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THE INFLUENCE OF THE Π-ELECTRON DISTRIBUTION AND Π-BOND STABILITY OF KETENE ACETALS ON THEIR REACTIVITY AND STEREOSELECTIVITY IN THERMAL (2 + 2) CYCLOADDITIONS WITH 1,1-DICYANOSTYRENES

HANS W. SCHEEREN*, ANTON J. R. VAN ROSSUM and RUTGER J. F. NIVARD
Department of Organic Chemistry, Catholic University, Toernooiveld, 6525 ED Nijmegen, The Netherlands

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Abstract—The reactions of a series of ketene acetals ($R^1R^2C{=}C(OMe)_2$) with dicyanostyrenes ($ArCH{=}C(CN)_2$) have been studied. Ketene acetals with a symmetrical Π-electron distribution give stable cyclobutanes *via* reactions in which no dipolar intermediates can be trapped. Ketene acetals with an unsymmetrical Π-electron distribution give unstable cyclobutanes or other products derived from dipolar intermediates. In this case, dipolar intermediates can be intercepted with H_2O. The results have been explained by supposing a different approach of the reactants in the cycloadditions of the two different types of ketene acetals. Further support for this supposition was obtained from the stereochemical course of the cycloaddition reactions with $R^1HC{=}C(OMe)_2$ (R^1=OMe, Me, Cl) and from the Hammett plots which show a better correlation with σ^+ for the symmetrically substituted $(MeO)_2C{=}C(OMe)_2$ and with σ for the unsymmetrical $MeCH{=}C(OMe)_2$.

The cycloaddition between electron-poor and electron-rich olefins has become a general method for the synthesis of cyclobutane derivates[1]. Weakly electron-poor alkenes having a single electron-withdrawing group at one or both sites of the olefinic bond react with strongly electron-rich olefins like enanimes only at elevated temperatures[2,3].

Weakly electron-rich alkenes like enole ethers react only with alkenes containing at least two electron-withdrawing substituents at the same site of the double bond, e.g. 1,1-dicyanoethene.[1,4] Ketene acetals ($R^1R^2C{=}C(OMe)_2$, **1**) belong to the electron-rich alkenes with an intermediate nucleophilicity between that of enole ethers and enamines. Recent investigations in our laboratory have shown that the scope of their (2 + 2)-cycloadditions with electron-poor alkenes can be extended to alkenes having only one electron-withdrawing substituent when a Lewis acid is used as a catalyst[5].

Results from the literature[1c,6–10] indicate that the nature of products from reactions of **1** with electron-poor alkenes is strongly determined by the Π-electron distribution in the ketene acetal and to a smaller extent by that in the electron-poor olefin. The symmetrically substituted ketene acetal **1f** (R^1=R^2=OMe) yielded in reactions with electron-poor olefins always cyclobutanes.[7] The unsymmetrically substituted ketene acetal $H_2C{=}C(OR)_2$, (R=Me or Et) has been reported to yield cyclohexane derivatives in the reactions with maleic anhydride[8a] and haloquinones,[8b] whereas cyclobutanes were isolated from the reactions with 1,1-dicyano-3-methylbutene[10] and methyl acrylate.[6]

We studied the influence of substituents R^1,R^2 in **1** on the outcome, velocity and stereochemistry of the cycloaddition reactions with dicyanostyrenes, $ArCH{=}C(CN)_2$. The substituents were varied systematically giving a series of compounds in which the symmetry of the Π-electron distribution and the HOMO-energy decrease according to R^1,R^2=OMe, OMe > OMe, H > Me, Me > Me, H > H, H or Cl, H. Dicyanostyrenes were chosen as the electron-poor component, because they react smoothly, give well defined products and are readily available by Knoevenagel condensations, so that the aryl group can be varied widely.

