Chemistry of Heterocyclic Compounds, Vol. 30, No. 3, 1994

5-[5-R-FURFURYLIDENE]-2,2-DIMETHYL-1,3-DIOXANE-4,6-DIONES

5.* NUCLEOPHILIC REPLACEMENT OF HALOGEN IN THE FURAN RING

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Halogen in positions 3 and 5 of the furan ring in furfurylidenedioxanediones is readily replaced by dithiocarbonate, dithiocarbamate, dithiophosphate, thiocyanate, and azide anions, and by thiourea, and secondary and tertiary amines. The conformation of the initial halogen derivative is retained in the substitution products.

Nucleophilic replacement of halogen in an α position of the furan ring is used extensively for the synthesis of various furan derivatives [2-6]. Such reactions proceed particularly readily when an electron-accepting substituent is present in the other α position of the furan ring [7-9].

It was shown in one of the previous communications [10] that an acyl ring conjugated with the furan nucleus through a carbon–carbon double bond displays powerful electron-accepting properties due to the combined action of the two carbonyl groups. In the same study [10] it was noted that "hard" nucleophiles, particularly OH^-, react reversibly with 5-furfurylidene-2,2-dimethyl-1,3-dioxanediones, adding at the carbon atom of the exocyclic bond. Consequently it seemed of interest to study the reaction of this series of compounds with nucleophiles softer than OH^-. The 3- and 5-halo and 4,5-dihalo derivatives, compounds (I)-(IV) containing good leaving nucleophilic halogen groups, were selected as subjects of investigation.

It turned out that soft nucleophiles [11] such as the anions of dithiocarbonic, dithiocarbamic, dithiophosphoric, and thiocyanic acids, the electrically neutral thiourea, and secondary and tertiary amines were not able to react with the exocyclic multiple bond of furfurylidenedioxanediones. When good leaving groups (halogens) were present in positions 3 and 5 of the furan ring replacement by the appropriate nucleophiles occurs. We noted that these groups were not replaced by hard nucleophiles possibly because the rate of addition of the hard nucleophile at the exocyclic multiple bond exceeded the rate of replacement of halogen or nitro group in the furan ring.

Reaction with salts of dithioacids occurs in acetone at 20-30°C in 0.5-2 h. Yields of the corresponding products (VII)-(XVIII) were 80-91% (Table 1).

Analysis of the constitution of the products of reaction with the ambident nucleophiles thiocyanate anion (acetone, room temperature) and thiourea (boiling ethanol) showed that the reaction occurs under conditions of orbital control through the soft nucleophile center, viz. the sulfur atom, with the formation of the corresponding thiocyanato derivative (XIX) (in 79% yield) and the thiouronium salts (XXI)-(XXIII) (in 90-93% yield). Boiling the pure thiocyanate (XIX) ($\nu_{SCN} = 2240\ cm^{-1}$) in acetone leads to the formation of the isothiocyanate (XX) ($\nu_{NCS} = 2080\ cm^{-1}$), which is seemingly caused by the known thiocyanate–isothiocyanate rearrangement.

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*For Communication 4 see [1].

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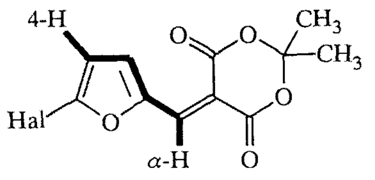
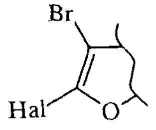
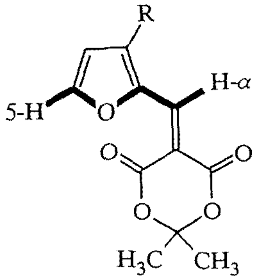


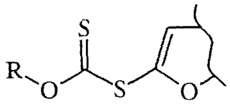
I–III



IV, V



VI, XLV



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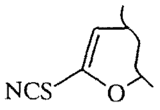

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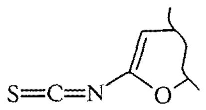
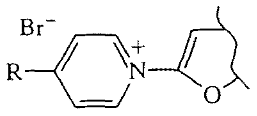
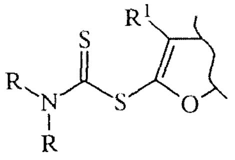


