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2,2-DIMETHYL-5-(5-R-FURFURYLIDENE)-1,3-dioxane-4,6 DIONES

7*. SYNTHESIS, STRUCTURE, AND PROPERTIES OF 2,2-DIMETHYL-5-(3-FURFURYLDIENE AND 3-THIENYLIDENE)-1,3-DIOXANE-4,6-DIONES

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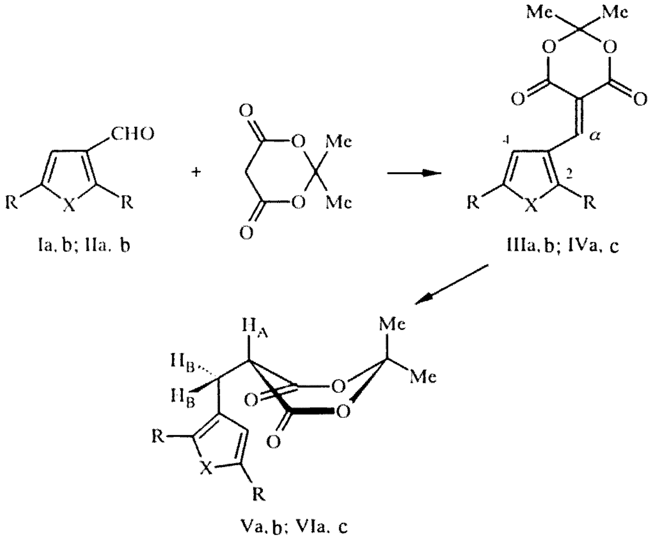
The corresponding 3-furfurylidene(thienylidene)-dioxanediones were obtained by the reaction of 2,5-R,R-furan(thiophen)-3-carbaldehydes with Meldrum's acid. It was shown by x-ray crystallographic analysis that they have the s-trans disposition at the $C_{(2)}=C_{(3)}$ *bond of the five-membered heterocycle and an exocyclic multiple bond. The character of the conjunction in their molecules was considered in the light of data of x-ray crystallographic analysis, electronic spectra, and NMR. The corresponding 3-[furfuryl(thienyl)]dioxanediones were obtained by the selective ionic hydrogenation of the exocyclic double bond.*

We showed previously that 2-furan and 2-thiophenecarbaldehydes react under mild conditions with 2,2-dimethyl-1,3-dioxane-4,6-dione (Meldrum's acid) and the resulting 2-furfuryldiene derivatives have the s-cis and the 2-thienylidene derivatives the s-trans conformation [1-5].

Processing from this it seemed of interest to synthesize the analogous derivatives of 3-furan- (Ia, b) and 3-thiophenecarbaldehydes (IIa, b), viz. the furfuryldiene-(IIIa, b) and thienyldienedioxanediones (IVa, c), and to study their stereochemistry.



I, III, V X = O; II, IV, VI X = S; I — VI a R = H, b R = Me, c R = Br

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*For part 6 see [1].

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TABLE 1. Characteristics of the Compounds Synthesized

Compound	Empirical formula	Found, % / Calculated, %		mp	UV spectrum,* λ_{max}, nm (lg ε)	IR spectrum, ν,cm^{-1}	Yield, %
		C	H				
IIIa	$C_{11}H_{10}O_5$	59.6 59,5	4.6 4,5	128...129	327 (4,14)	1788, 1774, 1740	93
IIIb	$C_{13}H_{14}O_5$	62.2 62,4	5.8 5.6	136...137	367 (4,58)	1720, 1710	80
IVa	$C_{11}H_{10}O_4S$	55.5 55,5	4.4 4,2	106...107	335 (4,22)	1723	95
IVc	$C_{11}H_8Br_2O_4S$	33.4 33,4	2.1 2,0	140...141	355 (3,80)	1740, 1724	70
Va	$C_{11}H_{12}O_5$	59.1 58,9	5.1 5,4	80...82	269 (3,48)	1760, 1745	85
Vb	$C_{13}H_{16}O_5$	61.7 61,9	6.5 6,4	81...82	275 (3,63)	1760, 1720	70
VIa	$C_{11}H_{12}O_4S$	55.2 55,0	5.2 5,0	83...84	271 (3,70)	1788, 1743	90
VIb	$C_{11}H_{10}Br_2O_4S$	33.3 33.2	2.7 2,5	104...105	262 (4,19)	1788, 1745	64

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*The only values given are of the long wave absorption characterizing the π,π^* transition of the conjugation system of the molecule.

