Chemistry of Tetra-alkoxyethenes. Part VI.[1] Cycloadditions with αβ-Unsaturated Carbonyl Compounds and Chemistry of the Resulting Tetra-alkoxydihydropyrans

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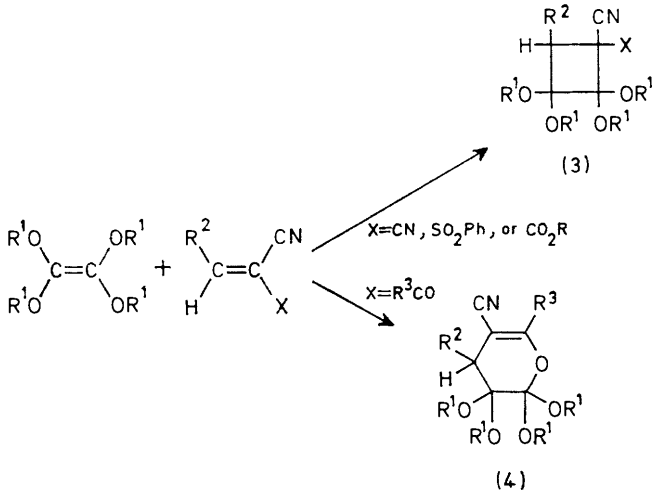
Heating tetra-alkoxyethenes (1) at 100 °C with α-cyano-αβ-unsaturated carbonyl compounds (2) gives [4 + 2] cycloaddition products in high yields. Mild acidic hydrolysis of the resulting 2,2,3,3-tetra-alkoxy-5-cyano-3,4-dihydro-2*H*-pyrans (4) gives separable mixtures containing a δ-oxo-ester (11), formed by ring opening, and an α-pyrone (12), which arises by recyclization of the δ-oxo-ester after hydrolysis of its acetal function. In concentrated sulphuric acid, compounds (4) are converted either into 3,3-dialkoxy-5-cyano-3,4-dihydro-2-pyrones (13) or into 3-alkoxy-5-cyano-2-pyrones (14), depending on the reaction temperature. Treatment of (4) with base yields 2,2,3-trialkoxy-5-cyano-2*H*-pyrans (15) by elimination of alcohol.

We have reported [2] that cycloadditions between electron-rich tetra-alkoxyethenes (1) and electron-poor cyanoethenes (2), activated by a second electron-withdrawing



(3)

(4)

SCHEME 1

α-substituent (X), yield cyclobutane derivatives,[3] when X = CN, SO_2Ph, or CO_2R. However, when X is an acyl group, [4 + 2] cycloadditions take place, yielding dihydropyran derivatives (4) (Scheme 1). Similar six-membered ring compounds have been obtained previously from several other types of electron-rich olefins, such as enol ethers,[3-5] enamines,[6,7] and keten acetals,[8,9] by reaction with an αβ-unsaturated carbonyl compound. Only the extremely nucleophilic tetra-aminoethene (5) has been shown to react in a different way. It yields [10] a five-membered ring compound, probably as a consequence of elimination of the highly stabilized diaminocarbene [11,12] (7) from an initially formed dipolar adduct (6) (Scheme 2).

Recently Bélanger and Brassard [13] succeeded in converting the cycloaddition products (9) from β-chloroketen acetals and αβ-unsaturated carbonyl compounds into α-pyrones (10), by elimination of hydrochloric acid and hydrolysis of the orthoester function (Scheme 3). In view of the wide occurrence of pyran and pyrone derivatives in nature,[14] and the applications of α-pyrones [15] in synthetic organic chemistry, such simple preparations of dihydropyrans and α-pyrones may be of value. We now give a more extensive report on the synthesis of dihydropyran derivatives from tetra-alkoxyethenes and αβ-unsaturated carbonyl compounds, and discuss the possibility of selective removal of the orthoester and acetal functions in these products.