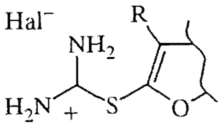
XX



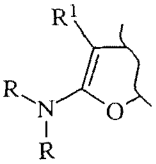
XXIX, XXX



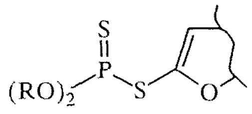
XIII–XV



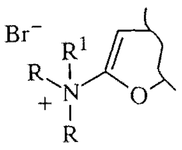
XXI–XXIII



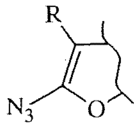
XXXI–XLII



XVI–XVIII



XXIV–XXVIII



XLIII, XLIV

I Hal = Cl; II, IV, XXI, XXII Hal = Br; III, V, XXIII Hal = I; VI, XXII, XXIII, XLIV R = Br; VII, XVI, XXIV, XXV, XXXI, XXXVIII R = CH_3; VIII, XIV, XV, XXXII, XXXIX R = C_2H_5; IX, XVII R = C_3H_7-n; X R = C_3H_7-*i*; XI R = C_4H_9-n; XII, XVIII R = C_4H_9-*i*; XXI, XXIX, XLIII R = H; XXX R = $N(CH_3)_2$; XXXIII R = C_2H_4OH; XLV R = N_3; XXXIV, XL R + R = $(CH_2)_4$; XIII, XXVII, XXXV, XLI R + R = $(CH_2)_5$; XXXVI R + R = $(CH_2)_8$; XXVI, XXXVII, XLII R+ R = $[(CH_2CH_2)_2O]$; XXVIII R + R + R^1 = $[(CH_2CH_2)_3N]$; XIII,XIV, XXIV, XXVI, XXVII, XXXI—XXXVII R^1 = H; XV, XXXVIII—XLII R^1 = Br; XXV R^1 = CH_3

The reaction of 5-halofurfurylidenedioxanediones (I)-(V) with such weak nucleophiles as thiourea indicates the exceptionally high lability of a halogen bound directly to the π-electron system of the furan ring. Similar reactions occur, although not always successfully, only with alkanes [12, 13]. This indicates the extremely high electron-accepting ability of the dioxanedione ring bound to furan through a multiple bond.

Secondary and tertiary amines give various products with the 5-halofurfurylidenedioxanediones (I)-(V) depending on the reaction conditions. The furylammonium salts (XXIV)-(XXX), which are crystalline compounds, are obtained in extremely high yield (86-94%) when using equimolar quantities of reactants and absolute solvents (benzene, pentane, hexane). They are very hygroscopic and are sensitive even to the moisture of the air but store well in the dry state without access to the air.

