taminated with succinimide; both compounds have nearly identical R_f values on TLC. Purification was achieved by repeated extraction of a dichloromethane solution of the mixture with 0.1 N $NaHCO_3$ solution. After the mixture was dried (Na_2SO_4) and the solvent evaporated, sultine **5b** was obtained in 32% yield.

5a: R_f 0.77 (eluent MeOH/CH_2Cl_2, 1/9 v/v); NMR ($CDCl_3$) δ 3.06 and 3.32 (AB part of ABX spectrum, J_{AX} = 1.2 Hz, J_{BX} = 6.3 Hz, J_{AB} = 13.2 Hz, 2 H, CH_2S), 4.67 and 4.84 (AB part of ABX spectrum, J_{AX} = 1.7 Hz, J_{BX} = 5.4 Hz, J_{AB} = 9.9 Hz, 2 H, CH_2O), 5.22–5.60 (m, 1 H, $CHCH_2O$), 7.17–8.11 (m, 6 H, C_6H_5 and NH); IR (KBr) 3280, 1640, 1535, 1060 cm^{-1}; mass spectrum, m/e 225 (M^+), 161 ($-SO_2$). Anal. Calcd for $C_{10}H_{11}NO_3S$: C, 53.32; H, 4.92; N, 6.22. Found: C, 53.12; H, 4.86; N, 6.19.

5b: R_f 0.40 (eluent MeOH/CH_2Cl_2, 1/9 v/v); NMR ($CDCl_3$) δ 3.24 and 3.60 (AB part of ABX spectrum, J_{AX} = 3 Hz, J_{BX} = 6.6 Hz, J_{AB} = 14 Hz, 2 H, CH_2S), 4.60 and 4.89 (AB part of ABX spectrum, J_{AX} = 1.5 Hz, J_{BX} = 4.6 Hz, J_{AB} = 10 Hz, 2 H, CH_2O), 5.00–5.29 (m, 1 H, $CHCH_2O$), 6.87 (d, 1 H, NH), 7.16–7.84 (m, 5 H, C_6H_5); IR (KBr) 3300, 1650, 1530, 1030 cm^{-1}; mass spectrum, 225 (M^+), 161 ($-SO_2$). Anal. Calcd for $C_{10}H_{11}NO_3S$: C, 53.32; H, 4.92; N, 6.22. Found: C, 53.26; H, 4.90; N, 6.22.

4-Benzamido-5,5-dideuterio-1,2-oxothiolane 2-Oxide (5a,b-d_2). The synthesis of **5a**-d_2 and **5b**-d_2 from **4**-d_2 was carried out as described above for **5a** and **5b**, yielding the compounds in 43% and 29%, respectively.

5a-d_2: R_f 0.77 (eluent MeOH/CH_2Cl_2, 1/9 v/v); NMR ($CDCl_3$) δ 3.06 and 3.32 (AB part of ABX spectrum, J_{AX} = 1.2 Hz, J_{BX} = 6.3 Hz, J_{AB} = 13.2 Hz, 2 H, CH_2S), 4.55–5.02 (residual protons CH_2O; 15% by integration), 5.44 (d of t, 1 H, $CHCH_2O$), 7.17–8.11 (m, 6 H, C_6H_5 and NH); mass spectrum, m/e 227 (M^+), 163 ($-SO_2$). Anal. Calcd for $C_{10}D_2H_9NO_3S$: C, 52.85; N, 6.16. Found: C, 52.67; N, 6.08.

5b-d_2: R_f 0.40 (eluent MeOH/CH_2Cl_2, 1/9 v/v); NMR ($CDCl_3$) δ 3.24 and 3.60 (AB part of ABX spectrum, J_{AX} = 3 Hz, J_{BX} = 6.6 Hz, J_{AB} = 14 Hz, 2 H, CH_2S), 4.59 and 4.89 (residual protons CH_2O; 15% by integration), 5.14 (d of t, 1 H, $CHCH_2O$), 6.82 (d, 1 H, NH), 7.16–7.84 (m, 5 H, C_6H_5); mass spectrum, m/e 227 (M^+), 163 ($-SO_2$). Anal. Calcd for $C_{10}D_2H_9NO_3S$: C, 52.85; N, 6.16. Found: C, 53.03; N, 6.28.

3-Benzamidoprop-1-ene (6), 3-Benzamido-(*Z*)-prop-2-ene (7), 3-Benzamido-(*E*)-prop-2-ene (8). The FVT of **5a** or **5b** (0.5 g, 2.2 mmol) was carried out as described above. The products were separated by HPLC (eluent CH_2Cl_2) to give **6**–**8** in yields of 40–50%, 2%, and 7%, respectively.

6: R_f 0.66 (MeOH/CH_2Cl_2, 1/9 v/v); NMR ($CDCl_3$) δ 4.08 (Y_2 part of $ABXY_2$ spectrum, J_{AY} = J_{BY} = 1.6 Hz, J_{XY} = $J_{Y\text{-}NH}$ = 5.6 Hz, 2 H, $NHCH_2$), 5.17 and 5.24 (AB part of $ABXY_2$ spectrum, J_{AB} = 3.2 Hz, J_{AX} = 17.2 Hz, J_{BX} = 10 Hz, 2 H, $C{=}CH_2$), 5.95 (X part of $ABXY_2$, spectrum 1 H, CH_2CH), 6.16–6.76 (br, 1 H, NH), 7.07–7.93 (m, 5 H, C_6H_5); IR ($CHCl_3$) 3460, 3360, 1660, 1520, 995, 930 cm^{-1}; mass spectrum, m/e 161 (M^+).

7: R_f 0.81 (MeOH/CH_2Cl_2, 1/9 v/v); NMR ($CDCl_3$) δ 1.70 (X_3 part of ABX_3 spectrum, d of d, J_{BX} = 6.9 Hz, J_{AX} = 1.7 Hz, 3 H, $CHCH_3$), 4.95 (B part of ABX_3 spectrum, J_{AB} = 8.4 Hz, 1 H, $CHCH_3$), 6.93 (A part of ABX_3 spectrum, J_{AX} = 1.8 Hz, $J_{A\text{-}NH}$ = 10.0 Hz, 1 H, NHCH), 7.30–7.96 (m, 6 H, C_6H_5, NH); mass spectrum, m/e 161 (M^+).

8: R_f 0.73 (MeOH/CH_2Cl_2, 1/9 v/v); NMR ($CDCl_3$) δ 1.74 (X_3 part of ABX_3 spectrum, d of d, J_{BX} = 6.8 Hz, J_{AX} = 11.6 Hz, 3 H, $CHCH_3$), 5.31 (B part of ABX_3 spectrum, J_{AB} = 13.8 Hz, 1 H, $CHCH_3$), 6.97 (A part of ABX_3 spectrum, $J_{A\text{-}NH}$ = 10.0 Hz, 1 H, NHCH), 7.30–8.00 (m, 6 H, C_6H_5, NH); mass spectrum, m/e 161 (M^+).

