

## Chemistry of Tetra-alkoxyethenes. Part VII.<sup>1</sup> Thermal [2 + 2] Cycloadditions with 1-Cyanobutadienes

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Acyclic 1-cyanobutadienes (2) having a second electron-withdrawing substituent at C-1 behave towards tetra-alkoxyethenes (1) like equally substituted simple olefins. The normal product is a [2 + 2], not a [4 + 2] cycloaddition product. The correspondence in reactivity of these electron-poor olefins and butadienes towards the nucleophilic tetra-alkoxyethenes is further exemplified by the similarity of substituent effects on the cycloadditions. A possible explanation is given.

We have shown previously<sup>2,3</sup> that under thermal conditions tetra-alkoxyethenes (1) give [2 + 2] cycloaddition products with electron-poor olefins having two electron-withdrawing groups at one of the olefinic carbon atoms. However, when one of the electron-withdrawing substituents in the electrophilic olefin is an acyl residue, as in  $\alpha$ -cyano- $\alpha\beta$ -unsaturated carbonyl compounds, only [4 + 2] cycloaddition products arise.

In connection with these results we have now investigated the behaviour of tetra-alkoxyethenes towards

butadienes having a low  $\pi$ -electron density. Preliminary experiments had revealed that two electron-withdrawing substituents (CN and X) were necessary in the diene (2) for sufficient reactivity.

*A priori*, two types of cyclization would be expected: formation of a cyclobutane derivative (3), as obtained with simple electron-poor olefins, or [4 + 2] cycloaddition, leading to a six-membered ring (4) (Scheme 1). The latter reaction, which corresponds to a Diels–Alder reaction with inverse electron demand,<sup>4-6</sup> has been

<sup>1</sup> Part VI, P. H. J. Ooms, L. P. C. Delbressine, J. W. Scheeren, and R. J. F. Nivard, preceding paper.

<sup>2</sup> R. W. Hoffmann, U. Bressel, J. Gehlhaus, and H. Häuser, *Chem. Ber.*, 1971, **104**, 873.

<sup>3</sup> P. H. J. Ooms, J. W. Scheeren, and R. J. F. Nivard, *Synthesis*, 1975, 260.

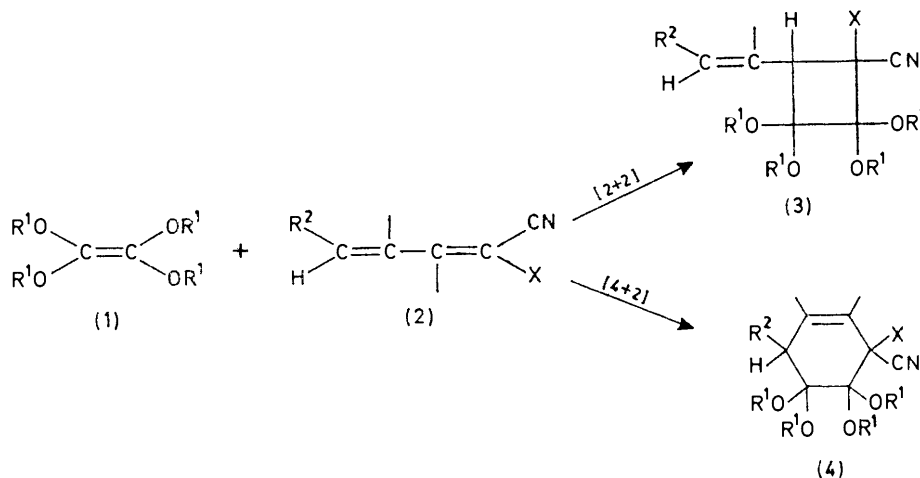
<sup>4</sup> Houben-Weyl, 'Methoden der Organischen Chemie,' 4 Aufl., Band V/c, Thieme Verlag, Stuttgart, 1968, p. 1040.

<sup>5</sup> J. Sauer, *Angew. Chem.*, 1966, **78**, 233; *Angew. Chem. Internat. Edn.*, 1966, **5**, 211.

<sup>6</sup> J. Sauer, *Angew. Chem.*, 1967, **79**, 76; *Angew. Chem. Internat. Edn.*, 1967, **6**, 16.

observed previously for other electron-rich olefins such as enol ethers,<sup>7</sup> keten acetals,<sup>8,9</sup> and enamines.<sup>10-12</sup> The [4 + 2] cycloadducts obtained with enol ethers and keten acetals, were derived however, from diene systems incorporated in an aromatic molecule (isoquinolinium salts