RESULTS

Tetramethoxyethene did not react with cinnamaldehyde or crotonaldehyde at 100 °C. With acrylaldehyde and methyl vinyl ketone at the same temperature only small amounts of a dihydropyran derivative were formed, together with large amounts of polymeric products. Higher temperatures, as used in cycloadditions of enol ethers [3,4] (150—200 °C) and keten

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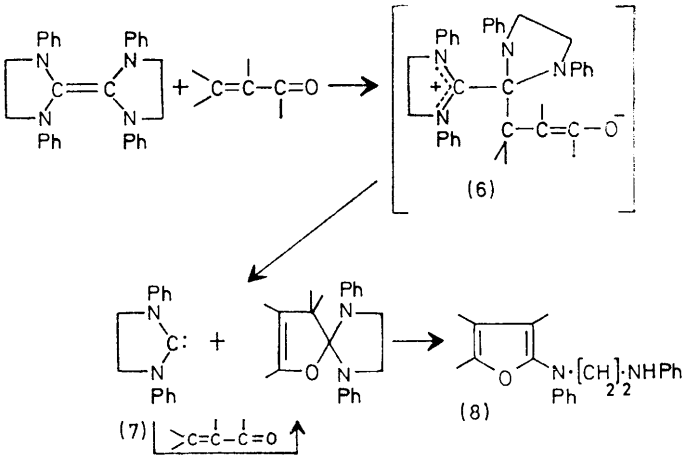
[12] R. W. Hoffmann, *Angew. Chem.*, 1968, **80**, 823; *Angew. Chem. Internat. Edn.*, 1968, **7**, 754.
[13] A. Bélanger and P. Brassard, *Canad. J. Chem.*, 1975, **53**, 195, 201.
[14] See, *e.g.*, F. M. Dean, 'Naturally Occurring Oxygen Ring Compounds,' Butterworths, London, 1963, ch. 4.
[15] N. P. Shusherina, N. D. Dmitrieva, E. A. Luk'yanets, and R. Ya. Levina, *Russ. Chem. Rev.*, 1967, **36**, 175.

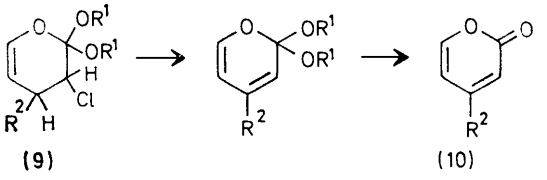
acetals [8,9] (150 °C) cannot be applied in reactions of tetramethoxyethene, since it decomposes [16] homolytically at about 150 °C.

Faster cycloadditions were found with αβ-unsaturated carbonyl compounds, $R^2CH = CY{\cdot}COR^3$, having an electron-withdrawing α-substituent. The reactivity at 100 °C towards tetra-alkoxyethenes was apparently still too low for practical use with Y = SO_2Ph, Bz, or CO_2R.



SCHEME 2

However, the cyano-derivatives (Y = CN) reacted smoothly, giving 2,2,3,3-tetra-alkoxy-5-cyano-3,4-dihydro-2*H*-pyrans (4). In this way several ring-substituted

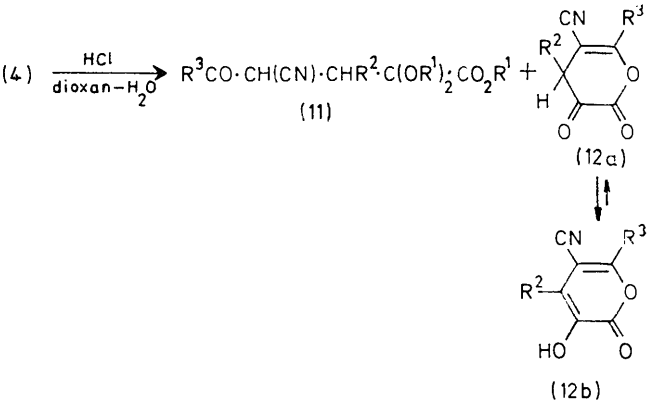


SCHEME 3

α-cyano-cinnamaldehydes and -benzylideneacetophenones could be converted into dihydropyran derivatives in yields of 80—95% (Table 1). Extension of the reaction to the preparation of compounds (4; R^2 = H or alkyl) was not studied, since useful syntheses of the necessary starting compounds are not available.