TABLE 1. Physicochemical Characteristics of the Compounds Synthesized

Compound	Empirical formula	Mp, °C	UV spectrum (ethanol), λ_{max}, nm (log ε)	IR spectrum, ν, cm^{-1}	Yield, %
1	2	3	4	5	6
IV	$C_{11}H_8Br_2O_5$	137...138	215 (3,18); 262 (4,23); 380 (4,53)	1691, 1719	80
V	$C_{11}H_8BrIO_5$	170...172	212 (4,04); 262 (3,95); 394 (4,31)	1696, 1732	90
VI	$C_{11}H_9BrO_5$	160...162	209 (3,98); 264 (3,64); 368 (4,30)	1738, 1760	81
VII	$C_{13}H_{12}O_6S_2$	116...117	215 (4,60); 267 (4,42); 373 (4,23)	1730, 1750	90
VIII	$C_{14}H_{14}O_6S_2$	103...105	215 (4,48); 267 (4,35); 373 (4,78)	1730, 1760	91
IX	$C_{15}H_{16}O_6S_2$	93...95	215 (4,40); 267 (4,18); 373 (4,60)	1730, 1752	86
X	$C_{15}H_{16}O_6S_2$	88...89	215 (4,31); 267 (3,99); 373 (4,56)	1730, 1750	89
XI	$C_{16}H_{18}O_6S_2$	57...58	215 (4,41); 267 (4,30); 373 (4,67)	1735, 1745	90
XII	$C_{16}H_{18}O_6S_2$	55...56	215 (4,16); 267 (3,95); 373 (4,47)	1725, 1755	87
XIII	$C_{17}H_{19}NO_5S_2$	159...160	223 (4,31); 283 (4,27); 380 (4,48)	1730, 1760	88
XIV	$C_{16}H_{19}NO_5S_2$	116...117	261 (4,26); 378 (4,37)	1730, 1760	82
XV	$C_{16}H_{18}BrNO_5S_2$	126...127	260 (4,40); 376 (3,93)	1729, 1755	80
XVI	$C_{13}H_{15}O_7PS_2$	63...64	217 (3,99); 260 (3,86); 385 (4,38)	1732, 1750	84
XVII	$C_{17}H_{23}O_7PS_2$	57...58	217 (3,96); 260 (3,88); 385 (4,36)	1732, 1750	86
XVIII	$C_{19}H_{27}O_7PS_2$	50...51	217 (3,93); 260 (3,83); 385 (4,39)	1732, 1740	87
XIX	$C_{12}H_9NO_5S$	97...98	360 (4,35)	1720, 1757, 2169	79
XX	$C_{12}H_9NO_5S$	90 (decomp.)	358 (4,28)	1719, 1750, 2080	75
XXI	$C_{12}H_{13}BrN_2O_5S$	230 (decomp.)	204 (3,57); 261 (3,95); 488 (4,39); 519 (4,53)	1738, 1770	90
XXII	$C_{12}H_{12}Br_2N_2O_5S$	230 (decomp.)	204 (4,01); 242 (3,85); 500 (4,12); 533 (4,21)	1720, 1740	93
XXIII*	$C_{12}H_{12}BrIN_2O_5S$	257...258	355 (4,27); 395 (4,33)	1711, 1740	91
XXIV*	$C_{13}H_{16}BrNO_5$	175...176	457 sh (4,47); 473 (4,68)	1711, 1730	94
XXV	$C_{14}H_{18}BrNO_5$	175...178	452 sh (4,47); 473 (4,66)	1710, 1730	91
XXVI*	$C_{15}H_{17}BrNO_6$	163...165	453 sh (4,39); 474 (4,62)	1680, 1710	90
XXVII*	$C_{16}H_{19}BrNO_5$	165 (decomp.)	453 sh (4,10); 471 (4,56)	1690, 1700	91
XXVIII*	$C_{17}H_{21}BrN_2O_5$	193...195	385 (3,98); 472 (4,07)	1720, 1740	92
XXIX*	$C_{16}H_{14}BrNO_5$	211 (decomp.)	377 (4,38)	1730, 1760	88

The use of a two-fold excess of a secondary amine and a polar solvent (ethanol, isopropyl alcohol) leads to the formation of the dialkylamino derivatives (XXXI)-(XLII), which are intensely colored compounds, extremely stable on storage (Table 1).

TABLE 1 (continued)

1	2	3	4	5	6
XXX*	$C_{18}H_{19}BrN_2O_5$	238...240	313 (3,98); 418 (4,26)	1705, 1735	86
XXXI	$C_{13}H_{15}NO_5$	176	236 (3,90); 271 (4,00); 456 sh (4,58); 461 (4,61)	1675, 1730	85
XXXII	$C_{15}H_{19}NO_5$	130...131	423 sh (4,65); 456(4,93)	1660, 1680	86
XXXIII	$C_{15}H_{19}NO_7$	250 (decomp.)	450 (4,77)	1635, 1660	84
XXXIV	$C_{15}H_{17}NO_5$	190...191	452 sh (4,67); 473 (4,97)	1635, 1685	92
XXXV	$C_{16}H_{19}NO_5$	160...161	427 sh (4,57); 461 (4,61)	1695, 1715	90
XXXVI	$C_{17}H_{21}NO_5$	120...122	454 sh (4,59); 475 (4,82)	1680, 1720	75
XXXVII	$C_{15}H_{17}NO_6$	182...183	422 sh (4,65); 464 (4,75)	1680, 1730	89
XXXVIII	$C_{13}H_{14}BrNO_5$	148...150	464 sh (4,68); 495 (4,94)	1661, 1701	79
XXXIX	$C_{15}H_{18}BrNO_5$	135 (decomp.)	465 sh (4,47); 490 (4,74)	1680, 1715	73
XL	$C_{15}H_{16}BrNO_5$	170 (decomp.)	463 sh (4,62); 490 (4,93)	1710, 1720	75
XLI	$C_{16}H_{18}BrNO_5$	158 (decomp.)	466 sh (4,62); 490 (4,88)	1680, 1720	74
XLII	$C_{15}H_{16}BrNO_6$	165 (decomp.)	456 sh (4,63); 493 (4,88)	1680, 1720	78
XLIII	$C_{11}H_9N_3O_5$	84...85	260 (4,12); 413 (4,14)	1720, 1751, 2142	76
XLIV	$C_{11}H_8BrN_3O_5$	106	260 (4,13); 427 (4,15)	1720, 1750, 2120	75
XLV	$C_{11}H_9N_3O_5$	147...148	215 (3,95); 303 (3,47); 386 (4,45)	1710, 1750, 2100	77

*The UV spectrum was drawn in acetic acid.