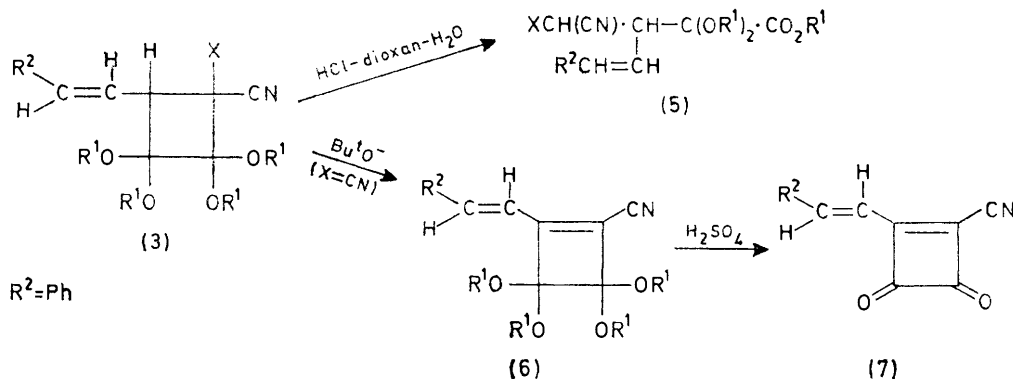
isolated in high yield (70–95%). Only compounds (2; R<sup>2</sup> = Me, X = CN, and R<sup>2</sup> = Ph, X = SO<sub>2</sub>Ph) gave mixtures of products, which could not be readily separated. The vinylcyclobutane structure of the products is apparent from spectroscopic data (Tables 1 and 2) and



SCHEME 1

and 4a-azonia-anthracenes, respectively) which are very unsuitable for giving [2 + 2] cycloaddition products. Reported [4 + 2] cycloadditions of enamines are described generally as two-step reactions, and in one case

chemical properties, which are similar to those of 1,1,2,2-tetra-alkoxy-3-cyanocyclobutanes. Heating the products (3) in dioxan–water under reflux with hydrogen chloride as catalyst<sup>14</sup> gave acetals of  $\alpha$ -oxo-esters (5)



SCHEME 2

the isolation of the supposed dipolar intermediate has been claimed.<sup>13</sup>

Our experiments with several acyclic, electron-poor dienes (2) revealed that their normal cycloadducts with tetra-alkoxyethenes are cyclobutane derivatives (3). In most cases the [2 + 2] cycloaddition product could be

(Table 3). Treatment of compound (3; R<sup>1</sup> = Me, R<sup>2</sup> = Ph, X = CN) with potassium t-butoxide in 1,2-dimethoxyethane<sup>15</sup> gave the 1-cyano-3,3,4,4-tetramethoxy-2-styrylcyclobutene (6). Dissolution of (6) in concentrated sulphuric acid at room temperature<sup>16</sup> caused

<sup>7</sup> C. K. Bradsher and F. H. Day, *Tetrahedron Letters*, 1971, 409.

<sup>8</sup> D. L. Fields and T. H. Regan, *J. Org. Chem.*, 1971, **36**, 2986, 2991.

<sup>9</sup> D. L. Fields and T. H. Regan, *J. Heterocyclic Chem.*, 1973, **10**, 195.

<sup>10</sup> S. Danishefsky and R. Cunningham, *J. Org. Chem.*, 1965, **30**, 3676.

<sup>11</sup> G. Märkl and R. Fuchs, *Tetrahedron Letters*, 1972, 4695.

<sup>12</sup> S. D. Darling and N. Subramanian, *J. Org. Chem.*, 1975, **40**, 2851.

<sup>13</sup> R. Gompper, *Angew. Chem.*, 1969, **81**, 348; *Angew. Chem. Internat. Edn.*, 1969, **8**, 312.

<sup>14</sup> P. H. J. Ooms, J. W. Scheeren, and R. J. F. Nivard, *Synthesis*, 1975, 662.

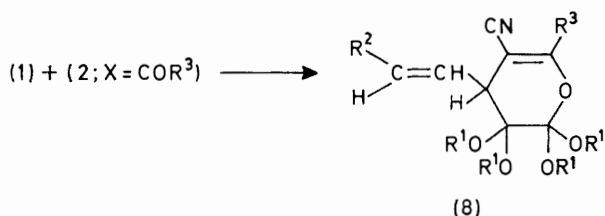
<sup>15</sup> P. H. J. Ooms, J. W. Scheeren, and R. J. F. Nivard, *Synthesis*, 1975, 263.

<sup>16</sup> P. H. J. Ooms, J. W. Scheeren, and R. J. F. Nivard, *Synthesis*, 1975, 639.

hydrolysis of both acetal functions, yielding 3-cyano-4-styrylcyclobut-3-ene-1,2-dione (7) (Scheme 2). Benzaldehyde was detected in the reaction mixture after ozonolysis of (3) with reductive work-up.