Hydrolysis of 2,2,3,3-*Tetra-alkoxy*-5-*cyano*-3,4-*dihydro*-2H-*pyrans* (4) *in the Presence of Acids.*—Acidic hydrolysis of compounds (4) yields different products according to the reaction conditions. Refluxing in dioxan–water with hydrogen chloride as catalyst yielded substituted δ-oxo-esters (11) as the main products. In all cases α-pyrone derivatives (12) were formed as principal side-products, in 20—25% yields (Scheme 4). The oxo-esters could be separated easily from the side-products, because of the low solubility of the latter. In general highest yields of oxo-esters (11) were obtained on heating the mixture under reflux for about 1 h (Table 2). Sulphuric acid and toluene-*p*-sulphonic acid are less effective catalysts for the conversion (4) ⟶ (11). In these cases the reaction mixture contained many more side-products, which were not identified.

I.r. data revealed that the side-products (12) exist in the enol (3-hydroxypyrone) form (12b), after crystallization (Table 3). Normally treatment of compounds (4) with concentrated sulphuric acid gave only products containing the α-pyrone ring (Scheme 5). Below 0 °C 3,3-dialkoxy-5-cyano-3,4-dihydropyrones (13) were obtained (Table 4). At higher temperatures these compounds apparently eliminate alcohol in the acidic medium; at 25 °C 3-alkoxy-5-cyano-2-pyrones (14) were isolated (Table 5). The same products were obtained when the pure compounds (13) were treated with concentrated sulphuric acid at 25 °C. These reactions failed with compounds (4; R^2 = α-furyl); in this case a complex mixture arose, perhaps owing to acidolytic cleavage of the



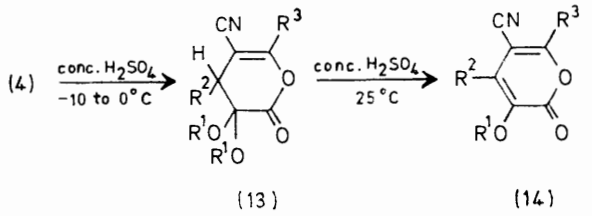
SCHEME 4

furyl group. Unsatisfactory results were also obtained in reactions with (4; R^3 = H).

Reactivity of 2,2,3,3-*Tetra-alkoxy*-5-*cyano*-3,4-*dihydro*-2H-*pyrans* (4) *towards Bases.*—Treatment of compounds

[16] R. W. Hoffmann, J. Schneider, and H. Hauser, *Chem. Ber.*, 1966, **99**, 1892.

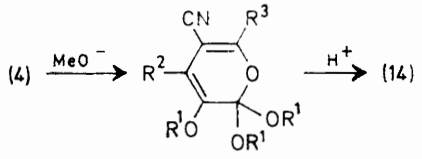
(4) with sodium methoxide in 1,2-dimethoxyethane usually caused elimination of alcohol, yielding 2,2,3-trialkoxy-5-cyano-2*H*-pyrans (15) (Table 6). Compounds



(13) (14)

SCHEME 5

(4; $R^3 = H$) did not react with methoxide. Use of a stronger base (t-butoxide) resulted in complex mixtures, independent of the nature of R^3. Hydrolysis of the



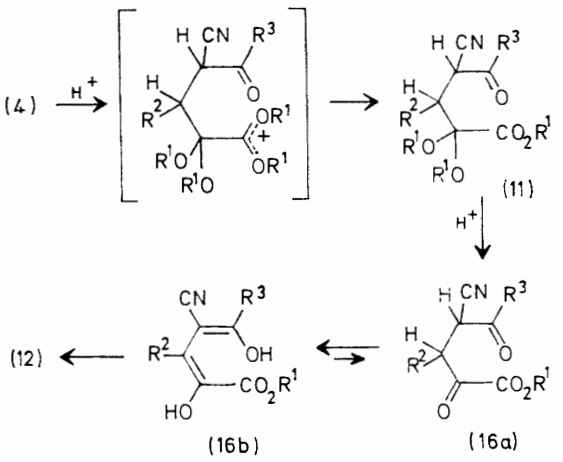
(15)

SCHEME 6

products (15) with sulphuric acid again yielded the α-pyrone derivatives (14) (Scheme 6).