TABLE 2. Data of PMR Spectra of Compounds (IIIa, b) and (IVa, c)

Compound	Chemical shifts in acetone-D_6, ppm, coupling constant (J), Hz				
	$(CH_3)_2C$ (6H, s)	α-H ($J_{\alpha4}$)	heteryl		
			2-H (J_{24})	4-H (J_{45})	5-H (J_{52})
IIIa	1,67	8.22 d $J_{\alpha5}$ = 0.6	8.62 d.d (0.8)	7.25 d.d (2.0)	7.60 d.d.d (1.6)
IIIb*	1,63	8.06 d (0.6)		6.95 d	
IVa	1,68	8.32 d.d $J_{\alpha2}$ = 1.0, $J_{\alpha5}$ = 0.8	8.82 d.d.d (1.2)	7.93 d.d (5.4)	7.53 d.d (3.0)
IVc	1,69	8.03 d (0.5)		8.13 d	

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*Other signals: 2.48 (3H, s, 2-CH_3), 2.22 (3H, s, 5-CH_3), J_{CH34} = 1.0.

As previously, the Knoevenagel reaction was used to obtain compounds (IIIa, b) and (IVa, c). The yields of the desired products were 70-95% (Table 1).

Analysis of the PMR spectra of compounds (IIIa, b) and (IVa, c) (Table 2) did not give an unequivocal answer to the problem of the conformation of the molecules although it was obvious that only the s-trans form may be practicable for the 2,5-dimethyl and 2,5-dibromo derivatives of this series. Consequently we carried out an x-ray structural investigation of the 2,5-unsubstituted (IIIa) and the 2,5-dimethyl substituted (IIIb) furfuryldienedioxanediones (see Tables 3 and 4 and Figs. 1 and 2).

Projections of spatial models of compounds (IIIa) and (IIIb) are represented in Figs. 1 and 2. As is seen, both molecules have the s-trans mutual disposition of the $C_{(\alpha)} = C_{(\beta)}$ bond of the furan ring and the exocyclic multiple bond with an intramolecular hydrogen bond between the $H_{(11)}$ and $O_{(4)}$ atoms. The parameters of the hydrogen bond for the molecules of (IIIa) and (IIIb) (in parentheses) were respectively: interatomic distances $H_{(11)}\ldots O_{(4)}$ and $C_{(11)}\ldots O_{(4)}$ equal to 2.219 and 2.895 (2.365 and 2.943 Å), valence angles $C_{(11)}-H_{(11)}\ldots O_{(4)}$ and $H_{(11)}\ldots O_{(4)}-C_{(3)}$ equal to 124.9 and 123.3 (126.4 and 127.7°). The internal stresses in the seven-membered ring containing the hydrogen bond are displayed mainly in an increase in the $C_{(2)}C_{(7)}C_{(8)}$ valence angle to 134.5 (134.2°) and an inversion of the furan ring from the $C_{(1)}C_{(2)}C_{(3)}$ plane by 1.3 (12.4°).

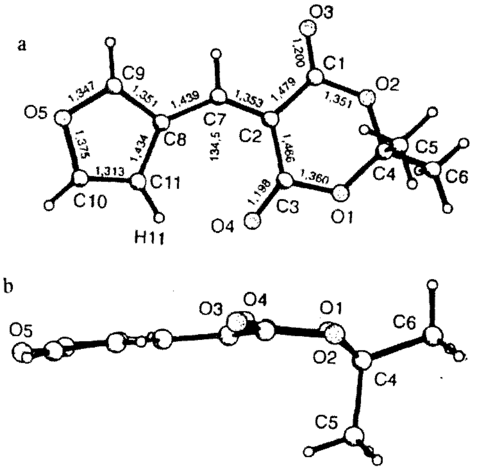

Fig. 1. Projections of spatial models of compound (IIIa) onto a) the plane of the "base of the bath" and b) the plane of symmetry of the dioxanedione ring.

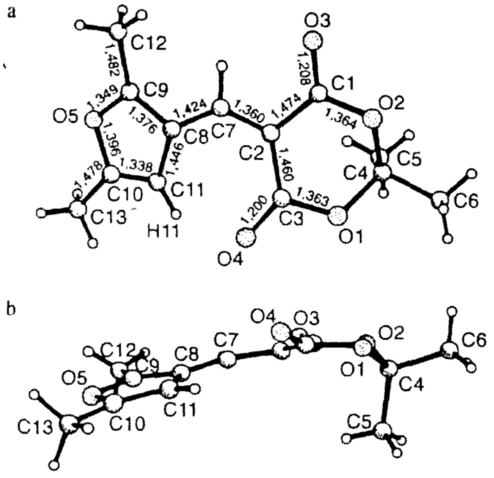

Fig. 2. Projections of spatial models of compound (IIIb) onto a) the plane of the "base of the bath" and b) the plane of symmetry of the dioxanedione ring.