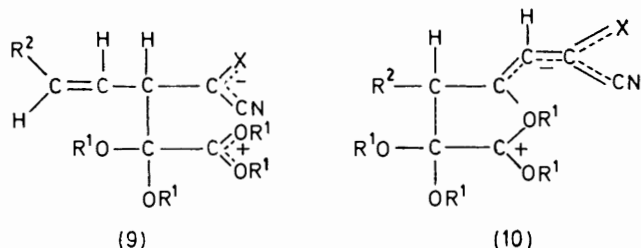
The similarity in reactivity of electrophilic olefins and dienes towards tetra-alkoxyethenes is also obvious from the influence of variations in  $R^2$  and X on the cycloadditions. In general they become slower as  $R^2$  becomes bulkier, or more electron-donating (Table 1), whereas variations in X lead to a decrease in the reaction rate in the order  $X = \text{CN} \sim \text{SO}_2\text{Ph} > \text{CO}_2\text{R} > \text{CO}\cdot\text{NH}_2$  (Table 2). It is probable, therefore, that the  $[2 + 2]$  cycloadducts arise *via* a polar mechanism. Dienes (2;  $X = R^3\text{CO}$ ) once again yielded tetra-alkoxydihydropyrans (8) (Scheme 3), in this case containing a vinyl substituent ( $R^2\text{CH}=\text{CH}-$ ) at C-4 (Table 4).

The high regioselectivity in the cycloadditions of the dienes (2) to tetra-alkoxyethenes, apparent from the absence of the thermodynamically more stable  $[4 + 2]$



SCHEME 3

cycloadducts in the products, may be ascribed to conformational and steric factors. True Diels-Alder reactions proceeding *via* a concerted mechanism are hampered when the parent diene has a preferred *transoid* conformation or when crowding occurs in the transition state, due to a large number of substituents in diene and dienophile.<sup>5,6</sup> Both factors are unfavourable for the conversion of (1) and (2) into (4) *via* a concerted process: (2) is a trisubstituted diene having a large preference for the *transoid* conformation and (1) is a tetrasubstituted



olefin. Non-concerted cycloadditions of (2) might proceed *via* dipolar intermediates (9) or (10). The formation of (9) would be followed by a fast ring closure since the intermediate arises and remains in the *U*-form repre-

sented.<sup>13,17-19</sup> This is not the case with (10), in which the *U*-form is less stabilized by coulombic interaction, and near approach of the terminal carbon atoms is hampered by the stiffened *transoid* conformation of the diene system.

## EXPERIMENTAL

All products were characterized by m.p.s and mass, i.e. (KBr pellets) and u.v. spectra (solutions in chloroform).

**1-Cyanobutadienes** [ $R^2\text{CH}:\text{CH}:\text{CH}:\text{C}(\text{CN})\text{X}$ ] (Table 5).—All butadienes used in the cycloaddition reactions were obtained by Knoevenagel condensations between appropriate  $\alpha\beta$ -unsaturated aldehydes and cyanomethylene compounds. The solvent, catalyst, and reaction times varied depending on the nature of  $R^2$  and X.

(a) ( $R^2 = \text{aryl}$ ,  $X = \text{CN}$ ). To a solution of 0.01 mol of each component in alcohol (25 ml), one drop of piperidine was added at room temperature. Next day the precipitate was filtered off and crystallized from alcohol.

(b) ( $R^2 = \text{Ph}$ ,  $X = \text{SO}_2\text{Ph}$ ). The same procedure was followed [piperidine-acetic acid (1 : 3) as catalyst].

(c) ( $R^2 = \text{Ph}$ ,  $X = \text{CO}\cdot\text{NH}_2$ ). Cinnamaldehyde (0.01 mol) was dissolved in alcohol (10 ml), and cyanoacetamide (0.01 mol) in water (10 ml). The solutions were mixed and treated as under (a).

(d) ( $R^2 = \text{Me}$ ,  $X = \text{CN}$ ). To a solution of crotonaldehyde (0.01 mol) and malononitrile (0.008 mol) in benzene (10 ml), one drop of diethylamine was added. After 15 h at room temperature the solution was extracted with dilute hydrochloric acid and water, dried ( $\text{CaSO}_4$ ), filtered, and evaporated. The residue was crystallized from petroleum (b.p. 80–100 °C). The yield (15%) is low as a consequence of polymerization.

(e) ( $R^2 = \text{Pr}^i$ ,  $X = \text{CN}$ ). A mixture containing 4-methylpent-2-enal (0.01 mol), malononitrile (0.01 mol), ammonium acetate (0.08 g), acetic acid (0.25 ml), and benzene (3 ml) was heated under reflux for 4 h. The solvents were evaporated off and the residue subjected to bulb-tube distillation at 125 °C and 0.01 Torr.