Acknowledgment. We thank Mr. J. M. J. Verlaak for his assistance in carrying out the FVT experiments, Professor Dr. B. Zwanenburg and Dr. A. J. H. Klunder for making available the FVT apparatus, and H. H. K. Brinkhof for the ^1H NMR spectra and helpful discussions. We are indebted to J. Zwinselman and Professor Dr. N. Nibbering (University of Amsterdam) for the electron-impact and field-ionization mass spectra. Part of the investigations was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research.

Registry No. **4**, 86290-15-5; **4**-d_2, 86290-17-7; **5a**, 86290-16-6; **5a**-d_2, 86290-18-8; **5b**, 86334-10-3; **5b**-d_2, 86334-11-4; **6**, 10283-95-1; **7**, 5500-46-9; **8**, 5202-76-6; *N*-benzoyl-L-cystine methyl ester, 5673-91-6.

Chemistry of Ketene Acetals. 7.† 2-Methoxy-4*H*-pyrans as Strong Hydride Donors in Reactions with Electrophilic Olefins

C. G. Bakker, C. J. J. M. Hazen, J. W. Scheeren,* and R. J. F. Nivard

Department of Organic Chemistry, Catholic University, Toernooiveld, 6525 ED Nijmegen, The Netherlands

Received October 26, 1982

The reactions of 2-methoxy-5,6-dihydropyrans (**2**) and 2-methoxy-4*H*-pyrans (**3**) with a variety of electrophilic olefins $R^4R^5C{=}C(CN)X$ have been studied. Cyclobutanes are formed in an equilibrium reaction from **2** as well as **3**. In general, the compounds **3** give ultimately the thermodynamically stable heptadienoic esters **10**. 2-Methoxy-4*H*-pyrans, substituted at carbon atom 6, yield, however, a pyrone derivative (**11**) when they react with strongly electrophilic olefins substituted with three or four electron-withdrawing groups. Both conversions are supposed to occur via the abstraction of a hydride ion from C(4) in a rate-determining step leading to a pyrylium ion (**14**). The further course of the process is determined by the character of the nucleophile formed in the addition of the hydride ion to the olefin and by the substitution pattern of **3**.

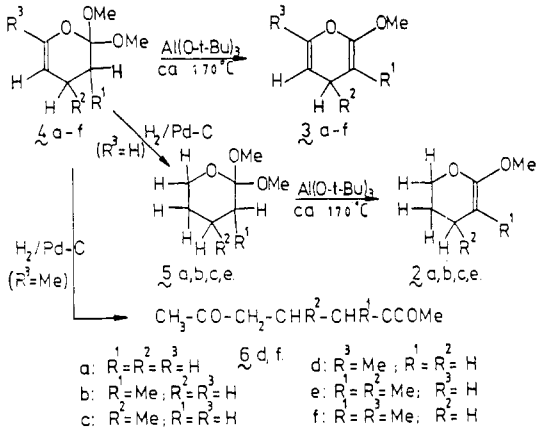
In combination with an investigation of cycloadditions between acyclic ketene acetals, $RR^1C{=}C(OMe)_2$ (**1**), and electrophilic alkenes or dienes[1] we studied the reactivity of two types of *cyclic* ketene acetals, viz., 2-methoxy-5,6-dihydropyrans (**2**) and 2-methoxy-4*H*-pyrans (**3**) toward electrophilic olefins. Apart from a possible effect of the second double bond on the rate and equilibrium constant of the expected cyclobutane formation, the investigation

† Part 6: C. G. Bakker, P. H. M. Ooms, J. W. Scheeren, and R. J. F. Nivard, *Recl. Trav. Chim. Pays-Bas*, **102**, 130 (1983).

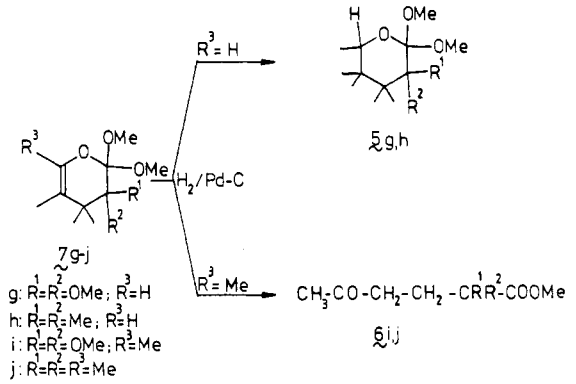
(1) H. W. Scheeren, A. J. R. van Rossum, and R. J. F. Nivard, *Tetrahedron*, **39**, 1345 (1983).

0022-3263/83/1948-2736$01.50/0

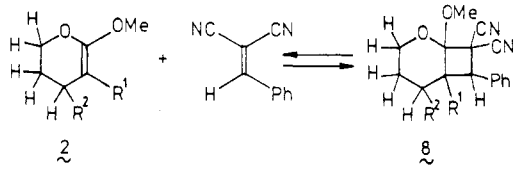
Scheme I



Scheme II



Scheme III



Scheme IV

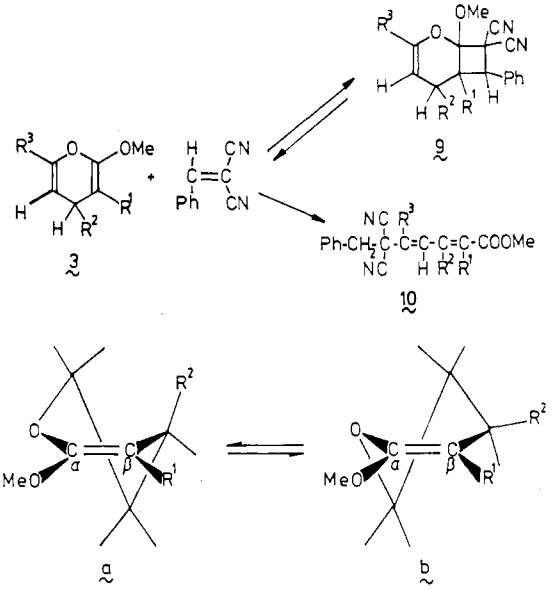


Figure 1. Conformational equilibrium of ketene acetals **2**.

of the reactivity of the compounds **3** seemed especially worthwhile, since competing ($2_\pi + 2_\pi + 2_\pi$) cycloadditions or ene reactions might be induced by the presence of the 1,4-pentadiene moiety in **3**. Until now, homo-Diels–Alder reactions of the related 1,4-cyclohexadienes have only been observed[2] with compounds having a rigid structure like norbornadiene, but ene reactions leading to benzene derivatives have recently been reported[3] for simple 1,3- and 1,4-cyclohexadienes in reaction with tetracyanoethylene (TCNE).

