14)}$	1,42 (2)	$C_{(12)}$—$C_{(13)}$—$C_{(14)}$	125,8 (12)
$C_{(13)}$—$C_{(15)}$	1,48 (2)	$C_{(12)}$—$C_{(13)}$—$C_{(15)}$	113,8 (11)
$O_{(7)}$—$C_{(14)}$	1,19 (2)	$C_{(14)}$—$C_{(13)}$—$C_{(15)}$	120,2 (12)
$O_{(8)}$—$C_{(15)}$	1,20 (2)	$O_{(7)}$—$C_{(14)}$—$C_{(13)}$	127,1 (12)
$O_{(9)}$—$C_{(14)}$	1,35 (2)	$O_{(8)}$—$C_{(15)}$—$C_{(13)}$	127,6 (13)
$O_{(10)}$—$C_{(15)}$	1,37 (2)	$O_{(9)}$—$C_{(16)}$—$O_{(10)}$	111,0 (11)
$O_{(9)}$—$C_{(16)}$	1,42 (2)	$O_{(9)}$—$C_{(16)}$—$C_{(17)}$	110,0 (11)
$O_{(10)}$—$C_{(16)}$	1,42 (2)	$O_{(10)}$—$C_{(16)}$—$C_{(17)}$	109,6 (11)
$C_{(16)}$—$C_{(17)}$	1,51 (2)	$C_{(17)}$—$C_{(16)}$—$C_{(18)}$	112,5 (12)
$C_{(16)}$—$C_{(18)}$	1,52 (2)	$C_{(15)}$—$O_{(10)}$—$C_{(16)}$	118,1 (10)

TABLE 6. Atomic Coordinates ($\text{Å}\times10^4$) and Temperature Factors ($\text{Å}^2\times10^3$) in Molecule of VIa

Atom	*x*	*y*	*z*	*U*[*2]
$O_{(1)}$	7197 (7)	1028 (8)	-1511 (3)	74 (4)
$O_{(2)}$	6078 (9)	795 (11)	-1004 (3)	115 (6)
$O_{(3)}$	8936 (7)	1610 (9)	-2740 (3)	68 (4)
$O_{(4)}$	10996 (7)	1632 (9)	-1575 (3)	71 (4)
$O_{(5)}$	11786 (6)	2224 (7)	-2144 (2)	56 (4)
$O_{(6)}$	10746 (7)	2217 (7)	-2716 (2)	59 (4)
$O_{(7)}$	10401 (6)	1107 (8)	-527 (2)	58 (4)
$O_{(8)}$	7313 (7)	978 (9)	291 (3)	73 (4)
$O_{(9)}$	10539 (6)	1657 (8)	80 (3)	52 (4)
$O_{(10)}$	9007 (7)	1662 (8)	492 (3)	56 (4)
$O_{(2)}$	-830 (2)	-2508 (2)	152 (2)	56 (1)
$C_{(1)}$	7056 (10)	950 (14)	-1123 (5)	51 (7)
$C_{(2)}$	8055 (10)	1076 (11)	-902 (4)	47 (6)
$C_{(3)}$	8890 (10)	1239 (11)	-1177 (4)	41 (5)
$C_{(4)}$	8417 (10)	1260 (11)	-1542 (5)	46 (6)
$C_{(5)}$	8772 (10)	1455 (11)	-1934 (4)	48 (6)
$C_{(6)}$	9770 (10)	1732 (11)	-2116 (4)	44 (5)
$C_{(7)}$	10847 (10)	1852 (11)	-1919 (4)	55 (6)
$C_{(8)}$	9726 (10)	1845 (12)	-2540 (4)	54 (6)
$C_{(9)}$	11636 (10)	2858 (12)	-2499 (4)	48 (5)
$C_{(10)}$	12692 (12)	2809 (14)	-2725 (4)	78 (7)
$C_{(11)}$	11467 (11)	4139 (13)	-2419 (4)	63 (6)
$C_{(12)}$	7981 (10)	1090 (11)	-488 (4)	44 (6)
$C_{(13)}$	8756 (10)	1266 (11)	-194 (4)	39 (5)
$C_{(14)}$	9922 (10)	1347 (12)	-242 (4)	51 (6)
$C_{(15)}$	8269 (12)	1265 (12)	201 (5)	54 (7)
$C_{(16)}$	10073 (11)	2285 (15)	384 (4)	56 (6)
$C_{(17)}$	9986 (11)	3562 (14)	255 (5)	74 (7)
$C_{(18)}$	10797 (11)	2266 (12)	746 (4)	68 (6)
N	4143 (8)	611 (10)	-1457 (3)	71 (5)
$Cn_{(1)}$	4225 (13)	1808 (12)	-1660 (4)	98 (7)
$Cn_{(2)}$	3265 (12)	485 (15)	-1134 (4)	104 (8)
$H_{(3)}$	982	145	-111	5
$H_{(5)}$	806	136	-213	5
$H_{(12)}$	708	111	-39	5
$Hn_{(1)}$	473	67	-133	5
$Hn_{(2)}$	383	-12	-162	5