(f) ( $R^2 = \text{Ph}$ ,  $X = \text{CO}_2\text{Et}$  or  $\text{Bz}$ ). These products were prepared according to literature procedures.<sup>20,21</sup>

**2,2,3,3-Tetra-alkoxy-4-vinylcyclobutane-1-carbonitriles** (3) (Tables 1 and 2).—A tetra-alkoxyethene (0.01 mol) was added to a solution of a 1-cyanobutadiene (2) (0.01 mol) in dry acetonitrile (5 ml) at room temperature. The butadienes with  $X = \text{CO}_2\text{Et}$  or  $\text{CO}\cdot\text{NH}_2$  were dissolved in a two-fold excess of a tetra-alkoxyethene without solvent. The mixture was heated at the temperature and for the time indicated in Tables 1 and 2. The solvent and the excess of tetra-alkoxyethene were then evaporated off and the residue was crystallized from methanol.

**2,2,3,3-Tetra-alkoxy-5-cyano-6-phenyl-4-styryl-3,4-dihydro-2H-pyrans** (8) (Table 4). A mixture of 1-benzoylbuta-1,3-dienonitrile (0.01 mol) and a tetra-alkoxyethene (0.02 mol) was heated at 100 °C for 1 h. The excess of tetra-alkoxyethene was evaporated off, and the residual oil was crystallized from methanol (ethanol for the ethoxy-compound).

**Acetals of  $\alpha$ -Oxo-esters** (5) (Table 3).—A solution of a cyclobutane (3) (3 mmol) in dioxan (35 ml), distilled water (35

<sup>17</sup> R. W. Hoffmann, *Angew. Chem.*, 1968, **80**, 823; *Angew. Chem. Internat. Edn.*, 1968, **7**, 745.

<sup>18</sup> H. K. Hall, jun., and P. Ykman, *J. Amer. Chem. Soc.*, 1975, **97**, 800.

<sup>19</sup> R. Schug and R. Huisgen, *J.C.S. Chem. Comm.*, 1975, 60.

<sup>20</sup> F. D. Popp and A. Catala, *J. Org. Chem.*, 1961, **26**, 2738.

<sup>21</sup> Nguyen Kim Son, R. Pinel, and Y. Mollier, *Bull. Soc. chim. France*, 1974, 471.