Preparation of the Cyclic Ketene Acetals 2 and 3. The cyclic ketene acetals **2a** and **3a** were obtained according to a procedure used by McElvain,[4] viz., by elimination of MeOH from the corresponding ortho esters (**4** and **5**, Scheme I). McElvain converted **4a** into **5a** by catalytic hydrogenation with Raney nickel. A general method for the preparation of 2,2-dimethoxy-3,4-dihydropyrans (**4**) by $ZnCl_2$-catalyzed cycloadditions of ketene acetals and α,β-unsaturated carbonyl compounds was recently described.[5] This hydrogenation using Pd on charcoal as a catalyst to the corresponding tetrahydropyrans (**5**) did not appear to be completely general; **4d** and **4f** underwent mainly hydrogenolysis of a MeO bond, yielding the δ-keto esters **6d** and **6f** (cf. ref 6). This deviant behavior may be due to the presence of a Me substituent (R^3) at the double bond; a similar hydrogenolysis of an ortho ester bond was observed with 2,2,3,3-tetramethoxy- and 2,2-dimethoxy-3,3-dimethyldihydropyrans (Scheme II) when a Me substituent is present at the olefinic bond (see Experimental Section and Table I). The cyclic ketene acetals are sensitive to oxygen (**3** more than **2**, especially when R^1 = H), giving brown syrupy liquids due to polymerization.[7] They can be stored indefinitely, however, under nitrogen at −30 °C.

Cycloadditions of 2 with Dicyanostyrene. Quite analogous to the acyclic ketene acetals **1**, the cyclic acetals **2** react in chloroform with an equivalent amount of dicyanostyrene to yield a cyclobutane (**8**) via a reversible cycloaddition[8] (Scheme III). With **2b** (R^1 = Me, R^2 = H) at room temperature, the ratio of **8**/**2b** at equilibrium (ca. 1) appeared, however, to be much lower than in the analogous reaction of $(Me)_2C{=}C(OMe)_2$ and dicyanostyrene (ratio ca. 9). This prevented isolation of **8**. The NMR spectrum of the product **8** (R^1 = Me, R^2 = H) could be derived, however, from the NMR spectrum of the equilibrium mixture: δ 1.25 (s, 3 H), 1.22–1.78 (m, 4 H), 3.20 (s, 1 H), 3.51 (s, 3 H), 4.00 (t, 2 H), 7.42 (s, 5 H). It showed only one sharp singlet for the OMe as well as the Me protons, indicating that a single isomer had been formed. Its configuration has not been established, but in view of the equilibration it may be supposed that it was the most stable isomer[1] (*trans,trans*-**8**).

Whereas **2b** reacted very smoothly with dicyanostyrene *at room temperature*, **2e** did not even react at 60 °C. An explanation might be that the conformational equilibrium of the cyclic ketene acetals **2** is shifted to the conformation **a** (Figure 1) when R^1 and R^2 are Me groups. In that conformation having R^2 in the pseudoaxial position, its

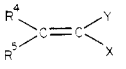
(2) G. N. Fickes and T. E. Metz, *J. Org. Chem.*, **43**, 4057 (1978).
(3) B. M. Jacobson, *J. Am. Chem. Soc.*, **95**, 2579 (1973); B. M. Jacobson, *ibid.*, **102**, 886 (1980).
(4) S. M. McElvain and G. R. McKay, Jr., *J. Am. Chem. Soc.*, **77**, 5601 (1955).
(5) C. G. Bakker, J. W. Scheeren, and R. J. F. Nivard, *Recl. Trav. Chim. Pays-Bas*, **100**, 13 (1981).
(6) L. Červený, S. Sabata and V. Růžička, *Collect. Czech. Chem. Commun.*, **45**, 3525 (1980).
(7) S. M. McElvain and C. L. Aldridge, *J. Am. Chem. Soc.*, **75**, 3993 (1953).
(8) R. Huisgen, *Pure Appl. Chem.*, **52**, 2283 (1980); R. Huisgen and G. Steiner, *Tetrahedron Lett.*, 3763 (1973); R. Huisgen and G. Steiner, *J. Am. Chem. Soc.*, **95**, 5054, 5056 (1973).

Table I. Products Obtained by Catalytic Reduction of Compounds 4 and 7

starting compd[a]	yield, %	bp, °C (mmHg)[b]	product	^{1}H NMR,[e] δ
4a	~90	69-70 (20)	5a	1.00-2.05 (m, 6 H), 3.16 (s, 3 H), 3.27 (s, 3 H), 3.50-3.70 (m, 2 H)
4d[c]	~60	82-88 (14)	6d	1.30-2.00 (m, 2 H), 2.00-2.65 (m, 4 H), 2.05 (s, 3 H), 3.56 (s, 3 H)
4c	80-90	50-55 (14)	5c	0.85 (d, 3 H, J = 7), 1.27-2.03 (m, 5 H), 3.18 (s, 3 H), 3.30 (s, 3 H), 3.53-3.70 (m, 2 H)
4e	80-90	60-62 (12)	5e	0.61 (d of d, 6 H, J = 7), 1.00-1.75 (m, 4 H), 3.10 and 3.17 (s, 3 H), 3.13 and 3.21 (s, 3 H), 3.38-3.50 (m, 2 H), cis-trans mixture (~3/1)
4f[c]	60-80	96-98 (13)	6f	1.09 (d, 3 H, J = 7), 1.40-2.10 (m, 2 H), 2.10-2.70 (m, 3 H), 2.05 (s, 3 H), 3.60 (s, 3 H)
7g	90-95	*d*	5g	1.15-2.00 (m, 4 H), 3.16 (s, 6 H), 3.28 (s, 6 H), 3.50-3.75 (m, 2 H)
7i[c]	80-90	*d*	6i	2.09 (s, 3 H), 1.90-2.70 (m, 4 H), 3.03 (s, 6 H), 3.86 (s, 3 H)
7h	~90	96-99 (13)	5h	0.97 (s, 6 H), 1.48-1.67 (m, 4 H), 3.27 (s, 6 H), 3.60-3.80 (m, 2 H)
7j[c]	50-60	*d*	6j	1.09 (s, 6 H), 1.45-1.95 (m, 2 H), 1.99 (s, 3 H), 1.95-2.50 (m, 2 H), 3.46 (s, 3 H)

[a] See Scheme I. [b] All mass spectra showed the characteristic peaks for M, M – Me, and M – OMe. Compounds 5 gave also M – H peaks. [c] IR ($\nu_{C=O}$) for 6d 1728, 1738 cm^{-1}; for 6f 1725, 1738 cm^{-1}; for 6i 1720, 1750 cm^{-1}; for 6j 1723; 1728 cm^{-1}. [d] Compounds were more than 95% pure after workup; distillation gave some decomposition and lowered the purity; determination of the boiling points was therefore not exact. [e] J values are given in hertz.