Azide anion smoothly replaces halogen in positions 3 and 5 of the furan ring in acetone at room temperature with the formation of the corresponding 3- and 5-azido derivatives (XLIII)-(XLV). These are crystalline compounds of various shades of yellow in color, unstable on storage, but extremely useful as synthons for obtaining other products.

Reaction of the 5- and 3-bromofurfurylidenedioxanediones (II), (IV), and (VI) with sodium azide leads to the formation of the corresponding azides (XLIII)-(XLV). The first two products are unstable on storage but the 3-azido derivative (XLV) is fairly stable.

There are two bands of different intensity for the stretching vibrations of the C=O groups in the IR spectra of compounds (I)-(XLV), which is characteristic of ylidene derivatives of β-dicarbonyl compounds [14]. The low frequency ν_{as} band is approximately twice as intense as the high frequency ν_s. Strong electron donors, such as amino groups, reduce the ν_{as} frequency to a larger extent than the ν_s (Table 1). Substituents such as thiocyanate, azide, and the thiouronium group have characteristic absorption bands in the IR spectra at 2169, 2140, and 1650 cm^{-1} respectively.

Analysis of the electronic, IR, and NMR spectra in combination with an analysis of the reactivity enabled us to subdivide all the compounds mentioned above into two groups. The first group comprises compounds with a normal alternation of multiple bonds in the conjugation system of the molecule, and the second comprises compounds with a resonating system of multiple bonds.

Compounds assigned to the first group contain a substituent atom directly bound to position 5 of the furan ring which has no or a weakly labile unshared electron pair (for example, ammonium nitrogen, halogen, sulfide sulfur, etc.).

Compounds assigned to the second group contain a substituent atom directly bound to position 5 of the furan ring which has a highly labile unshared electron pair, such as an amine nitrogen.

TABLE 2. PMR Spectra in Deuteroacetone of Compounds (IV)-(XIII), (XVI)-(XIX), (XXI), (XXIX), (XXXII), (XXXIV), (XXXV), (XXXVII), (XXXVIII), (XL), (XLII)-(XLIV)