DISCUSSION

Comparison of the reactivity of tetra-alkoxyethenes with that of other electron-rich olefins reveals that enamines add much faster to αβ-unsaturated carbonyl compounds. In general, enamines give six-membered cycloaddition products at room temperature, even with less activated αβ-unsaturated ketones.[6,7] The reactivity of enol ethers and keten acetals seems not very different from that of tetra-alkoxyethenes. Ethyl vinyl ether and 1,1-dialkoxyisobutene add smoothly to 2-benzylidene-2-cyanoacetophenone. They both even add to less activated carbonyl compounds, *e.g.* cinnamaldehyde and acrylaldehyde, although at higher temperatures. However, the presence of the acetal function in the cycloaddition products (4) from tetra-alkoxyethenes provides these compounds with a much more varied reactivity than the related dihydropyrans without this group. In general 2,2-dialkoxydihydropyrans give only open-chain products, *viz.* δ-oxo-esters, on acidic hydrolysis,[8,13] without formation of side-products corresponding to (12). The formation of the compounds (12) on acidic hydrolysis of 2,2,3,3-tetra-alkoxydihydropyrans may be ascribed to hydrolysis of the acetal function in the primarily formed δ-oxo-ester (11). The resulting product (16) will enolize [(16a) ⇄ (16b)], favouring recyclization by intramolecular transesterification (Scheme 7).

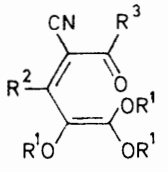


(16b) (16a)

SCHEME 7

The hydrolysis of the acetal function in (11) is slow in comparison with the hydrolysis of the orthoester function in (4). The products (11) can be obtained in higher yields when compounds (4) are subjected to brief treatment with dilute hydrochloric acid; compounds (12) are obtained only after longer reaction times. The cyclization of (16), giving (12) in acidic medium is apparently complete. The occurrence of the α-oxo-ester (16a) or its tautomer (16b) in the reaction mixture has never been observed. Similarly, acidic hydrolysis of (15) yields only the cyclic product (14); the α-alkoxy-analogue of (16b), which must be an intermediate in this reaction, could not be detected.

An alternative route for the conversion of (15) into (14) may be *via* valence isomerization of (15) into the dienones (17), as described for several other α-pyran derivatives.[9,17,18] However, compounds (15), dissolved in



(17)

phenyl cyanide, are apparently completely stable at 200 °C, whereas the isomerization products (17), being keten acetals, should decompose at this temperature.[16,19,20] The thermal stability of (15) may be explained by arguments similar to those used for 4,6,6-trialkylpyrans.[21]

[17] A. Roedig and H. A. Renk, *Chem. Ber.*, 1973, **106**, 3877.
[18] P. Schiess and H. L. Chia, *Helv. Chim. Acta*, 1970, **53**, 485.
[19] P. H. J. Ooms, J. W. Scheeren, and R. J. F. Nivard, *Synthesis*, 1975, 263.
[20] S. M. McElvain and C. L. Stevens, *J. Amer. Chem. Soc.*, 1946, **68**, 1917.
[21] A. F. Kluge and C. P. Lillija, *J. Org. Chem.*, 1971, **36**, 1977.