TABLE 1

## 2,2,3,3-Tetra-alkoxy-4-vinylcyclobutane-1,1-dicarbonitriles (3; X = CN)

R <sup>1</sup>	R <sup>2</sup> <sup>a</sup>	Reaction temp/time	Yield (%)	M.p. (°C)	<i>m/e</i>	$\nu_{\max}$ (KBr)/ cm <sup>-1</sup> <sup>b</sup>	$\lambda_{\max}$ (CHCl <sub>3</sub> )/ nm ( $\epsilon$ ) <sup>c</sup>		Analyses (%)			
									C	H	N	
Me	Me <sup>d</sup>	25 °C/24 h	70	(Oil)	266 ( <i>M</i> ), 251 ( <i>M</i> - CH <sub>3</sub> ), 235 ( <i>M</i> - OCH <sub>3</sub> )							
Me	Pr <sup>1</sup>	25 °C/48 h	70	(Oil)	279 ( <i>M</i> - CH <sub>3</sub> ), 263 ( <i>M</i> - OCH <sub>3</sub> )	2 240 (C≡N), 980 (C-H)						
Me	<i>p</i> -NO <sub>2</sub> ·C <sub>6</sub> H <sub>4</sub>	70 °C/2 h	95	153	358 ( <i>M</i> - CH <sub>3</sub> ), 342 ( <i>M</i> - OCH <sub>3</sub> )	2 240 (C≡N), 1 604 (C=C), 978 (C-H)	309 (18 300)	C <sub>18</sub> H <sub>19</sub> N <sub>3</sub> O <sub>6</sub>	Reqd. 57.9 Found 57.9	5.15 5.1	11.2 11.1	
Me	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	70 °C/4 h	86	99	333/331 ( <i>M</i> - OCH <sub>3</sub> )	2 240 (C≡N), 1 592 (C=C), 982 (C-H)	265	C <sub>18</sub> H <sub>19</sub> ClN <sub>2</sub> O <sub>4</sub>	Reqd. 59.6 Found 60.0	5.3 5.3	7.7 7.8	
Me	Ph	70 °C/5 h	88	105	313 ( <i>M</i> - CH <sub>3</sub> ), 297 ( <i>M</i> - OCH <sub>3</sub> )	2 243 (C≡N), 1 600 (C=C), 978 (C-H)	259 (20 700)	C <sub>18</sub> H <sub>20</sub> N <sub>2</sub> O <sub>4</sub>	Reqd. 65.85 Found 65.8	6.15 6.2	8.5 8.7	
Me	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	70 °C/6 h	85	114	327 ( <i>M</i> - CH <sub>3</sub> ), 311 ( <i>M</i> - OCH <sub>3</sub> )	2 243 (C≡N), 1 605 (C=C), 980 (C-H)	266	C <sub>19</sub> H <sub>22</sub> N <sub>2</sub> O <sub>4</sub>	Reqd. 66.65 Found 66.3	6.5 6.5	8.2 8.1	
Me	<i>p</i> -MeO·C <sub>6</sub> H <sub>4</sub>	70 °C/7 h	80	121	358 ( <i>M</i> ), 343 ( <i>M</i> - CH <sub>3</sub> ), 327 ( <i>M</i> - OCH <sub>3</sub> )	2 245 (C≡N), 1 610 (C=C), 973 (C-H)	274 (23 800)	C <sub>19</sub> H <sub>22</sub> N <sub>2</sub> O <sub>5</sub>	Reqd. 63.7 Found 63.6	6.2 6.2	7.8 7.8	
Me	2-Furyl	70 °C/6 h	85	125	303 ( <i>M</i> - CH <sub>3</sub> ), 287 ( <i>M</i> - OCH <sub>3</sub> )	2 242 (C≡N), 1 659 (C=C-O), 967 (C-H)	279	C <sub>18</sub> H <sub>16</sub> N <sub>2</sub> O <sub>5</sub>	Reqd. 60.35 Found 60.0	5.7 5.7	8.8 8.8	
Et	Pr <sup>1</sup>	25 °C/48 h	70	(Oil)	321 ( <i>M</i> - C <sub>2</sub> H <sub>5</sub> ), 305 ( <i>M</i> - OC <sub>2</sub> H <sub>5</sub> )	2 240 (C≡N), 980 (C-H)						
Et	<i>p</i> -NO <sub>2</sub> ·C <sub>6</sub> H <sub>4</sub>	70 °C/2 h	80	127	429 ( <i>M</i> ), 400 ( <i>M</i> - C <sub>2</sub> H <sub>5</sub> ), 384 ( <i>M</i> - OC <sub>2</sub> H <sub>5</sub> )	2 240 (C≡N), 1 600 (C=C), 979 (C-H)	310	C <sub>22</sub> H <sub>27</sub> N <sub>3</sub> O <sub>6</sub>	Reqd. 61.55 Found 61.3	6.35 6.3	9.7 9.7	
Et	Ph	70 °C/5 h	76	90	355 ( <i>M</i> - C <sub>2</sub> H <sub>5</sub> ), 339 ( <i>M</i> - OC <sub>2</sub> H <sub>5</sub> )	2 239 (C≡N), 1 600 (C=C), 970 (C-H)	260 (20 400)	C <sub>22</sub> H <sub>23</sub> N <sub>2</sub> O <sub>4</sub>	Reqd. 68.75 Found 68.3	7.35 7.4	7.2 7.3	
Et	<i>p</i> -MeO·C <sub>6</sub> H <sub>4</sub>	70 °C/7 h	78	96	414 ( <i>M</i> ), 385 ( <i>M</i> - C <sub>2</sub> H <sub>5</sub> ), 369 ( <i>M</i> - OC <sub>2</sub> H <sub>5</sub> )	2 240 (C≡N), 1 606 (C=C), 971 (C-H)	271	C <sub>23</sub> H <sub>30</sub> N <sub>2</sub> O <sub>5</sub>	Reqd. 66.65 Found 66.7	7.3 7.3	6.7 6.8	

<sup>a</sup> <sup>1</sup>H N.m.r. spectra, measured in CS<sub>2</sub> for compounds with R<sup>2</sup> = Ph show  $J_{AB}$  16 and  $J_{BX}$  9 Hz for the ABX system PhCH<sub>2</sub>CH·CH.

<sup>b</sup> The C-H out-of-plane deformation absorption lies in the range 960–990 cm<sup>-1</sup>, characteristic of *trans*-protons. <sup>c</sup> The values for  $\lambda_{\max}$  and  $\epsilon$  are as expected for a styrene unit. <sup>d</sup> Not isolated in pure form.

TABLE 2

2,2,3,3-Tetra-alkoxy-4-styrylcyclobutane-1-carbonitriles (3; R<sup>2</sup> = Ph)