Table II. Relative Reaction Rates ($t_{1/2}$) of the Formation of the Product 10 (or 11) from 1.8 mmol of 3 and 1.8 mmol of an Electrophilic Olefin ($R^4R^5C{=}CXY$) in 0.7 mL of $CDCl_3$



expt	3	R^1	R^2	R^3	R^4	R^5	X	Y	product	temp, °C	$t_{1/2}$
1	3d	H	H	Me	H	Ph	CN	CN	10	20	8 d
2	3b	Me	H	H	H	Ph	CN	CN	10	20	6 h
3	3e	Me	Me	H	H	Ph	CN	CN	10	20	55 m
4	3f	Me	H	Me	H	Ph	CN	CN	10	20	30 m
5	3f	Me	H	Me	Me	Ph	CN	CN	10[a]	50	8 h
6	3f	Me	H	Me	Ph	Ph	CN	CN	10[a]	50	~48 h
7	3f	Me	H	Me	$(CH_2)_5$		CN	CN	10[a]	50	~12 h
8	3f	Me	H	Me	H	Ph	CN	COOEt	10[a]	20	2.5 h
9	3f	Me	H	Me	H	*p*-NO_2Ph	CN	CN	10[a]	20	15 m
10	3f	Me	H	Me	H	*p*-NO_2Ph	CN	COOEt	10[a]	20	1 h
11	3b	Me	H	H	COOEt	CN	CN	COOEt	10[a]	20	<10 s
12	3e	Me	Me	H	COOEt	CN	CN	COOEt	10[a]	20	<10 s
13	3b	Me	H	H	CN	CN	CN	CN	10[a]	20	<1 s
14	3f	Me	H	Me	CN	Ph	CN	CN	10[a] and 11 + 12	20	<20 s
15	3f	Me	H	Me	CN	H	CN	COOEt	10[a] and 11 + 12	*b*	
16	3f	Me	H	Me	COOEt	H	COOEt	CN	10[a] and 11 + 12	*b*	
17	3f	Me	H	Me	COOEt	CN	CN	COOEt	11 and 13	20	<10 s
18	3f	Me	H	Me	CN	CN	CN	CN	11 and 13	20	<1 s

[a] Corresponding to compound 10, but with other substituents. [b] These experiments were executed at 60 °C to secure completion of the reaction.

interaction with R^1 is minimized, but approach of the electrophile to C(β) is hindered at both sides of the olefinic bond.

Reactions of 3 with Electrophilic Olefins. When the reaction of equimolar amounts of **3d** and dicyanostyrene dissolved in chloroform was followed by NMR at room temperature, after ca. 30 min the cyclobutane derivative **9** ($R^1 = R^2 = H$; R^3 = Me) had formed: ca. 95% yield; NMR δ 2.00 (br s, 3 H), 1.90–2.20 (m, 2 H), 2.30-2.80 (m, 1 H), 3.15–3.30 (m, 1 H), 3.60 (s, 3 H), 4.60–4.90 (m, 1 H), 7.40 (s, 5 H). The sharp singlets for OMe (3.60 ppm) and C_6H_5 (7.40 ppm) indicated that again only one isomer had been formed. After longer reaction times the cyclobutane gradually disappeared, until ultimately the α,β,γ,δ-unsaturated ester **10** ($R^1 = R^2 = H$; R^3 = Me), probably the cis-α,β-trans-γ,δ isomer (see further), remained. This product would be expected from an "ene" reaction[3,9] followed by ring opening.

Apparently, the cyclobutane derivative is formed in a fast equilibrium reaction, whereas the formation of the ester is a much slower process (Scheme IV). In the reactions of **3b,e,f** with dicyanostyrene under similar conditions the corresponding, unsaturated esters **10** were obtained, but in these cases previous formation of a cyclobutane (**9**) was not observed at room temperature.

In order to study the influence of substituents in the reactants on the rate of the ester formation, we measured half-life times ($t_{1/2}$) for the formation of **10** using standardized and equal concentrations of **3** and electrophilic olefin at 20 °C. Under these conditions reciprocal $t_{1/2}$ values can be used as relative rate constants. The results (Table II) show that Me substituents at C(4) or C(6) in **3** accelerate the formation of **10** considerably (expts 3 and 4, relative to 2). The effect of Me at C(6) is about twice as large as Me at C(4). The effect of a Me group at C(3) on the formation of **10** is less clear; the ester formation from **3d** (expt 1) is slowed down by the lowering of the concentration of **3** during the experiment as a consequence of the cyclobutane formation. It seems quite certain, however, that a Me substituent at C(3) retards the cyclobutane formation considerably; even with the compound **3b** ($t_{1/2}$ = 6 h) no cyclobutane formation was observed.

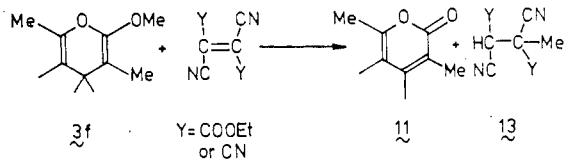
In similar experiments we studied the influence of the composition of the electrophilic olefin on $t_{1/2}$. Olefins in which both R^4 and R^5 are alkyl or aryl residues react much

(9) H. M. R. Hoffman, *Angew. Chem.*, 81, 597 (1969).

Table III. Preparation of Cyclic Ketene Acetals 2 and 3

product	reaction time, h	yield, %	bp, °C (mmHg)	^{1}H NMR ($CDCl_3$), δ
3b	6	25	50-54 (15)	1.53 (s, 3 H, C(3)-CH_3), 2.60-2.73 (m, 2 H, C(4)-H_2), 3.61 (s, 3 H, C(2)-OCH_3), 4.64-4.87 (m, 1 H, C(5)-H), 6.16-6.33 (m, 1 H, C(6)-H)
3e	4	50	60-64 (15)	1.08 (d, 3 H, J = 7, C(4)-CH_3), 1.57 (s, 3 H, C(3)-CH_3), 2.67-2.91 (m, 1 H, C(4)-H), 3.61 (s, 3 H, C(2)-OCH_3), 4.61-4.78 (m, 1 H, C(5)-H), 6.17-6.31 (m, 1 H, C(6)-H)
3f	3	65	62-64 (15)	1.52 (s, 3 H, C(3)-CH_3), 1.76 (br s, 3 H, C(6)-CH_3), 1.56-2.72 (m, 2 H, C(4)-H_2), 3.62 (s, 3 H, C(2)-OCH_3), 4.42-4.58 (m, 1 H, C(5)-H)
3c	4	35	50-55 (15)	1.08 (d, 3 H, J = 7, C(4)-CH_3), 2.74-3.24 (m, 1 H, C(4)-H), 3.54-3.81 (m, 1 H, C(3)-H), 3.59 (s, 3 H, C(2)-OCH_3), 4.54-4.88 (m, 1 H, C(5)-H), 6.11-6.31 (m, 1 H, C(6)-H)
3d	4	35	48-52 (15)	1.76 (br s, 3 H, C(6)-CH_3), 2.64-2.91 (m, 2 H, C(4)-H_2), 3.55-3.82 (m, 1 H, C(3)-H), 3.58 (s, 3 H, C(2)-OCH_3), 4.43-4.66 (m, 1 H, C(5)-H)
2b	6	40	52-56 (15)	1.22-1.78 (m, 2 H, C(5)-H_2), 1.56 (s, 3 H, C(3)-CH_3), 1.89 (br t, 2 H, J = 4.5, C(4)-H_2), 3.58 (s, 3 H, C(2)-OCH_3), 4.00 (br t, 2 H, J = 4.5, C(6)-H_2)
2e	4	60	64-66 (15)	1.02 (d, 3 H, J = 7, C(4)-CH_3), 1.24-1.80 (m, 2 H, C(5)-H_2), 1.56 (br s, 3 H, C(3)-CH_3), 1.67-2.11 (m, 1 H, C(4)-H), 3.57 (s, 3 H, C(2)-OCH_3), 3.99 (t, 2 H, J = 5, C(6)-H_2)