TABLE 1

2,2,3,3-Tetra-alkoxy-5-cyano-3,4-dihydro-2*H*-pyrans (4; R^1 = Me) (Scheme 1)

R^2	R^3	Yield (%)	M.p. (°C)	*m/e*	$\nu_{max.}$(KBr)/cm^{-1}			Analyses (%) C	H	N
p-$O_2N{\cdot}C_6H_4$	Ph	87	158	426 (*M*), 411 (*M* − CH_3), 395 (*M* − OCH_3)	2 212 (C≡N), 1 620 (C=C–O)	$C_{22}H_{22}N_2O_7$	Reqd.	61.95	5.2	6.55
							Found	62.1	5.3	6.55
p-ClC_6H_4	Ph	90	134	416/414 (*M*), 401/399 (*M* − CH_3), 385/383 (*M* − OCH_3)	2 210 (C≡N), 1 625 (C=C–O)	$C_{22}H_{22}ClNO_5$	Reqd.	63.55	5.35	3.35
							Found	63.7	5.4	3.4
p-MeO·C_6H_4	Ph	95	120	411 (*M*), 396 (*M* − CH_3), 380 (*M* − OCH_3)	2 208 (C≡N), 1 618 (C=C–O)	$C_{23}H_{25}NO_6$	Reqd.	67.15	6.1	3.4
							Found	66.9	6.2	3.4
2-Furyl	Ph	88	81	371 (*M*), 356 (*M* − CH_3), 340 (*M* − OCH_3)	2 218 (C≡N), 1 640/1 632 (C=C–O)	$C_{20}H_{21}NO_6$	Reqd.	64.7	5.7	3.75
							Found	65.0	5.9	3.8
p-MeO·C_6H_4	H	80	122	335 (*M*), 320 (*M* − CH_3), 304 (*M* − OCH_3)	2 212 (C≡N), 1 646 (C=C–O)	$C_{17}H_{21}NO_6$	Reqd.	60.9	6.3	4.2
							Found	61.0	6.4	4.2

TABLE 2

αα-Dialkoxy-γ-cyano-δ-oxo-esters (11; R^3 = Ph) (Scheme 4)

R^1	R^2	Yield (%)	M.p. (°C)	*m/e*	$\nu_{max.}$(KBr)/cm^{-1}			Analyses (%) C	H	N
Me	*p*-$NO_2{\cdot}C_6H_4$	75	67	381 (*M* − OCH_3), 353 (*M* − $COOCH_3$)	2 235 (C≡N), 1 735 (C=O), 1 692 (C=O)	$C_{21}H_{20}N_2O_7$	Reqd.	61.15	4.9	6.8
							Found	60.5	4.9	6.7
Me	*p*-ClC_6H_4	70	120	403/401 (*M*), 372/370 (*M* − OCH_3), 344/342 (*M* − CO-OCH_3)	2 237 (C≡N), 1 735(C=O), 1 693 (C=O)	$C_{21}H_{20}ClNO_5$	Reqd.	62.75	5.0	3.5
							Found	63.0	4.9	3.4
Me	Ph	70	125	367 (*M*), 336 (*M* − OCH_3), 308 (*M* − $COOCH_3$)	2 240 (C≡N), 1 760 (C=O), 1 696 (C=O)	$C_{21}H_{21}NO_5$	Reqd.	68.65	5.75	3.8
							Found	68.8	5.8	3.8
Me	*p*-MeO·C_6H_4	80	122	397 (*M*), 366 (*M* − OCH_3), 338 (*M* − $COOCH_3$)	2 239 (C≡N), 1 761 (C=O), 1 690 (C=O)	$C_{22}H_{23}NO_6$	Reqd.	66.5	5.85	3.5
							Found	66.7	5.9	3.6
Me	2-Furyl	45	109	357 (*M*), 326 (*M* − OCH_3), 298 (*M* − $COOCH_3$)	2 240 (C≡N), 1 731 (C=O), 1 692 (C=O)	$C_{19}H_{19}NO_6$	Reqd.	63.85	5.35	3.9
							Found	63.8	5.4	4.0
Et	Ph	85	83	409 (*M*), 364 (*M* − OC_2H_5), 336 (*M* − $COOC_2H_5$)	2 239 (C≡N), 1 731 (C=O), 1 692 (C=O)	$C_{24}H_{27}NO_5$	Reqd.	70.4	6.65	3.4
							Found	70.1	6.7	3.4