R <sup>1</sup>	X	Reaction temp/time	Yield (%)	M.p. (°C)	<i>m/e</i>	$\nu_{\max}$ (KBr)/ cm <sup>-1</sup> <sup>b</sup>	$\lambda_{\max}$ (CHCl <sub>3</sub> )/ nm ( $\epsilon$ ) <sup>c</sup>		Analyses (%)		
									C	H	N
Me	SO <sub>2</sub> Ph <sup>d</sup>	70 °C/5 h	75		443 ( <i>M</i> ), 428 ( <i>M</i> - CH <sub>3</sub> ), 412 ( <i>M</i> - OCH <sub>3</sub> ), 302 ( <i>M</i> - SO <sub>2</sub> C <sub>6</sub> H <sub>5</sub> )						
Me	CO <sub>2</sub> Et	100 °C/15 h	82	101	360 ( <i>M</i> - CH <sub>3</sub> ), 344 ( <i>M</i> - OCH <sub>3</sub> )	2 240 (C≡N), 1 733 (C=O), 1 595 (C=C), 971 (C-H)	257 (24 300)	C <sub>20</sub> H <sub>25</sub> NO <sub>6</sub>	Reqd. 64.0 Found 64.0	6.7 6.8	3.7 3.7
Me	CO·NH <sub>2</sub>	100 °C/30 h	50	183	346 ( <i>M</i> ), 331 ( <i>M</i> - CH <sub>3</sub> ), 315 ( <i>M</i> - OCH <sub>3</sub> )	2 240 (C≡N), 1 685 (C=O), 1 615 (C=C), 985 (C-H)	257 (22 500)	C <sub>18</sub> H <sub>22</sub> N <sub>2</sub> O <sub>5</sub>	Reqd. 62.4 Found 62.3	6.4 6.4	8.0 8.1
Et	SO <sub>2</sub> Ph <sup>d</sup>	70 °C/5 h	80		470 ( <i>M</i> - C <sub>2</sub> H <sub>5</sub> ), 454 ( <i>M</i> - OC <sub>2</sub> H <sub>5</sub> ), 358 ( <i>M</i> - SO <sub>2</sub> C <sub>6</sub> H <sub>5</sub> )						
Et	CO <sub>2</sub> Et	100 °C/15 h	80	(Oil)	402 ( <i>M</i> - C <sub>2</sub> H <sub>5</sub> ), 386 ( <i>M</i> - OC <sub>2</sub> H <sub>5</sub> )	2 240 (C≡N), 1 748 (C=O), 1 614 (C=C), 970 (C-H)	258	C <sub>21</sub> H <sub>33</sub> NO <sub>6</sub>	Reqd. 66.8 Found 67.5	7.7 7.7	3.2 3.3

For footnotes, see Table 1.

TABLE 3  
 Acetals of  $\alpha$ -oxo-esters (5)<sup>a</sup>

R <sup>1</sup>	R <sup>2</sup>	X	Yield (%)	<i>m/e</i>	$\nu_{\max.}$ (KBr)/ cm <sup>-1</sup>	$\lambda_{\max.}$ (CHCl <sub>3</sub> )/ nm	Analyses (%)				
							C	H	N		
Me	<i>p</i> -O <sub>2</sub> N·C <sub>6</sub> H <sub>4</sub>	CN	88	359 ( <i>M</i> ),	2 220 (C≡N),	300					
				328 ( <i>M</i> - OCH <sub>3</sub> ),	1 750 (C=O),						
				300 ( <i>M</i> - COOCH <sub>3</sub> )	1 598 (C=C)						
Me	Ph	CN	90	314 ( <i>M</i> ),	2 222 (C≡N),	255	C <sub>17</sub> H <sub>18</sub> N <sub>2</sub> O <sub>4</sub>	Reqd.	64.95	5.75	8.9
				283 ( <i>M</i> - OCH <sub>3</sub> ),	1 757 (C=O),						
				255 ( <i>M</i> - COOCH <sub>3</sub> )	1 606 (C=C)						
Me	<i>p</i> -MeO·C <sub>6</sub> H <sub>4</sub>	CN	85	344 ( <i>M</i> ),	2 222 (C≡N),	269	C <sub>18</sub> H <sub>20</sub> N <sub>2</sub> O <sub>5</sub>	Reqd.	62.8	5.85	8.15
				313 ( <i>M</i> - OCH <sub>3</sub> ),	1 750 (C=O),						
				285 ( <i>M</i> - COOCH <sub>3</sub> )	1 605 (C=C)						
Me	Ph	CO <sub>2</sub> Et	75	361 ( <i>M</i> ),	2 220 (C≡N),	252					
				330 ( <i>M</i> - OCH <sub>3</sub> ),	1 777 (C=O),						
				302 ( <i>M</i> - COOCH <sub>3</sub> )	1 743 (C=O)						
Et	Ph	CN	85	311 ( <i>M</i> - OC <sub>2</sub> H <sub>5</sub> ),	2 222 (C≡N),	249	C <sub>20</sub> H <sub>24</sub> N <sub>2</sub> O <sub>4</sub>	Reqd.	67.4	6.8	7.85
				283 ( <i>M</i> - COOC <sub>2</sub> H <sub>5</sub> )	1 750 (C=O),						
					1 609 (C=C)						
Et	Ph	CO <sub>2</sub> Et	80	358 ( <i>M</i> - OC <sub>2</sub> H <sub>5</sub> ),	2 220 (C≡N),	250					
				330 ( <i>M</i> - COOC <sub>2</sub> H <sub>5</sub> )	1 773 (C=O),						
					1 740 (C=O)						

<sup>a</sup> All compounds were obtained as oils, which were not further purified.