The dioxanedione ring in the crystals of both molecules has the conformation of a distorted bath in which the angles between the planes of the "base of the bath" ($O_{(1)}O_{(2)}C_{(1)}C_{(3)}$) and the "sides of the bath" ($C_{(1)}C_{(2)}C_{(3)}$ and $O_{(1)}O_{(2)}C_{(4)}$) are equal to 9.2 and 40.5 (15.4 and 41.0°) respectively.

Seemingly a rapid inversion of the bath-like conformation of the dioxanedione ring occurs in solutions of compounds (III) and (IV), as only one singlet signal from the six protons of the methylene groups is observed even at $-80°C$ in the PMR spectra of these compounds. This was reported previously for the 2-furfurylidene derivatives.

The conjugation in molecules (IIIa, b) is displayed in changes to the interatomic distances but the normal alternation of formally double and single bonds is retained in the bond system from the furan ring oxygen $O_{(5)}$ through the atoms $C_{(9)}$, $C_{(8)}$, $C_{(7)}$, and $C_{(2)}$ to a carbonyl group of the dioxanedione ring. The multiple bond $C_{(10)}{=}C_{(11)}$ does not participate in conjugation as indicated by the interatomic distances $O_{(5)}-C_{(10)}$ and $C_{(8)}-C_{(11)}$, which are extremely large for a furan ring.

TABLE 3. Coordinates of Atoms (C, O × 10^4; H × 10^3) of the Compound (IIIa) Molecule, and Temperature Factors (× 10^3)

Atom	x	y	z	U
$O_{(1)}$	5060(2)	5262(1)	2247(1)	57(1)
$O_{(2)}$	7677(2)	6194(1)	3007(1)	63(1)
$O_{(3)}$	7426(2)	6750(1)	5073(1)	69(1)
$O_{(4)}$	2155(2)	4886(1)	3561(2)	67(1)
$O_{(5)}$	1178(3)	7027(1)	8490(2)	71(1)
$C_{(1)}$	6528(3)	5865(1)	1783(2)	58(1)
$C_{(2)}$	8282(5)	5574(2)	871(4)	86(1)
$C_{(3)}$	5236(6)	6377(2)	1009(3)	79(1)
$C_{(4)}$	6520(3)	6336(1)	4220(2)	51(1)
$C_{(5)}$	3706(3)	5330(1)	3394(2)	48(1)
$C_{(6)}$	4327(3)	5933(1)	4389(2)	43(1)
$C_{(7)}$	2843(3)	6038(1)	5446(2)	46(1)
$C_{(8)}$	2779(3)	6538(1)	6614(2)	46(1)
$C_{(9)}$	951(4)	6518(1)	7460(2)	60(1)
$C_{(10)}$	4254(4)	7117(1)	7181(2)	59(1)
$C_{(11)}$	3251(4)	7387(1)	8281(3)	62(1)
$H_{(21)}$	903(5)	523(2)	148(3)	13(1)
$H_{(22)}$	754(4)	535(1)	3(3)	10(1)
$H_{(23)}$	940(4)	596(1)	56(3)	10(1)
$H_{(31)}$	440(4)	612(1)	16(2)	9(1)
$H_{(32)}$	615(4)	677(1)	68(3)	9(1)
$H_{(33)}$	406(4)	654(1)	160(3)	8(1)
$H_{(7)}$	148(3)	571(1)	541(2)	5(1)
$H_{(9)}$	-46(3)	623(1)	743(2)	7(1)
$H_{(10)}$	564(3)	727(1)	681(2)	6(1)
$H_{(11)}$	362(4)	772(1)	894(3)	8(1)

The fairly significant and reliable increase (~0.025 Å) in the length of the formally multiple bonds of the furan ring on going from an unsubstituted furan to the 2,5-dimethyl derivative must also be noted. This is possibly linked with the transfer of electron density from the methyl groups and its concentration in these particular bonds.

The electronic spectra of compounds (III) and (IV) (see Table 1) have the same broad and symmetrical absorption bands, possessing positive solvatochromicity, as the spectra of their 2-furfurylidene analogs. It is interesting to note the closeness of the position of the absorption maxima for the corresponding pairs of 2- and 3-furfurylidene derivatives. This, it would seem, is contradicted by the x-ray structural data on the nonparticipation in conjugation of one of the formally multiple bonds of compounds (I)-(IV). However if one takes into account that excitation of compounds (III) and (IV) is linked with the separation of charges, then possibly in the excited state the isolated multiple bond participates in conjugation through the partially positive oxygen atom of the furan ring.