TABLE 3

5-Cyano-3-hydroxy-2-pyrones (12b) (Scheme 4)

R^2	Yield (%)	M.p. (°C)	*m/e*	$\nu_{max.}$(KBr)/cm^{-1}	$\lambda_{max.}$($CHCl_3$)/nm			Analyses (%) C	H	N
p-$NO_2{\cdot}C_6H_4$	25	216	334 (*M*), 306 (*M* − CO), 277 (*M* − CO − COH)	2 222 (C≡N), 1 710 (C=O), 1 625 (C=C–O)	345	$C_{18}H_{10}N_2O_5$	Reqd.	64.65	3.0	8.4
							Found	63.05	3.1	8.2
p-ClC_6H_4	22	226	325/323 (*M*), 297/295 (*M* − CO), 268/266 (*M* − CO − COH)	3 352 (OH), 2 230 (C≡N), 1 710 (C=O), 1 627 (C=C–O)	331	$C_{18}H_{10}ClNO_3$	Reqd.	66.8	3.1	4.35
							Found	66.7	3.1	4.15
Ph	20	197	289 (*M*), 261 (*M* − CO), 232 (*M* − CO − COH)	3 350 (OH), 2 225 (C≡N), 1 710 (C=O), 1 620 (C=C–O)	331	$C_{18}H_{11}NO_3$	Reqd.	74.75	3.85	4.85
							Found	74.1	3.9	4.8
p-MeO·C_6H_4	25	228	319 (*M*), 304 (*M* − CH_3), 288 (*M* − OCH_3), 291 (*M* − CO), 262 (*M* − CO − COH)	3 355 (OH), 2 228 (C≡N), 1 710 (C=O), 1 620 (C=C–O)	342	$C_{19}H_{13}NO_3$	Reqd.	71.45	4.1	4.4
							Found	71.3	4.0	4.35

EXPERIMENTAL

All products were characterized by m.p.s, mass spectra, and i.r. data (KBr pellets).

α-Cyano-αβ-unsaturated Carbonyl Compounds [$R^2CH{:}C(CN){\cdot}COR^3$].—The compounds with R^3 = Ph were prepared by Knoevenagel condensations between an appropriate aldehyde and cyanoacetophenone, with piperidine as catalyst.[22] In all cases only one isomer, probably the *trans*, was isolated. New compounds are those with R^2 = *p*-ClC_6H_4 (m.p. 87°; yield 80%) and R^2 = α-furyl (m.p. 117°; yield 75%).

[22] H. Kauffmann, *Ber.*, 1917, **50**, 527.

TABLE 4

3,3-Dialkoxy-5-cyano-3,4-dihydro-2-pyrones (13; R^3 = Ph) (Scheme 5)