 TABLE 4  
 2,2,3,3-Tetra-alkoxy-5-cyano-6-phenyl-4-styryl-3,4-dihydro-2*H*-pyrans (8; R<sup>2</sup> = R<sup>3</sup> = Ph)

R <sup>1</sup>	Yield (%)	M.p. (°C)	<i>m/e</i>	$\nu_{\max.}$ (KBr)/cm <sup>-1</sup>	$\lambda_{\max.}$ (CHCl <sub>3</sub> )/ nm	Analyses (%)				
						C	H	N		
Me	90	126	407 ( <i>M</i> ),	2 205 (C≡N),	274	C <sub>24</sub> H <sub>26</sub> NO <sub>5</sub>	Reqd.	70.75	6.2	3.45
			392 ( <i>M</i> - CH <sub>3</sub> ),	1 622 (C=C-O),						
			376 ( <i>M</i> - OCH <sub>3</sub> )	977 (C-H)						
Et	85	106	463 ( <i>M</i> ),	2 208 (C≡N),	273	C <sub>28</sub> H <sub>33</sub> NO <sub>5</sub>	Reqd.	72.55	7.2	3.0
			434 ( <i>M</i> - C <sub>2</sub> H <sub>5</sub> ),	1 628 (C=C-O),						
			418 ( <i>M</i> - OC <sub>2</sub> H <sub>5</sub> )	973 (C-H)						

 TABLE 5  
 1-Cyanobutadienes (2) by Knoevenagel condensation of  $\alpha\beta$ -unsaturated aldehydes and substituted acetonitriles

R <sup>2</sup>	X	Yield (%)	M.p. (°C)	<i>m/e</i>	$\nu_{\max.}$ (KBr)/ cm <sup>-1</sup> <sup>a</sup>	$\lambda_{\max.}$ (CHCl <sub>3</sub> )/ nm	Analyses (%)				
							C	H	N		
Me	CN	15	52	118 ( <i>M</i> ), 91 ( <i>M</i> - HCN)	22 20 (C≡N),	286	C <sub>7</sub> H <sub>8</sub> N <sub>2</sub>	Reqd.	71.15	5.1	23.7
					1 634 (C=C),						
Pr <sup>i</sup>	CN <sup>b</sup>	65	(Oil)	146 ( <i>M</i> ), 131 ( <i>M</i> - CH <sub>3</sub> ),	2 220 (C≡N),	288					
				104 ( <i>M</i> - CH <sub>3</sub> - HCN)	1 640 (C=C),						
<i>p</i> -O <sub>2</sub> N·C <sub>6</sub> H <sub>4</sub>	CN	75	184	225 ( <i>M</i> ), 179 ( <i>M</i> - NO <sub>2</sub> ),	2 220 (C≡N),	349	C <sub>12</sub> H <sub>7</sub> N <sub>3</sub> O <sub>2</sub>	Reqd.	64.0	3.15	18.65
				152 ( <i>M</i> - NO <sub>2</sub> - HCN)	1 612 (C=C),						
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	CN	76	201	216/214 ( <i>M</i> ), 189/187	2 220 (C≡N),	360	C <sub>12</sub> H <sub>7</sub> ClN <sub>2</sub>	Reqd.	67.15	3.3	13.05
				( <i>M</i> - HCN)	1 609 (C=C),						
Ph	CN <sup>c</sup>	80	130	180 ( <i>M</i> ), 153 ( <i>M</i> - HCN)	2 220 (C≡N),	355	C <sub>12</sub> H <sub>8</sub> N <sub>2</sub>	Reqd.	80.0	4.45	15.55
					1 609 (C=C),						
<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	CN	75	135	194 ( <i>M</i> ), 167 ( <i>M</i> - HCN)	2 220 (C≡N),	370	C <sub>13</sub> H <sub>10</sub> N <sub>2</sub>	Reqd.	80.4	5.2	14.4
					1 599 (C=C),						
<i>p</i> -MeO·C <sub>6</sub> H <sub>4</sub>	CN	85	161	210 ( <i>M</i> ), 183 ( <i>M</i> - HCN)	2 220 (C≡N),	396	C <sub>13</sub> H <sub>10</sub> N <sub>2</sub> O	Reqd.	74.25	4.8	13.35
					1 597 (C=C),						
2-Furyl	CN	80	105	170 ( <i>M</i> ), 143 ( <i>M</i> - HCN)	2 220 (C≡N),	389	C <sub>10</sub> H <sub>6</sub> N <sub>2</sub> O	Reqd.	70.6	3.55	16.45
					1 604 (C=C),						
Ph	SO <sub>2</sub> Ph <sup>d</sup>	93	146	295 ( <i>M</i> ), 153 ( <i>M</i> - HSO <sub>2</sub> C <sub>6</sub> H <sub>5</sub> )	2 218 (C≡N),	349	C <sub>17</sub> H <sub>13</sub> NO <sub>2</sub> S	Reqd.	69.15	4.45	4.75
					1 611 (C=C),						
Ph	CO·NH <sub>2</sub>	65	153	198 ( <i>M</i> ), 182 ( <i>M</i> - NH <sub>2</sub> ),	2 210 (C≡N),	345	C <sub>12</sub> H <sub>10</sub> N <sub>2</sub> O	Reqd.	72.7	5.1	14.15
				171 ( <i>M</i> - HCN)	1 680 (C=O),						
					1 602 (C=C),						
					978 (C-H)						