Conjugation in the molecules of compounds (III) and (IV) must *a priori* activate the halogen atom in position 2 (but not 5) of the five-membered heterocycle. However all attempts to replace either of the bromine atoms in the dibromide (IV) by nucleophiles proved to be unsuccessful.

Soft nucleophiles add reversibly at the carbon atom of the exocyclic multiple bond, confirming the existence of properties of electroneutral Lewis π-acids [2] for the series of compounds being considered. This enables the selective ionic hydrogenation of this bond in dioxanediones (III) and (IV), using the sodium borohydride–hydrochloric acid system described previously [4], by which compounds (V) and (VI) (Table 1) were obtained.

The color of the reaction mixture disappears on hydrogenation, and is a visual indicator of the end of the reaction. Absorption bands for carbonyl groups were observed in the IR spectra of compounds (V) and (VI) at a higher frequency compared with the position of the analogous bands in the spectra of the initial compounds (III) and (IV) (see Table 1). A similar shift was also observed in the case of the 2-furfuryl(thienyl) derivatives [4].

The PMR spectra of compounds (V)-(VI) (Table 5) are analogous to the spectra of the corresponding 2-furfuryl(thienyl)dioxanediones [4] and have a characteristic set of signals. There are two singlet anisochronic signals for the methyl group protons of the isopropylidene unit, a multiplet signal for the AB_2 system of the $CH-CH_2$ group protons and also signals for the protons of the five-membered heterocycle and its substituents. Consequently, the 3-furfuryl(thienyl)dioxanediones,

TABLE 4. Coordinates of Atoms (C, × 10^4; H × 10^3) of the Compound (IIIb) Molecule, and Temperature Factors (× 10^3)

Atom	x	y	z	U
$O_{(1)}$	8428(2)	5709(2)	7836(1)	54(1)
$O_{(2)}$	7193(2)	4114(2)	9197(1)	53(1)
$O_{(3)}$	6975(4)	1297(3)	8907(2)	70(1)
$O_{(4)}$	9680(3)	4497(2)	6299(2)	58(1)
$O_{(5)}$	7426(2)	-1095(2)	3550(2)	43(1)
$C_{(1)}$	7271(4)	2583(3)	8490(2)	47(1)
$C_{(2)}$	7788(3)	2652(3)	7290(2)	40(1)
$C_{(3)}$	8671(4)	4290(3)	7059(2)	43(1)
$C_{(4)}$	6993(3)	5596(3)	8638(2)	49(1)
$C_{(5)}$	4952(4)	5479(4)	7994(2)	65(1)
$C_{(6)}$	7540(5)	7138(4)	9602(3)	73(1)
$C_{(7)}$	7513(3)	1151(3)	6508(2)	40(1)
$C_{(8)}$	7671(3)	698(3)	5277(2)	37(1)
$C_{(9)}$	7309(3)	-986(3)	4721(2)	39(1)
$C_{(10)}$	7873(3)	565(3)	3331(2)	42(1)
$C_{(11)}$	8039(3)	1673(3)	4352(2)	40(1)
$C_{(12)}$	6844(4)	-2625(3)	5142(2)	49(1)
$C_{(13)}$	8101(4)	713(4)	2088(2)	57(1)
$H_{(51)}$	468(4)	447(4)	744(2)	9(1)
$H_{(51)}$	483(5)	648(4)	754(3)	10(1)
$H_{(53)}$	411(4)	552(3)	855(2)	7(1)
$H_{(61)}$	880(4)	713(4)	1004(3)	11(1)
$H_{(62)}$	670(3)	713(3)	1020(2)	7(1)
$H_{(63)}$	747(4)	824(3)	928(2)	11(1)
$H_{(7)}$	706(3)	21(2)	688(2)	5(1)
$H_{(11)}$	835(2)	280(2)	444(1)	4(1)
$H_{(121)}$	555(4)	-316(3)	489(2)	9(1)
$H_{(122)}$	708(4)	-247(4)	598(3)	9(1)
$H_{(123)}$	759(4)	-347(4)	480(2)	8(1)
$H_{(131)}$	843(4)	189(4)	204(2)	8(1)
$H_{(132)}$	918(4)	6(3)	180(2)	8(1)
$H_{(133)}$	687(4)	32(3)	156(2)	7(1)

like their 2-furfuryl(thienyl) analogs, have a structure characteristic of this group of compounds. The dioxane ring has a "rigid bath" conformation, the methyl group being disposed on axial and equatorial bonds (which causes the nonequivalence of the proton signals of these groups), and the five-membered heterocycle is located on an equatorial bond in the mirror symmetry plane of the dioxanedione ring. It is most probable that the multiple α,β-bond of the five-membered heterocycle is shielded by the saturated bond as occurs in solutions of the 2-furfuryl(thienyl) derivatives [4].