---

[*] The coordinates of the methyl group hydrogen atoms are not presented but may be obtained from the authors.

[*2] The equivalent isotropic factors were determined as one third of the projection of the orthogonalized $U_{(i,j)}$ tensor.

leads to separation of absorption bands corresponding to the absorption of the "mother dyes." In the present case, the separation is so great that the short-wavelength band undergoes a hypsochromic shift to the ultraviolet region, in which it is masked by other high-energy transition bands.

EXPERIMENTAL

The IR spectra for vaseline mulls were taken on an IR-71 spectrometer. The PMR spectra were taken on a Tesla BS-467A spectrometer at 60 MHz and on Bruker WM-250 spectrometer at 250 MHz. The electronic absorption spectra were taken on a Specord M-40 spectrophotometer for solutions in ethanol and water.

Silica gel (40/100 mesh) was used for the chromatographic separation and purification of products. The purity of products and reaction course were monitored by thin-layer chromatography on Silufol UV-254 plates using 1:1 acetone—chloroform as the eluent.

X-ray diffraction study of III and VIb. Light yellow monoclinic crystals of III grown from ethanol solution have the following unit cell parameters: $a = 6.420(2)$, $b = 14.178(5)$, $c = 8.769(3)$ Å, $\gamma = 100.28(2)°$, $V = 785.4(0.8)$ Å^3, space group P2(1)/b, $Z = 4$. The unit cell parameters and intensities of 734 independent reflections with $I > 3\sigma(I)$ were obtained on a Syntex P1 automatic diffractometer using MoKα radiation and θ/2θ scanning. The structure was solved by the direct method using the SHELXTL program package [15] and refined anisotropically for nonhydrogen atoms and isotropically for hydrogen atoms to $R = 0.043$ and $R_w = 0.044$.

Violet monoclinic crystals of VIa grown from 50% aq. ethanol have the following unit cell parameters: $a = 12.215(2)$, $b = 11.122$, $c = 0.0*(9)$ Å, $\gamma = 99.36(1)°$, $V = 4593.6(2.9)$ Å^3, space group P2$_1$/n, $Z = 8$. The unit cell fparameters and intensities of 2278 independent reflections with $I > 3\sigma(I)$ were obtained on a Syntex P1 automatic diffractometer using MoKα radiation and θ/2θ scanning. The structure was solved by the direct method using the SHELXTL program package [15] and refined anisotropically for nonhydrogen atoms and isotropically for hydrogen atoms to $R = 0.081$ and $R_w = 0.079$.

(3-Dimethylaminomethylen-2-oxo-5(3H)-furanyl)methylenimmonium perchlorate (II). 29.14 ml (0.31 mole) of $POCl_3$ were added under vigorous stirring to 47.9 ml (0.62 mole) of N,N-dimethylformamide cooled to 0°C. The mixture was stirred for 0.5 h at room temperature and recooled to 0°C. Then 10.59 ml (0.15 mole) of 2(5H)-furanone were slowly added dropwise. The reaction mixture was maintained for 2 h at 60-70°C and cooled to 0°C. Then, 150 ml of cold ethanol were added, the mixture was thoroughly stirred and 20 ml of 70% perchloric acid were added dropwise. The light yellow crystalline precipitate was filtered off, washed with cold ethanol, and dried in the absence of moisture.

3-Dimethylaminomethylene-5-formyl-2(3H)-furanone (III). A solution of 2 g (6.7 mmoles) of salt II in 70 ml of water was stirred at 60-70°C for 1 h, cooled, and extracted with three 25 ml portions of chloroform. The combined abstract was dried over Na_2SO_4. The solvent was evaporated in vacuum and the residue was recrystallized from ethanol.

Potassium 3,5-diformyl-2-furanolate (IV). To solution of 2 g (6.7 mmoles) of salt II in 100 ml of 50% aq. methanol 3.2 g (13.4 mmoles) of KOH were added. The mixture was heated at reflux for 4-5 h. After cooling, the solvent was evaporated at room temperature in vacuum and the solid residue was recrystallized from methanol.