RESULTS

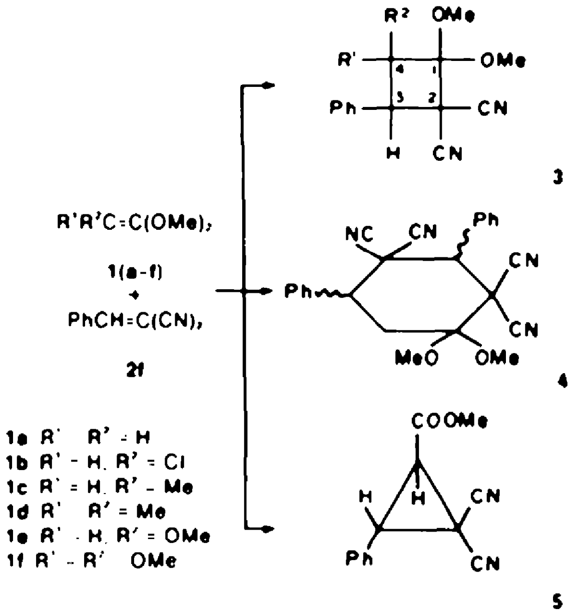
When the ketene acetals **1a–f** were treated with dicyanostyrene (**2f**) in acetonitrile as the solvent the products given in Scheme 1 could be isolated. Stable cyclobutanes (**3e** and **3f**) were only obtained in good yields from the reaction of **2f** with **1e** and **1f**. The NMR spectrum (and sharp m.p.) of **3e** indicated that only one isomer was formed from **1e** and **2f**. It was not possible to deduce from the NMR spectrum whether it had the *cis*- or *trans*-configuration. X-ray analysis established, however, that the *trans* product had been formed.[11]

The (2 + 2) cycloadditions of the other ketene acetals led to equilibria. Removal of the solvent (acetonitrile) from the reaction mixtures of **1c** or **1d** with **2f** resulted in simultaneous, partial removal of the ketene acetal from the equilibrium mixture, so that the remaining products (**3c** and **3d**) were always contaminated with **2f**. On keeping **3c** or **3d** in solution the amount of **2f** increased, because the ketene acetal was removed from the equilibrium mixture by polymerization.

The NMR spectrum of **3c** showed only one doublet for the Me group at C(4) (δ, 1.27 ppm). The Me signals of **3d** are at δ, 1.20 and δ, 1.37 ppm. From these results it cannot be deduced whether **3c** is a *cis*- or *trans*-compound. Due to the instability of **3c** it was not possible to obtain pure crystals for X-ray analysis. From the X-ray analysis of the hydrolysed product it could be deduced, however, that the *trans* cyclobutane had been formed (see further).

An impure sample of **3a** could be isolated by precipitation from a reaction mixture in tetrahydrofuran with pentane. Reaction of **1a** and **2f** in a more polar solvent or using longer reaction times led, however, to a stable cyclohexane derivative **4**.

The mixture of **1b** and **2f** appeared rather complex; the presence of a cyclobutane derivative could not be demonstrated. Evaporation of the solvent and crystallization of the residue from methanol gave the cyclo-



3

4

5

1a R' R' = H
1b R' - H, R' = Cl
1c R' = H, R' - Me
1d R' R' = Me
1e R' - H, R' = OMe
1f R' - R' OMe

R'	R'	reaction conditions	compound
H	H	20 min*, 20°	3a
H	Me	1 hr , 20°	3c(*trans*)
Me	Me	2 hrs , 80°	3d
H	MeO	3 hrs , 20°	3e(*trans*)
MeO	MeO	2 hrs , 80°	3f
H	H	5 hrs, 20°	4(*cis* and *trans*)
H'	Cl	3 hrs, 20°	5(*trans*)

*in THF

Scheme 1

propane derivative 5 as the main product (~50%). A similar result has recently been found in the reaction of bromoketene diethyl acetal and 1-carboethoxy-1-cyanoethene.[9]