Compound	Chemical shift, δ, ppm				J, Hz		Other signals and coupling constants
	$C(CH_3)_2$	α-H	3-H	4-H	$J_{\alpha\text{-}4}$	$J_{3\text{-}4}$	
IV	1,68	7,97	8,27	—	—	—	$J_{\alpha\text{-}3} = 0,4$
V	1,67	7,97	8,18	—	—	—	$J_{\alpha\text{-}3} = 0,4$
VI	1,72	7,90	—	6,87	—	—	$J_{4,5} = 2,0$, $J_{\alpha\text{-}5} = 0,6$
VII	1,72	8,06	8,28	7,16	0,8	4,0	4,13 (3H, s, OCH_3)
VIII	1,70	8,07	8,30	7,13	0,7	4,0	1,27 (3H, t, $J = 7,0$, CH_3); 4,60 (2H, q, $J = 7,0$, OCH_2)
IX	1,70	8,06	8,26	7,15	0,7	4,0	0,93 (3H, t, $J = 7,2$, CH_3); 1,80 (2H, m, CH_2); 4,52 (2H, t, $J = 6,8$, OCH_2)
X	1,72	8,06	8,32	7,16	0,9	4,0	1,03 (6H, d, $J = 7,8$, $2CH_3$); 4,06 (1H, q, $J = 7,8$, CH)
XI	1,68	8,08	8,35	7,15	0,7	3,9	0,8...1,5 (7H, m, $(CH_2)_2CH_3$); 4,50 (2H, t, $J = 6,1$, OCH_2)
XII	1,70	8,07	8,32	7,13	0,8	4,0	0,96 (6H, d, $J = 6,7$, 2CH); 2,23 (1H, m, CH); 4,56 (2H, d, $J = 7,0$, OCH_2)
XIII	1,68	8,07	8,25	7,05	0,7	4,0	1,22 (3H, t, CH_3); 1,33 (3H, t, CH_3); 3,82 (2H, q, NCH_2); 3,93 (2H, q, NCH_2)
XVI	1,68	8,01	8,22	6,88	0,7	3,9	4,52 (6H, d, $J_{Ph} = 11,0$, $2OCH_3$)
XVII	1,68	8,06	8,25	6,88	0,7	3,9	0,82 (6H, m, $2CH_3$); 1,80 (4H, m, CH_2CH_2); 3,60 (4H, m, $2OCH_2$)
XVIII	1,70	8,03	8,24	6,78	0,7	4,0	0,78 (12H, d, $J = 7,2$, $4CH_3$); 2,04 (2H, m, 2CH); 3,66 (4H, m, $2OCH_2$)
XIX	1,69	7,98	8,30	6,75	0,7	4,0	
XXI*	1,42	7,85	7,95	6,97	—	3,8	
XXIX**	1,65	8,25	8,12	7,68	—	4,0	9,48 (2H, 2 Hα); $J_{\alpha\beta} = 6,0$; 8,28 (2H, 2 Hβ); $J_{\beta\gamma} = 8,0$; 8,73 (1H, Hγ); $J_{\alpha\gamma} = 1,5$
XXXII	1,63	7,93	8,78	5,87	0,7	5,0	1,23 (6H, t, $J = 7,2$, $2CH_3$); 3,48 (4H, q, $N(CH_2)_2$)
XXXIV	1,63	7,82	8,87	5,70	0,8	5,0	2,03 (4H, m, CH_2CH_2); 3,53 (4H, m, $N(CH_2)_2$)
XXXV	1,55	7,70	8,87	6,10	0,9	5,0	1,65 (6H, m, $(CH_2)_3$); 3,63 (4H, m, $N(CH_2)_2$)
XXXVII	1,55	7,87	8,97	6,22	0,9	4,8	3,70 (8H, m, $N(CH_2CH_2)_2O$)
XXXVIII	1,58	7,68	8,78	—	—	—	3,38 (6H, s, $N(CH_3)_2$)
XL	1,55	7,67	8,83	—	—	—	3,87 (8H, m, $(CH_2)_4$)
XLII	1,58	7,70	8,57	—	—	—	3,82 (8H, m, $N(CH_2CH_2)_2O$)
XLIII	1,75	7,96	8,41	6,38	0,4	4,1	
XLIV	1.68	8.00	8.48	—	—	—	

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*In CF_3COOD.

**In DMSO-D_6.

Both groups of compounds have the same conformational structure. Furfurylidene derivatives have the s-cis disposition of the furan ring and the exocyclic multiple bond which is confirmed by the presence of regioselective long-range coupling constants between the α-H and 4-H protons [15-17] of 0.6-0.8 Hz in the PMR spectra (Table 2).

The introduction of a bulky substituent into position 3 of the furan ring makes the s-cis conformation impossible and transforms the molecule into the s-trans form. As a result no long range coupling is observed in the spectra of compounds (VI) and (XLV) between the α-H and 4-H protons but there is a long-range interaction between the α-H and 5-H protons [according to the other spectral characteristic compounds (VI) and (XLV) may be assigned to the first group in the classification mentioned above]. Another characteristic feature of the s-cis conformation of the furfurylidene derivatives of the first and second groups is the strong low-field displacement of the signal of the 3-H proton to 7.9-8.4 ppm for compounds of the first group and to

8.5-8.9 ppm for compounds of the second, as a result of the intramolecular contact of this proton with the oxygen of the carbonyl group [15]. In addition, on going from the first group of compounds to the second the coupling constant between the β protons of the furan ring changes from 4.0 ± 0.1 to 5.0 ± 0.3 Hz, which is probably linked with an increase in the multiplicity of the β,β-carbon–carbon bond.

The clearest difference (readily observed experimentally) in the spectral characteristics of the compounds of these two groups is the position and shape of the long-wave absorption band in the electronic spectra and also the influence of solvent polarity on the position of this absorption band.

Compounds of the first group have wide ($\Delta\nu_{1/2}$ ~4000 cm^{-1}) smooth and symmetrical long-wave absorption bands (K bands), undergoing a bathochromic shift on increasing the solvent polarity (positive solvatochromia), which is characteristic of compounds with a more polar excited state [19].