Scheme V



3f 11 13

slower with **3f** than dicyanostyrene (expts 5–7); in all three cases the reaction rates were unmeasurably low at room temperature. Replacement of a CN group in dicyanostyrene by the weaker electron-withdrawing COOEt group (expt 8) has a small retarding effect; the introduction of a *p*-nitro group in the phenyl ring (expts **9** and **10**) has a reversed influence. Strongly electrophilic olefins, containing three or four electron-withdrawing groups, react extremely fast with the compounds **3** at room temperature. With **3b** and **3e**, unsaturated esters corresponding to **10** are obtained (expts 11–13); **3f** in reaction with tricyanostyrene gave, however, an α-pyrone (**11**) as a second product [together with (1,2,2-tricyanopropyl)benzene (**12**) (expt 14)].

In the reactions of **3f** with diethyl α,β-dicyanoethenedicarboxylate or TCNE formation of the α-pyrone **11** was the only observed reaction (expts 17 and 18; see Scheme V). The formation of a product mixture, containing **10** and **11** (+**12**) as observed in expt 14 was also found in reactions of **3f** with other olefins containing three electron-withdrawing groups (expts 15 and 16). Determination of the relative amounts of the products by integration of the characteristic NMR signals for double bond protons at C(3) and C(4) in **11** (δ 5.90 and 7.06, J = 7 Hz) and in **10** (δ 6.25–6.65 and 7.30–7.65, J = 11 Hz) showed that the **11**/**10** ratio increased with the electrophilicity of the olefin used. The formation of the α-pyrone **11** (in expts 14–18) and the very large influence of the number and nature of electron-withdrawing substituents in the electrophilic olefin on the rate of the formation of **10** and **11** make it rather improbable that the reactions proceed as real, concerted ene reactions,[9] followed by ring-opening or elimination. It is more probable that the primary and rate-determining step is the abstraction[10] of a hydride ion from **3**, leaving a pyrylium cation **14**, stabilized by aromatization.[11] On the basis of this supposition, we tentatively postulate Scheme VI for the reactions of **3** with electron-poor olefins. The reversible formation of a cycloaddition product (**9**) is only observed when the cyclobutane formation is sufficiently fast in comparison with the hydride abstraction from **3**. The anion **15**, formed in the latter reaction, can add to the pyrylium cation **14** at C(2), C(4), or C(6), giving **17**–**18**, respectively. The esters **10** arise when the addition at C(6) is followed by ring-opening of **18**. It yields **10** in only one configuration.[12] A similar ring-opening reaction of **17** has not been observed, whereas ring opening of **16** cannot be expected. Nucleophilic substitution of **15** on the MeO group of **14** yields an α-pyrone (**11**).

A rate-determining step as formulated explains the accelerating effects of Me substituents at C(4) and C(6) (R^2 = Me or R^3 = Me) as they cause additional stabilization of **14**; after correction of the rates of the **3e** → **14** and **3f** → **14** reactions for a statistical factor, the effects of R^3 = Me and R^2 = Me appear nearly equal, as expected.

In order to consolidate the formation of the ionic intermediates **14** and **15** as the initial step in the mechanism of the formation of **10** (and **11**), we repeated several experiments at considerably lower temperatures, in the hope of finding indications for the occurrence of proposed intermediates.

All these experiments revealed that during the course of the reaction (at low temperature) transient NMR signals appear which cannot be ascribed to the starting compounds or the final products. In most cases, however, further identification was not possible. Repetition of experiments 4 and 17 at low temperature, which will be described in more detail, were exceptional, however.

The reaction of **3f** with dicyanostyrene (expt 4) was followed in an NMR tube at −30 °C. After 3 days signals of the product **10** were still not observed; the presence of a cyclobutane derivative **9** (not observed at room temperature) was, however, apparent from the occurrence of a novel set of signals different from that of **3f** (see Table

(10) T. Nishiguschi, A. Ohki, H. Sahakibara, and K. Fukuzumi, *J. Org. Chem.*, **43**, 2803 (1978).

(11) H. Perst in "Oxonium Ions in Organic Chemistry", Verlag Chemie, Weinheim/Bergstr., Germany, 1971, Chapter 7.4, p 149.

(12) S. Bersani, G. Doddi, S. Fornarini, and F. Stegel, *J. Org. Chem.*, **43**, 4112 (1978); G. Doddi, S. Fornarini, G. Illuminati, and F. Stegel, *ibid.*, **44**, 4496 (1979); T. A. Gosink, *ibid.*, **39**, 1942 (1974).

Table IV. Preparation of 2,4-Heptadienoic Methyl Esters 10 from 3 and Electrophilic Olefins