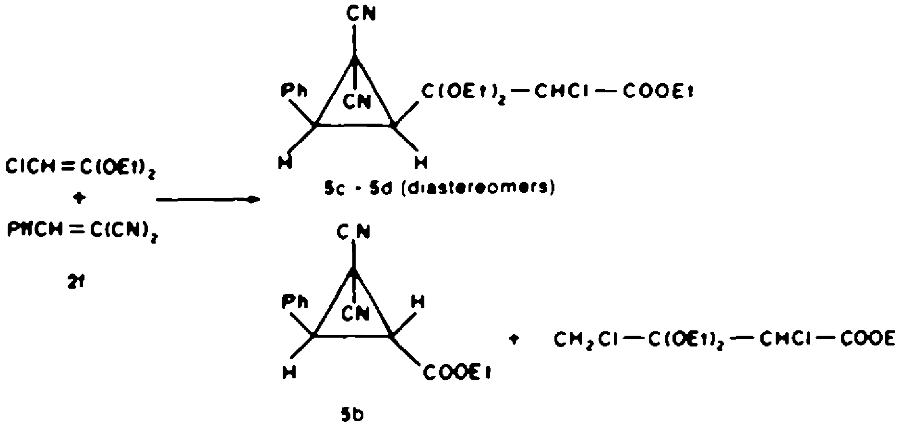
The product 5 was obtained as the racemate of a single diastereomer. We analysed the mother liquor for the presence of the epimeric form; complete separation by HPLC could not be realized, but from NMR spectra of mixtures of the side-products it could be deduced that the other diastereomer could only be present in a very small amount.

The coupling constant of the ring protons in 5 ($J=8$ Hz) is not very indicative for either the *cis*- or *trans*-configuration. Gosselck *et al.*[17] found for the corresponding diethyl acetal and several related cyclopropanes $J_{trans} = 8 - 8.1$ Hz, $J_{cis} = 9.2 - 9.3$ Hz, what suggests that 5 is the *trans* isomer. This was confirmed by the outcome of the reaction of **2f** with an excess of the diethyl acetal corresponding to **1b**, viz $ClCH{=}C(OEt)_2$. After filtration of polymeric products and evaporation of the solvent, the reaction mixture could be separated by HPLC in this case, yielding four compounds (Scheme 2). The amount of **5c** + **5d** was about four times that of **5b**.

The coupling constant of both diastereomers **5c** and **5d** was 9.1 Hz, significantly higher than the coupling constant of **5b**, J=8.0 Hz as previously reported. By analogy it may be deduced that the cyclopropane 5 from **1b** and **2f**, which corresponds to **5b** is a *trans* compound.

Cycloaddition rate constants. Second order rate constants (k) were determined in various solvents for the cycloadditions of the whole series of dicyanostyrenes (**2a-h**, given in Scheme 3) with **1b** (at 40°), **1c** (at 20°) and **1f** (at various temperatures between 20 and 60°). To that aim the decrease of the concentration of **2** with time was followed spectroscopically. The results are given in Tables 1-3.

It appeared that electron-withdrawing substituents in **2** accellerate the reaction, whereas electron-donating substituents are retarding. The reactivity of the ketene acetals decreases in the order **1c** ≫ **1b** > **1f**. (For the cycloadditions with **2c** in acetonitrile at 20° the relative rates are 10^{3}, 3 and 1, respectively.) As mentioned before



Scheme 2

Substituent

2a	**2b**	**2c**	**2d**	**2e**	**2f**	**2g**	**2h**
pNO$_2$	mNO$_2$	mCl	pCl	pF	-	pMe	pOMe

Scheme 1

the (2 + 2)-cycloadditions of **1b** and **1c** lead to equilibria. The equilibrium constants (K_{eq}) are generally large, but decrease in going from dicyanosytrenes having electron-withdrawing substituents to dicyanostyrenes containing donating substituents (footnotes at Tables 1 and 2)[11]

Hammett plots showed satisfactory, linear correlations between log k-values and substituent constants[14] for the cycloadditions of **1f** and **1c**; for **1f** the better correlation is found when σ^+-values are used; with **1c** good linearity is only found, using σ-values. A Hammett plot of the rate constants of cycloadditions between **2a-h** and **1b** showed a lower correlation coefficient both when σ- and σ^+-values are used. In Table 4 ρ-values and correlation coefficients, derived from the Hammett plots are given.