R^1	R^2	Yield (%)	M.p. (°C)	*m/e*	$\nu_{max.}$(KBr)/cm^{-1}			Analyses (%)		
								C	H	N
Me	*p*-$O_2N{\cdot}C_6H_4$	95	163	380 (*M*), 349 (*M* − OCH_3), 334 (*M* − H_3COCH_3)	2 212 (C≡N), 1 745 (C=O), 1 630 (C=C–O)	$C_{20}H_{16}N_2O_6$	Reqd.	63.15	4.25	7.35
							Found	63.0	4.25	7.3
Me	*p*-ClC_6H_4	90	125	370/368 (*M*), 339/337 (*M* − OCH_3), 324/322 (*M* − H_3COCH_3)	2 210 (C≡N), 1 745 (C=O), 1 630 (C=C–O)	$C_{20}H_{16}ClNO_4$	Reqd.	64.95	4.3	3.8
							Found	65.2	4.3	3.8
Me	Ph	90	154	335 (*M*), 304 (*M* − OCH_3), 289 (*M* − H_3COCH_3)	2 216 (C≡N), 1 757 (C=O), 1 635 (C=C–O)	$C_{20}H_{17}NO_5$	Reqd.	71.65	5.1	4.2
							Found	71.4	5.1	4.1
Me	*p*-$MeOC_6H_4$	90	164	365 (*M*), 334 (*M* − OCH_3), 319 (*M* − H_3COCH_3)	2 202 (C≡N), 1 753 (C=O), 1 631 (C=C–O)	$C_{21}H_{19}NO_5$	Reqd.	69.05	5.25	3.85
							Found	68.9	5.2	3.8
Et	Ph	88	121	363 (*M*), 318 (*M* − OC_2H_5), 289 (*M* − $H_5C_2OC_2H_5$)	2 210 (C≡N), 1 751 (C=O), 1 636 (C=C–O)	$C_{22}H_{21}NO_4$	Reqd.	72.7	5.8	3.85
							Found	72.5	5.8	3.9

TABLE 5

3-Alkoxy-5-cyano-2-pyrones (14; R^3 = Ph) (Scheme 5)

R^1	R^2	Yield (%)	M.p. (°C)	*m/e*	$\nu_{max.}$(KBr)/cm^{-1}	$\lambda_{max.}$(CHCl$_3$)/nm			Analyses (%)		
									C	H	N
Me	*p*-$O_2N{\cdot}C_6H_4$	97	228	348 (*M*), 333 (*M* − CH_3), 317 (*M* − OCH_3)	2 229 (C≡N), 1 732 (C=O), 1 606 (C=C–O)	295	$C_{19}H_{12}N_2O_5$	Reqd.	65.5	3.45	8.05
								Found	65.7	3.45	8.1
Me	*p*-ClC_6H_4	98	152	339/337 (*M*), 324/322 (*M* − CH_3), 308/306 (*M* − OCH_3)	2 232 (C≡N), 1 731 (C=O), 1 611 (C=C–O)	300	$C_{19}H_{12}ClNO_3$	Reqd.	67.55	3.6	4.15
								Found	67.2	3.6	4.2
Me	Ph	90	153	303 (*M*), 288 (*M* − CH_3), 272 (*M* − OCH_3)	2 225 (C≡N), 1 735 (C=O), 1 611 (C=C–O)	301	$C_{19}H_{13}NO_3$	Reqd.	75.25	4.3	4.6
								Found	75.1	4.36	4.7
Me	*p*-MeO·C_6H_4	50	194	333 (*M*), 318 (*M* − CH_3), 302 (*M* − OCH_3)	2 220 (C≡N), 1 732 (C=O), 1 609 (C=C–O)	294	$C_{20}H_{15}NO_4$	Reqd.	72.05	4.55	4.2
								Found	71.9	4.5	4.2
Et	Ph	92	124	317 (*M*), 288 (*M* − C_2H_5), 272 (*M* − OC_2H_5)	2 230 (C≡N), 1 726 (C=O), 1 610 (C=C–O)	303	$C_{20}H_{15}NO_3$	Reqd.	75.7	4.75	4.4
								Found	75.7	4.85	4.4

TABLE 6

2,2,3-Trialkoxy-5-cyano-2*H*-pyrans (15) (Scheme 6)