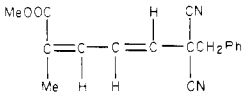
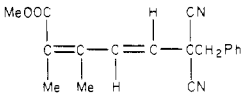
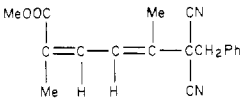
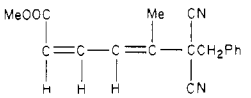
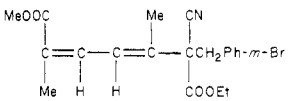
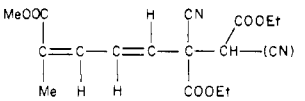
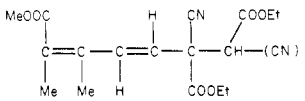
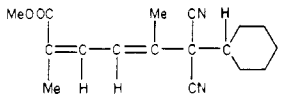
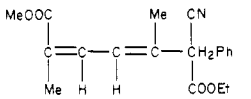
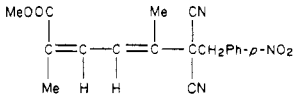
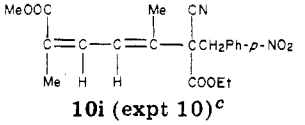
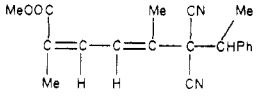
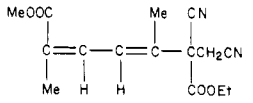
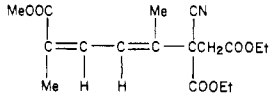
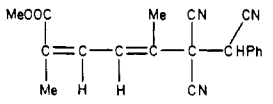
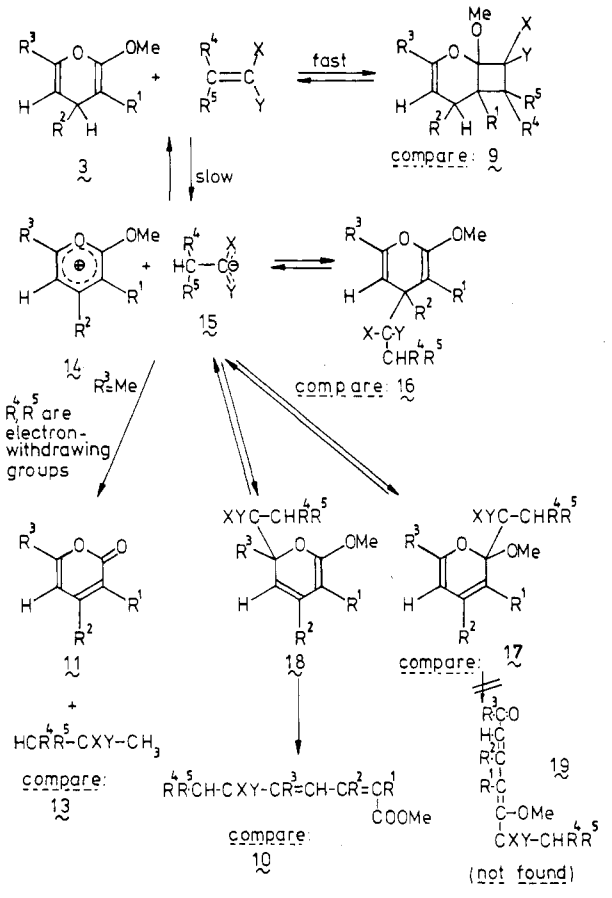
compd	formula	time	temp, °C	yield, %	^{1}H NMR ($CDCl_3$),[f] δ
 10a (expt 2)[a,b,d]	$C_{17}H_{26}O_2N_2$	3 h	60	90	2.02 (br s, 3 H, C(2)-CH_3), 3.29 (s, 2 H, C(7)-H_2), 3.78 (s, 3 H, C(1)-OCH_3), 5.68 (d, 1 H, J' = 15, C(5)-H), 6.37 (br d, 1 H, J'' = 11, C(3)-H), 7.36 (s, 5 H, C(7)-Ph); 7.69 (dd, 1 H, J' = 15, J'' = , C(4)-H)
 10b (expt 3)[b]	$C_{18}H_{26}O_2N_2$	1 h	40	90	1.91 (br s, 3 H, C(3)-CH_3), 2.02 (br s, 3 H, C(2)-CH_3), 3.32 (s, 2 H, C(7)-H_2), 3.80 (s, 3 H, C(1)-OCH_3), 5.66 (d, 1 H, J = 15, C(5)-H), 7.40 (s, 5 H, C(7)-Ph), 7.52 (d, 1 H, J = 15, C(4)-H)
 10c (expt 4)[a,b]	$C_{18}H_{18}O_2N_2$	1 h	40	90	2.02 (br s, 6 H, C(2)-CH_3, C(5)-CH_3), 3.29 (s, 2 H, C(7)-H_2), 3.72 (s, 3 H, C(1)-OCH_3), 6.61 (br d, 1 H, J = 11, C(3)-H), 7.34 (s, 5 H, C(7)-Ph, 7.52 (br d, 1 H, J = 11, C(4)-H)
 10d (expt 1)[b]	$C_{17}H_{16}O_2N_2$	24 h	60	80	2.10 (br s, 3 H, C(5)-CH_3), 3.36 (s, 2 H, C(7)-H_2), 3.76 (s, 3 H, C(1)-OCH_3), 5.93 (d, 1 H, J = 11, C(2)-H), 6.82 (t, 1 H, J = 11, C(3)-H), 7.39 (s, 5 H, C(7)-Ph), 7.87 (br d, 1 H, J = 11, C(4)-H)
 10j[b]	$C_{20}H_{22}O_4NBr$	4 h	60	70	1.27 (t, 3 H, J = 7, EtO), 1.96 (br d, 3 H, C(5)-CH_3), 2.04 (br s, 3 H, C(2)-CH_3), 3.16 and 3.50 (AB pattern, 2 H, J = 14, C(7)-H_2), 3.77 (s, 3 H, C(1)-OCH_3), 4.25 (q, 2 H, J = 7, EtO), 6.67 (br d, 1 H, J'' = 11, C(3)-H), 7.07-7.60 (m, 5 H, C(4)-H, C(7)-Ph)
 10m (expt 11)[a,b,e]	$C_{17}H_{20}O_6N_2$	10 min	25	80	1.37 (t, 6 H, J = 7, EtO), 2.03 (br s, 3 H, C(2)-CH_3), 3.82 (s, 3 H, C(1)-OCH_3), 4.37 (q, 4 H, J = 7, EtO), 4.47 (s, 1 H, C(7)-H), 5.85 (br d, 1 H, J' = 15, C(5)-H), 6.46 (br d, 1 H, J'' = 11, C(3)-H), 7.90 (dd, 1 H, J' = 15, J'' = 11, C(4)-H); for the other diastereoisomer 6.02 (br d, 1 H, J' = 15, C(5)-H), 6.46 (br d, 1 H, J'' = 11, C(3)-H), 7.86 (dd, 1 H, J' = 15, J'' = 11, C(4)-H)
 10p (expt 12)[b]	$C_{18}H_{22}O_6N_2$	10 min	25	80	1.37 (t, 6 H, J = 7, EtO), 1.94 (br s, 3 H, C(3)-CH_3), 2.02 (br s, 3 H, C(2)-CH_3), 3.82 (s, 3 H, C(1)-OCH_3), 4.37 (q, 4 H, J = 7, EtO), 4.51 (s, 1 H, C(7)-H), 5.72 (d, 1 H, J' = 15, C(5)-H), 7.58 (br d, 1 H, J' = 15, C(4)-H); the other diastereoisomer 5.88 (d, 1 H, J' = 15, C(5)-H), 7.40 (br d, 1 H, J' = 15, C(4)-H)
 10g (expt 7)[c]					1.70-2.10 (m, 10 H), 2.05 (br s, 6 H), 3.75 (s, 3 H), 6.49 and 7.42 (AB pattern, 2 H, J = 11); tertiary proton hidden beyond multiplets (1.70-2.10)
 10h (expt 8)[c]					1.33 (t, 3 H, J = 7), 2.00 (br s, 6 H), 3.46 (s, 2 H), 3.68 (s, 3 H), 4.13 (q, 2 H, J = 7), 6.63 (br d, 1 H, J = 11), 7.27 (s, 5 H), 7.58 (br d, 1 H, J = 11)
 10f (expt 9)[c]					2.10 (br s, 6 H), 3.45 (s, 2 H), 3.75 (s, 3 H), 6.58 (br d, 1 H, J = 11), 7.48 (br d, 1 H, J = 11), 7.53 and 8.22 (AB pattern, 4 H, J = 9)
 10i (expt 10)[c]					1.33 (t, 3 H, J = 7), 2.05 (br s, 6 H), 3.40 (s, 2 H), 3.75 (s, 3 H), 4.13 (q, 2 H, J = 7), 6.62 (br d, 1 H, J = 11), 7.53 and 8.22 (AB pattern, 4 H, J = 9), one proton hidden beyond the aromatic AB pattern at ~7.50 (H-C(4))
 (expt 5)[c]					1.66 (s, 3 H), 2.02 (br s, 6 H), 3.43 (s, 1 H), 3.72 (s, 3 H), 6.34 (d, 1 H, J = 11), 7.34 (s, 5 H), 7.59 (d, 1 H) J = 11)