<sup>a</sup> The values of the C≡N absorptions point to conjugation of the nitrile groups. <sup>b</sup> Purified by bulb-tube distillation at 100 °C and 0.1 Torr. <sup>c</sup> This compound has previously been synthesized with sodium ethoxide as catalyst; (F. W. Hinrichsen and O. Lohse, *Annalen*, 1917, **336**, 325), m.p. 128 °C. <sup>d</sup> Formerly obtained with sodium hydroxide as catalyst; (J. Tröger and A. Prochnow, *J. prakt. Chem.*, 1909, (2) **78**, 123), 148 °C

ml), and concentrated hydrochloric acid (0.3 ml), was heated under reflux for 5 h. The solvent was then evaporated off and the residue dissolved in ether. The solution was extracted with 10% sodium hydrogen carbonate, and the aqueous layer extracted twice with ether. The combined ethereal extracts were washed three times with saturated sodium chloride solution (until neutral), dried ( $\text{Na}_2\text{SO}_4$ ), filtered, and evaporated. The  $\alpha$ -oxo-ester acetals, obtained as oils, were not purified further; bulb-tube distillation at 125 °C and 0.1 Torr caused decomposition. Several samples, however, gave correct elemental analyses. The purity of the others is at least 90% (based on n.m.r. spectra).

**3,3,4,4-Tetramethoxy-2-styrylcyclobut-1-ene-1-carbonitrile (6).**—Potassium t-butoxide (0.04 mol) was added to a solution of compound (3) in dry, 1,2-dimethoxyethane (25 ml), and the mixture was stirred for 1 h at room temperature. The solvent was then evaporated off at room temperature. The mixture was dissolved in water and extracted three times with ether. The combined ethereal extracts were washed three times with water, dried ( $\text{Na}_2\text{SO}_4$ ), filtered, and evaporated. The remaining oil was purified by bulb-tube distillation at 125 °C and 0.1 Torr (yield 80%);  $\nu_{\text{max}}$  (KBr) 2 202 ( $\text{C}\equiv\text{N}$ ), 1 625 ( $\text{C}=\text{C}$ ), and 979  $\text{cm}^{-1}$  ( $\text{C}-\text{H}$ );  $\lambda_{\text{max}}$  ( $\text{CHCl}_3$ ) 326 nm;  $m/e$  301 ( $M$ ), 286 ( $M - \text{CH}_3$ ), and 270 ( $M - \text{OCH}_3$ ).

**3-Cyano-4-styrylcyclobut-3-ene-1,2-dione (7).**—Finely divided compound (6) (0.01 mol) was dissolved in concentrated sulphuric acid (20 ml) with stirring. After 1 h the mixture was poured onto crushed ice, and the cyclobutenedione was obtained as a yellow-brown precipitate. The mixture was extracted three times with chloroform, and the combined extracts were washed three times with saturated sodium chloride solution (until neutral), dried ( $\text{Na}_2\text{SO}_4$ ), filtered, and evaporated, leaving (7) as a crystalline mass, which was not purified further; yield 70%; m.p. 97–99 °C;  $\nu_{\text{max}}$  (KBr) 2 210 ( $\text{C}\equiv\text{N}$ ), 1 773 ( $\text{C}=\text{O}$ ), 1 602 ( $\text{C}=\text{C}$ ), and 975 ( $\text{C}-\text{H}$ )  $\text{cm}^{-1}$  (the strong carbonyl absorption near 1 780  $\text{cm}^{-1}$  is characteristic of carbonyl functions in four-membered ring systems<sup>8,22</sup>);  $\lambda_{\text{max}}$  ( $\text{CHCl}_3$ ) 364 nm;  $m/e$  209 ( $M$ ), 181 ( $M - \text{CO}$ ), and 153 ( $M - 2\text{CO}$ ).

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<sup>22</sup> W. Ried and A. H. Schmidt, *Angew. Chem.*, 1972, **84**, 1048; *Angew. Chem. Internat. Edn.*, 1972, **11**, 997.