3-(3-Dimethylaminomethylene-5-(2,2-diethoxycarbonylvinyl)-2(3H)-furanone (Va). A. To solution of 2.95 g (10 mmoles) of salt II in 100 ml of ethanol 1.6 g (10 mmoles) of diethylmalonate and two or three drops of trimethylamine were added. The reaction mixture was heated at 60°C for 1-2 h, monitoring consumption of the starting compound by thin-layer chromatography. The solvent was evaporated to 20-30 ml and the solution was cooled. The crystalline precipitate was filtered off and recrystallized from ethanol.

B. To solution of 1.67 g (10 mmoles) of aldehyde III in 30 ml of ethanol 1.6 g (10 mmoles) of diethyl malonate and two or three drops of triethylamine were added. The reaction was then carried out as described in procedure A.

Products Vb-Vg were obtained analogously.

Dimethylammonium 3,5-di(2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidenemethyl)-2-furanolate (VIa). A. To a solution of 5.9 g (0.02 mole) of salt II in 60 ml of ethanol 5.76 g (0.04 mole) of Meldrum's acid and two or three drops of triethylamine were added. The reaction mixture was maintained at room temperature and violet crystals began to precipitate out after 3-4 h. The mixture was cooled. The crystalline precipitate was filtered off and recrystallized from ethanol.

B. To a solution of 1.67 g (10 mmoles) of aldehyde III in 40 ml of ethanol 2.88 g (20 mmoles) of Meldrum's acid and two or three drops of triethylamine were added. The mixture was moderately heated until all the Meldrum's acid dissolved. The reaction was then carried out as described for procedure A.

Products Vb and Vc were synthesized analogously.

REFERENCES

1. N. D. Kozhina, G. D. Krapivin, V. E. Zavodnik, T. Gratsza, D. Vegh, L. A. Chernousenko, and L. A. Badovskaya, Khim. Geterotsikl. Soedin., No. 1, 135 (1995).
2. L. N. Sorotskaya, L. A. Badovskaya, T. Ya. Kaklyugina, L. I. Belen'kii, A. V. Ignatenko, A. Krutoshikova, and L. A. Pantseva, Zh. Org. Khim., **25**, 175 (1989).
3. G. F. Muzychenko, V. G. Glukhovtsev, L. A. Badovskaya, N. D. Kozhina, A. V. Ignatenko, O. B. Kravchenko, and G. I. Nikitin, Zh. Org. Khim., **17**, 481 (1981).
4. E. Yoshii, N. Koizumi, and E. Kitatsuji, Heterocycles, **4**, 1663 (1976).
5. A. Vilsmeier and A. Haak, Ber., **60**, 121 (1927).
6. M. A. Kira, Z. M. Nofal, and K. Z. Gadolla, Tetrahedron Lett., No. 48, 4215 (1970).
7. K. Kiyomi and M. Ichino, J. Org. Chem., **37**, 284 (1972).
8. A. I. Kitaigorodskii, P. M. Zorkii, and V. K. Bel'skii, Structure of Organic Compounds (Structural Data 1971-1973) [in Russian], Nauka, Moscow (1982).
9. G. D. Krapivin, N. I. Val'ter, V. E. Zavodnik, T. Ya. Kaklyugina, and V. G. Kul'nevich, Khim. Geterotsikl. Soedin., No. 3, 335 (1994).
10. A. Gordon and R. Ford, Chemist's Handbook [Russian translation], Mir, Moscow (1976), p. 129.
11. K. A. Coulson, Theoretical Organic Chemistry. Reports Presented at the Kekule Symposium Organized by the Chemical Society, London, September, 1958 [Russian translation], Moscow (1963), p. 66.
12. G. D. Krapivin, N. I. Val'ter, V. E. Zavodnik, V. E. Bel'skii, and V. G. Kul'nevich, Khim. Geterotsikl. Soedin., No. 11, 1453 (1988).
13. G. D. Krapivin, N. I. Val'ter, V. E. Zavodnik, D. Vegh, L. Fishera, and V. G. Kul'nevich, Khim. Geterotsikl. Soedin., No. 7, 899 (1995).
14. A. I. Kiprianov, Usp. Khim., **11**, 1283 (1971).
15. G. M. Sheldrick, Computational Crystallography, Oxford Univ. Press, New York—Oxford (1982), p. 506.