Table IV (*Continued*)

compd	formula	time	temp °C	yield, %	^{1}H NMR ($CDCl_3$),[f] δ
 (expt 15)[c]					2.02 (br s, 6 H), 3.72 (s, 3 H), 6.25 (d, 1 H, *J* = 11), 7.60 (d, 1 H, *J* = 11)
 (expt 16)[c]					1.27 (t, 3 H, *J* = 7), 1.32 (t, 3 H, *J* = 7); 2.02 (br s, 6 H), 3.72 (s, 3 H), 4.16 (q, 2 H, *J* = 7), 4.27 (q, 2 H, *J* = 7), 6.66 (d, 1 H, *J* = 11), 7.42 (d, 1 H, *J* = 11)
 (expt 14)[c]					2.02 (br s, 6 H), 3.70 (s, 3 H), 6.32 (d, 1 H, *J* = 11), 7.05 (d, 1 H, *J* = 11), 7.30 (s, 5 H)

[a] Compounds **10a,c,m** gave satisfactory elemental analyses for C, H, and N. [b] All compounds showed as characteristic IR absorptions $\nu_{C\equiv N}$ between 2240 and 2255 cm^{-1} and $\nu_{C=O}$ at 1710 cm^{-1} (conjugated ester). [c] Only performed on an NMR scale; products were not further purified. [d] Mp 85–86 °C (from diisopropyl ether). [e] Mp 103–104 °C (from chloroform). [f] *J* values are given in hertz.

Scheme VI



III) and corresponding to that previously given for the cyclobutane **9** from **3d** and dicyanostyrene: δ 1.40 (s, 3 H, C(3)–CH_3), 1.90–2.2 (m, 2 H, $H_2C(4)$), 2.00 (br s, 3 H, C(6)–CH_3), 3.18 (s, 1 H, cyclobutane proton), 3.60 (s, 3 H, OCH_3), 4.64–4.90 (m, 1 H, C(5)–H), 7.35 (s, 5 H, Ph).

Repetition of the experiment at −10 °C gave after 1 day a more complex spectrum. Careful analysis showed that **3f** was still present and that **10** had already been formed. Subtraction of the spectra of **3f** and **10** from the complete spectrum left a set of weak signals (±10%) at δ 1.70 (s, 3 H), 2.04 (s, 3 H), 3.29 (s, 2 H), 3.72 (s, 3 H), 3.93–4.13 (m, 1 H), 4.90–5.14 (m, 1 H), and 7.34 (s, 5 H).

In comparison with **3f** the signals of C(3)–CH_3, C(6)–CH_3, and OCH_3 are at lower field (Δδ 0.1–0.3): the olefinic proton C(5)–H is even more shifted downfield (Δδ ca. 0.5).

Instead of the *multiplet* at 2.56–2.72 (C(4)–H_2) a novel *singlet* is present at δ 3.29 (2 H) and a multiplet (1 H) at δ 3.93–4.13. If one accepts the notion that the compound is an adduct of **3f** and dicyanostyrene, the most probable structure[11,12] is **16**; for the isomers **17** and **18** containing two olefinic protons the signal for HC(4) at δ 3.93–4.13 would be at lower field.

In a similar way we repeated experiment 17 at −60 °C. On mixing of the reactants a purple coloration, due to charge-transfer complexation, was immediately observed. After ca. 5 min the coloration disappeared, and after 30 min a complex NMR spectrum was traced, in which no signals of the final product (**11**) could be detected. Apart from the starting compound **3f** careful analysis showed the presence of probably two other compounds. One set of signals [δ 1.3 (s, 3 H), 1.84 (m, 2 H), 2.05 (br s, 3 H), 3.65 and 3.70 (2 s, 3 H), 4.60–4.78 (m, 1 H), 4.05–4.45 (m, 4 H), 1.20–1.45 (m, 6 H)] pointed to a cycloaddition product (**9**). The remaining signals [δ 1.94 (br s, 6 H), 3.25 (s, 3 H), 4.90 (s, 1 H), 4.80–5.15 (m, 1 H), 5.95–6.15 (m, 1 H), 4.05–4.45 (m, 4 H), 1.20–1.45 (m, 6 H)] might best be ascribed to the "ene product" **17** because of the presence of two olefinic protons. On longer reaction times both compounds disappeared with formation of polymeric products.

The results show that even in extremely fast reactions (expt 17) a cyclobutane derivative (**9**) may arise as the kinetically determined product.

The cycloaddition is a reversible process, and as the cyclobutane formation in most cases cannot be observed at room temperature, it seems that the equilibium is much more in favor of the cyclobutane at lower temperatures. The abstraction of a hydride ion,[3,10] from **3** by the electrophilic olefin leads ultimately via an irreversible step to more stable end products. The occurrence of **17** as in intermediate in experiment 4 shows that the ions **14** and **15** can recombine in several ways. Attack of **15** at C(4) of **14**, which is the preferential position, when it is unsubstituted[11] could not be substantiated because the resulting product (**16**) cannot react further. The fast ring opening of **18** to an α,β,γ,δ-unsaturated methyl ester (**10**) is probably caused by the formation of the thermodynamically

stable ester function of **10**. This appears to be the generally observed product. Deviations of this main route are only observed in reactions of ketene acetals, in which position 6 is methylated, with strongly electrophilic olefins. In those cases the intermediate anions (**15**) are very soft nucleophiles,[13] particularly useful in nucleophilic substitution. The increased nucleophilicity causes substitution at the MeO group, leading to the α-pyrones.

Experimental Section

Melting points are uncorrected. IR spectra were recorded on a Perkin-Elmer 297 spectrophotometer. ^{1}H NMR spectra were measured with a Varian T-60 or a Bruker 90-Mc spectrometer in CCl_4 or $CDCl_3$ solution and with Me_4Si (δ 0) as an internal standard (J values are given in hertz). Mass spectra were obtained by using a double-focussing Varian Associates SM-1B spectrometer.

The starting compounds **4a**[4], **4b**[5], **4e**[5], and **4f**[5] have been described previously: **4c** and **4d** were prepared according to the general procedure given in ref 4. **4c**: yield 40%; bp 48–50 °C (14 mmHg); NMR δ 1.01 (d, 3 H, J = 7, C(4)–CH_3), 1.36–2.69 (m, 3 H, C(3)–H_2, C(4)–H), 3.26 (s, 3 H, C(2)–OCH_3), 3.36 (s, 3 H, C(2)–OCH_3), 4.49–4.72 (m, 1 H, C(5)–H), 6.02–6.25 (m, 1 H, C(6)–H). **4d**: yield 60%; bp ~50 °C (14 mmHg); NMR δ 1.61–2.28 (m, 4 H, C(3)–H_2, C(4)–H_2), 1.78 (br s, 3 H, C(6)–CH_3); 3.31 (s, 6 H, C(2)–OCH_3), 4.36–4.63 (m, 1 H, C(5)–H).