EXPERIMENTAL

The electronic spectra of solutions in ethanol of the compounds synthesized were recorded on a Specord M 40 spectrophotometer, IR spectra on Specord IR 75 and M 80 spectrometers in KBr disks or as a Nujol suspension (IIIb), and the PMR spectra on Tesla BS 467A (60 MHz) and Bruker WM 250 (250 MHz) spectrometers, the internal standard being TMS. A check on the progress of reactions and the purity of products was effected by TLC on Silufol UV-254 plates in the system toluene–ethanol 20:3.

X-Ray Structural Investigation of Compounds (IIIa, b). Bright yellow transparent monoclinic crystals of compound (IIIa) of composition $C_{11}H_{10}O_5$ were grown from an ethanolic solution. Cell parameters were a = 6.6064(2), b = 18.950(3), c = 9.188(2) Å; γ = 96.42(2)°, V = 1049.2(0.8) Å^3. Space group P $2_{1/n}$, Z = 4. The experimental data were obtained on a PT Syntex automatic diffractometer (MoKα radiation, β filter, $\theta/2\theta$ scanning to $2\theta_{\max}$ = 48°), and consisted of 1050 reflec-

TABLE 5. Data of PMR Spectra of Compounds (Va, b) and (VIa, c)

Compound	Chemical shifts in acetone-D_6, ppm, coupling constants (J), Hz							
	$(CH_3)_2C$		CH(A) d	CH_2 (2B) t	J_{AB}	heteryl		
	a-CH_3, s	e-CH_3, s				4-H	2-H	5-H
Va	1,64	1,85	4,38	3,20	5,2	6.35 d.d	7.30-7.35 m	
Vb*	1,50	1,72	4,70	3,00	4,7	5.72 s	7.10 d	7.23 d.d*2
VIa	1,52	1,77	4,35	3,35	5,0	6.95 d*2		
VIc	1,74	1,92	4,44	3,31	5,0	7.13 s		

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*Other signals: 2.05 (3H, s, 2-CH_3), 2.10 (3H, s, 5-CH_3)

*2J_{45} = 4.8.

tions with I > 3σ (I). The structure was solved by the direct method with the SHELXTL set of programs [6] and refined in an anisotropic (isotropic for H atoms) approach to divergence factors R = 0.028 and R_w = 0.032.

Bright yellow transparent triclinic crystals of compound (IIIb) of composition $C_{13}H_{14}O_5$ were grown from solution in a mixture of ethanol–chloroform, 1:1. Cell parameters were a = 6.897(2), b = 7.969(2), c = 11.504(4) Å; α = 99.15(2), β = 96.77(2), γ = 95.83(2)°, V = 615.2(3) Å^3. Space group P-1, Z = 2. The experimental data were obtained on a NICOLET P3 automatic diffractometer (MoKα radiation, θ/2θ scanning to $2\theta_{max}$ = 45° and consisted of 1184 reflections with I > 3σ (I). The structure was solved by the direct method with the SHELXTL set of programs [6] and refined in an anisotropic (isotropic for H atoms) approach to divergence factors R = 0.030 and R_w = 0.034.

5-(3-Furfurylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (IIIa). Furan-3-carbaldehyde (Ia) 0.96 g (10 mmole) and triethylamine (1-2 drops) were added to a solution of Meldrum's acid (1.44 g: 10 mmole) in alcohol (20 ml). The reaction mixture was maintained at room temperature for 2-3 h and then cooled to 0°C. The precipitated crystals of the product were filtered off and purified by recrystallization from ethanol.

Compounds (IIIb) and (IVa, c) were obtained analogously from aldehydes (Ib) and (IIa, b) respectively.

5-(3-Furfuryl)-2,2-dimethyl-1,3-dioxane-4,6-dione (Va). Sodium borohydride (0.2 g: 5 mmole) was added in small portions at room temperature with vigorous stirring to a solution of compound (IIIa) (2.22 g: 10 mmole) in ethanol (50 ml) until decolorization of the solution. The reaction mixture was then cooled, crushed ice (100 g) added, and the solution acidified to pH ~6 with dilute (1:10) hydrochloric acid. The colorless solid product which precipitated was filtered off, washed with water, and crystallized from alcohol.

Compounds (Vb) and (VIa, c) were obtained analogously from dioxanediones (IIIb) and (IVa, c) respectively.

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