R^1	R^2	Yield (%)	M.p. (°C)	*m/e*	$\nu_{max.}$(KBr)/cm^{-1}	$\lambda_{max.}$(CHCl$_3$)/nm			Analyses (%)			Reaction temp./time
									C	H	N	
Me	*p*-ClC_6H_4	73	96	385/383 (*M*), 370/368 (*M* − CH_3), 354/352 (*M* − OCH_3)	2 218 (C≡N), 1 639 (C=C–O)	332	$C_{21}H_{18}ClNO_4$	Reqd.	65.7	4.75	3.65	25 °C/
								Found	65.9	4.8	3.7	8 h
Me	Ph	92	102	349 (*M*), 334 (*M* − CH_3), 318 (*M* − OCH_3)	2 210 (C≡N), 1 636 (C=C–O)	332	$C_{21}H_{19}NO_4$	Reqd.	72.2	5.5	4.0	Reflux/
								Found	72.4	5.6	3.9	3 h
Me	MeO·C_6H_4	90	152	379 (*M*), 364 (*M* − CH_3), 348 (*M* − OCH_3)	2 210 (C≡N), 1 639 (C=C–O)	336	$C_{22}H_{21}NO_5$	Reqd.	69.65	5.6	3.7	Reflux/
								Found	69.3	5.5	3.6	8 h
Me	2-Furyl	90	95	339 (*M*), 324 (*M* − CH_3), 308 (*M* − OCH_3)	2 210 (C≡N), 1 638 (C=C–O)	331	$C_{19}H_{17}NO_5$	Reqd.	67.25	5.05	4.15	Reflux/
								Found	67.6	5.1	4.1	3 h
Et	Ph	75	Oil	391 (*M*), 362 (*M* − C_2H_5), 346 (*M* − OC_2H_5)	2 215 (C≡N), 1 635 (C=C–O)	342						Reflux/ 3 h

β-Cyanocinnamaldehydes ($R^3 = H$) were prepared as described by Wasserman.[23] The *p*-methoxy-compound ($R^2 = p$-MeO·C_6H_4) was obtained in 33% yield and had m.p. 137°.

2,2,3,3-*Tetra-alkoxy-5-cyano-3,4-dihydro-2H-pyrans* (4) (*Table* 1).—A mixture of a tetra-alkoxyethene (0.02 mol) and a β-acyl-β-cyanostyrene (0.01 mol) was heated without solvent at 100 °C. After 1 h the excess of tetra-alkoxyethene was evaporated off and the residual oil crystallized from methanol.

αα-*Dialkoxy-γ-cyano-δ-oxo-esters* (11) (*Table* 2).—The product (4) from the previous preparation (3 mmol), dissolved in dioxan (35 ml) and water (35 ml), was treated with concentrated hydrochloric acid (0.3 ml) and refluxed for 1 h. Evaporation left a residue which was dissolved in chloroform. The solution was washed three times with a saturated sodium chloride solution (until neutral), dried (Na_2SO_4), filtered, and evaporated. The residue was crystallized from methanol.

5-*Cyano-3-hydroxy-2-pyrones* (12b) (*Table* 3).—The same procedure was used as in the foregoing preparation, but refluxing was continued for 24 h. The solvent was then removed, and on addition of chloroform to the oily residue the crystalline product (12b) was precipitated.

3,3-*Dialkoxy-5-cyano-3,4-dihydro-2-pyrones* (13) (*Table* 4).—Finely divided tetra-alkoxycyanodihydropyran (4) (1 mmol) was dissolved in concentrated sulphuric acid (5 ml) at 0 °C with stirring. After 1 h the solution was poured on to crushed ice. The mixture was then extracted three times with chloroform, and the combined extracts were washed three times with saturated sodium chloride solution (until neutral), dried (Na_2SO_4), filtered, and evaporated. The residual oil was crystallized from methanol.

3-*Alkoxy-5-cyano-2-pyrones* (14) (*Table* 5).—The procedure was the same as the foregoing, but the reaction mixture was stirred for 1 h at 25 °C.

2,2,3-*Trialkoxy-5-cyano-2H-pyrans* (15) (*Table* 6).—Sodium methoxide (2 mmol) was added to a solution of the tetra-alkoxycyanodihydropyran (4) (1 mmol) in dry 1,2-dimethoxyethane (10 ml). The mixture was stirred for the time and at the temperature indicated in Table 6. The solution was then evaporated and the residue dissolved in water. This solution was extracted three times with chloroform and the combined extracts were washed three times with saturated sodium chloride solution, dried (Na_2SO_4), filtered, and evaporated. The residue was crystallized from methanol.

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