The electrophilic olefins mentioned in Table II were prepared by methods described in ref 14.

Catalytic Reduction of Compounds 4 and 7.[4,15] A 2,2-dimethoxy-3,4-dihydropyran (25 mmol) was dissolved in dry dioxane (50 mL), to which 5 mol % of Pd/C was added. The mixture was shaken at room temperature, whereas an atmosphere of hydrogen was maintained in the vessel until 1 equiv of hydrogen had been consumed. Then the catalyst was removed by filtration, the solvent evaporated in vacuo, and the residue distilled into a receiver, previously washed with alkali. Yields and physical and spectroscopic data of the products (**5** and **6**) are given in Table I.

Preparation of 2-Methoxy-5,6-dihydro-4*H*-pyrans (2) and 2-Methoxy-4*H*-pyrans (3).[4] A cyclic ortho ester (**4** or **5**, 30 mmol) was slowly added during 30 min to an equivalent amount of Al(O-*t*-Bu)$_3$, which was heated to 170 °C. The mixture was left at that temperature for the time given in Table III. After completion of the reaction, *tert*-butyl alcohol and the desired product were successively distilled in vacuo from the reaction mixture. The products (**2** and **3**) were redistilled but remained contaminated with small amounts of the starting compound (**4** or **5**). Yields, boiling points and NMR data are given in Table III.

2,4-Heptadienoic Methyl Esters from Compounds 3 and Electrophilic Olefins. An appropriate electrophilic olefin (3.6 mmol, $R^4R^5C{=}CXY$; see Table II) was dissolved in chloroform (5 mL) in a round-bottomed flask, previously washed with alkali. The solution was heated to 40–60 °C, and then a cyclic ketene acetal (**3**, 4.0 mmol) was added. The mixture was left at the temperature given in Table IV and then cooled to room temperature, and the solvent and excess of **3** were removed by distillation in vacuo. In some cases (see Table IV) the product could be crystallized from the residue. In most other cases the product could not be obtained analytically pure and was only characterized by IR, mass, and NMR spectroscopy (at a purity of about 95%).

In the reactions of **3f** with PhC(CN)=C(CN)$_2$, EtOOC(CN)-C=C(CN)COOEt, and (NC)$_2$C=C(CN)$_2$ the reagents were mixed at room temperature, and the residue which was left after removal of the solvent was extracted several times with pentane. The combined extracts were concentrated in vacuo. Column chromatography of the residue (silica gel; eluent CCl_4/diisopropyl ether, 2/3) gave in all three cases pure 3,6-dimethyl-α-pyrone (**11**): ca. 70% yield; mp 58–60 °C; IR 1715 (C=O), 1645 and 1590 (C=C); NMR δ 2.07 (s, 3 H), 2.23 (s, 3 H), 5.88 (d, 1 H, J = 7), 7.02 (d, 1 H, J = 7); mass spectrum, m/e 124 (M^+), 96 (M^+ – CO). Anal. Calcd for $C_7H_8O_2$ (M_r = 124.134): C, 67.72; H, 6.49. Found; C, 67.50; H, 6.40.

Registry No. 2b, 86289-98-7; **2e**, 86289-99-8; **3b**, 86289-93-2; **3c**, 86289-96-5; **3d**, 86289-97-6; **3e**, 86289-94-3; **3f**, 86289-95-4; **4a**, 86290-14-4; **4c**, 86289-87-4; **4d**, 86289-86-3; **4e**, 77998-71-1; **4f**, 77998-73-3; **5a**, 66607-28-1; **5c**, 86289-88-5; **5e**, 86289-89-6; **5g**, 86289-90-9; **5h**, 86289-91-0; **6d**, 13984-50-4; **6f**, 38872-30-9; **6i**, 43227-82-3; **6j**, 86289-92-1; **7g**, 77998-83-5; **7h**, 77998-76-6; **7i**, 77998-84-6; **7j**, 77998-79-9; (*Z*,*E*)-**10a**, 86290-02-0; (*Z*,*E*)-**10b**, 86307-81-5; (*Z*,*E*)-**10c**, 86290-03-1; (*Z*,*E*)-**10d**, 86290-04-2; (*Z*,*E*)-**10f**, 86290-09-7; (*Z*,*E*)-**10g**, 86290-07-5; (*Z*,*E*)-**10h**, 86290-08-6; (*Z*,*E*)-**10i**, 86290-10-0; (*Z*,*E*)-**10j**, 86290-05-3; (*Z*,*E*)-**10m**, 86290-06-4; (*Z*,*E*)-**10p**, 86307-82-6; 11, 53034-20-1; β,β-dicyanostyrene, 2700-22-3; β,β-dicyano-α-methylstyrene, 5447-87-0; β,β-dicyano-α-phenylstyrene, 10394-96-4; cyclohexylidenepropanedinitrile, 4354-73-8; (*E*)-ethyl 2-cyano-3-phenyl-2-propenoate, 2169-69-9; β,β-dicyano-4-nitrostyrene, 2700-23-4; (*E*)-ethyl 2-cyano-3-(4-nitrophenyl)-2-propenoate, 2017-89-2; (*Z*)-diethyl 2,3-dicyanobutendioate, 86290-00-8; 1,1,2,2-tetracyanoethene, 670-54-2; α,β,β-tricyanostyrene, 4364-80-1; (*Z*)-ethyl 2,3-dicyano-2-propenoate, 54797-28-3; (*E*)-diethyl cyanobutendioate, 86290-01-9; (*Z*,*E*)-methyl 6,6-dicyano-2,5-dimethyl-7-phenyl-2,4-octadienoate, 86290-11-1; (*Z*,*E*)-2-(methoxycarbonyl)-5-methyl-6,7-dicyano-6-(ethoxycarbonyl)-2,4-heptadiene, 86290-12-2; (*Z*,*E*)-2-(methoxycarbonyl)-5-methyl-6-cyano-6,7-bis(ethoxycarbonyl)-2,4-heptadiene, 86290-13-3; (*Z*,*E*)-methyl 2,5-dimethyl-7-phenyl-6,6,7-tricyano-2,4-heptadienoate, 86307-83-7.

(13) H. Perst in "Oxonium Ions in Organic Chemistry", Verlag Chemie, Weinheim/Bergstr., Germany, 1971, Chapter 5.

(14) G. Jones in *Org. React.* (*N.Y.*), **15**, 204 (1967); C. J. Ireland and J. S. Pizey, *J. Chem. Soc., Chem. Commun.*, 4 (1972); G. K. Noren and H. K. Hall, Jr., *J. Polym. Sci.*, **10**, 3183 (1972); H. K. Hall, Jr., and P. Ykman, *J. Am. Chem. Soc.*, **97**, 800 (1975).

(15) R. Scarpati, M. Cioffi, G. Scherillo, and R. A. Nicolaus, *Gazz. Chim. Ital.*, **96**, 1164 (1966); H. Adkins and H. R. Billica, *J. Am. Chem. Soc.*, **70**, 695 (1948).