Compounds of the second group, like the merocyanine dyes, have a narrow ($\Delta\nu_{1/2}$ ~1600 cm^{-1}) more intense band in the visible region of the spectrum on the short-wave slope of which a second maximum is observed (often as a shoulder) located at a distance of 1000-2000 cm^{-1} from the main maximum and linked with the vibrational O-1′ transition. The latter, like the O-O′ transition, is polarized along the chain of conjugation. The difference of the frequencies of the O-O′ and O-1′ transitions corresponds to the frequency of the fully symmetric vibration of the carbon atoms of the chromophore chain in the excited state, causing splitting of the purely electronic transition [18]. The long-wave absorption of this group of substances possesses negative solvatochromia which is characteristic of compounds in which the ground state is more polar than the excited state [19]. The ground state corresponds best to a resonance structure with charge separation and as a result with rapidly alternating multiple bonds in the conjugation chain.

EXPERIMENTAL

The UV spectra were drawn on a Specord M 40 instrument in ethanol, IR spectra were taken on UR 20 and Specord IR 71 spectrophotometers in Nujol suspensions. The PMR spectra were drawn on Tesla BS 467A (60 MHz) and Bruker WP 200 SY (200 MHz) spectrometers in deuteroacetone. A check on the progress of reactions and the homogeneity of the compounds synthesized was carried out by TLC on Silufol UV-254 plates in the system toluene–ethanol, 20:3.

Compounds (I)-(VI) were obtained according to [10].

O-Methyl S-[5-(2,2-Dimethyl-4,6-dioxo-1,3-dioxan-5-ylidenemethyl)-2-furyl] Dithiocarbonate (VII). Potassium O-methyl dithiocarbonate (1.46 g, 10 mmole) was added to a solution of compound (I) (3.01 g, 10 mmole) in absolute acetone (40 ml) and the mixture stirred at room temperature for 3 h. The precipitate of KBr was filtered off, the filtrate evaporated in vacuum, and the residue recrystallized from alcohol.

Compounds (VIII)-(XIX) were prepared analogously.

5-(5-Isothiocyanatofurfurylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (XX). A solution of the thiocyanate (XIX) in dry acetone was boiled for 1-1.5 h. The solvent was evaporated in vacuum and the residue recrystallized from dioxane.

5-(2,2-Dimethyl-4,6-dioxo-1,3-dioxan-5-ylidenemethyl)-2-furylthiouronium Bromide (XXI). A hot solution of bromide (II) (3.02 g, 10 mmole) in ethanol (20 ml) was added to a boiling solution of thiourea (0.76 g, 10 mmole) in ethanol (20 ml). The precipitated solid was filtered off, and washed with cold ethanol and with ether.

Compounds (XXII) and (XXIII) were obtained analogously.

N-[5-(2,2-Dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene-methyl)-2-furyl]dimethylammonium Bromide (XXIV). A Solution of compound (II) (10 mmole) in absolute pentane (100 ml) was saturated with dry dimethylamine. After 1 h the precipitated solid was filtered off without access to the moisture of the air, washed with pentane, and dried in vacuum.

Compound (XXV) was obtained analogously.

N-[5-(2,2-Dimethyl-4,6-dioxo-1,3-dioxan-5-ylidenemethyl)-2-furyl]morpholinium Bromide (XXVI). Absolute morpholine (0.87 g, 10 mmole) was added to a solution of compound (II) (10 mmole) in dry benzene or hexane (100 ml). After 2 h the precipitated crystals were filtered off without exposure to the moisture of the air, washed with dry hexane, and dried in vacuum.

The salts (XXVII)-(XXX) were obtained analogously.

5-(5-N,N-Diethylaminofurfurylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (XXXII). Diethylamine (2.2 ml: 20 mmole) was added to a solution of compound (II) (10 mmole) in alcohol (50 ml), the mixture stirred at room temperature for 3 h, and cooled to 0 to −5°C. The precipitated solid was filtered off and recrystallized from alcohol.

Compounds (XXXI) and (XXXIII)-(XLII) were obtained analogously.

5-(5-Azidofurfurylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (XLIII). A solution of sodium azide (0.65 g: 10 mmole) in water (5 ml) was poured into a solution of compound (II) (10 mmole) in acetone (50 ml). The mixture was stirred at room temperature for 3 h then cooled to 0 to −5°C. The precipitated crystals were filtered off, washed with dry alcohol, and dried in vacuum.

Compounds (XLIV) and (XLV) were obtained analogously.

The synthesized azides (XLIII) and (XLIV) were unstable on storage and must be used for further syntheses.

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