Solvent effects. The rate constants for the cycloadditions of **2c** with **1b**, **1c** and **1f** were measured in several solvents (Tables 1-3). For the correlation of log k-values

Table 1. Rate constants (k)* for the cycloaddition of 1,1-dimethoxypropene **1c** with ringsubstitututed β,β-dicyanostyrenes **2a-h** at 20°

compound	solvent	[illegible]	k [illegible]	k average [illegible]	[illegible] measured at [illegible] (nm)
2a	acetonitrile	1.8·10[illegible]	[illegible]		[illegible]
2b	acetonitrile	1.8·10[illegible]	[illegible]		[illegible]
2c	acetonitrile	8.2·10[illegible]	[illegible]	[illegible]	300
2c	acetonitrile	4.2·10[illegible]	[illegible]		
2c	dioxan	4.3·10[illegible]	4.1	4	
2c	dioxan	4.3·10[illegible]	[illegible]		
2c	dichloroethane	9.8·10[illegible]	[illegible]	[illegible]	
2c	dichloroethane	9.8·10[illegible]	[illegible]		
2c	acetonitrile	[illegible]	[illegible]	[illegible]	316
2d	acetonitrile	4.2·10[illegible]	40		
2e	acetonitrile	8.2·10[illegible]	24		[illegible]
2f	acetonitrile	8.2·10[illegible]	[illegible]	23	306
2f	acetonitrile	4.2·10[illegible]	[illegible]		
2g	acetonitrile	[illegible]	[illegible]		[illegible]
2h	acetonitrile	[illegible]	10		348

*The cycloaddition leads to an equilibrium so that in fact k_{obs} has to be corrected for the reverse reaction however [illegible] as appears from

K_{eq} = ca 4·10[illegible] (for 2a in acetonitrile)

ca 6[illegible] (for 2h in acetonitrile)

Table 2. Rate constants (k)* for the cycloaddition of 1,1-dimethoxy-2-chloroethene **1b** with ringsubstituted β,β-dicyanostyrenes **2b-g** at 40°

compound	solvent	[illegible]	k [illegible]	k average [illegible] mol⁻¹ min⁻¹
2b	acetonitrile	[illegible]	1.29	
2c	acetonitrile	0.12	0.76	0.73
	acetonitrile	0.12	0.59	
	[illegible] (20:1)	0.12	[illegible]	
2c	dioxan	[illegible]	0.094	0.091
	dioxan	[illegible]	[illegible]	
2c	1,2-dichloroethane	0.19	0.49	0.54
	1,2-dichloroethane	0.19	0.58	
2d	acetonitrile	0.20	0.53	
2e	acetonitrile	0.20	0.37	0.36
	acetonitrile	0.20	0.35	
2f	acetonitrile	0.20	[illegible]	0.30
	acetonitrile	0.20	0.33	
2g	acetonitrile	0.20	0.16	0.15
	acetonitrile	0.20	0.14	

*The reaction leads to an equilibrium so that in fact k_{obs} has to be corrected for the reverse reaction, however [illegible] as appears from

K_{eq} ca 10[illegible] (for 2c in acetonitrile)

ca [illegible] (for 2g in acetonitrile)

Table 3. Rate constants (k) for the cycloaddition of tetramethoxyethene **1f** with ringsubstituted β,β-dicyanostyrenes **2a–g**

compound	solvent	°C	[illegible]	[illegible]	average [illegible]
2a	acetonitrile	60	0.100	[illegible]	[illegible]
2a	acetonitrile	60	[illegible]	[illegible]	
2c	chlorobenzene	60	0.200	[illegible]	
2c	dioxan	60	0.200	0.036	
2c	1,2-dichloroethane	60	0.200	0.21	
2c	acetonitrile	60	0.200	[illegible]	[illegible]
2c	acetonitrile	60	0.109	[illegible]	
2c	acetonitrile	45	0.200	[illegible]	[illegible]
2c	acetonitrile	45	0.200	[illegible]	
2c	acetonitrile	30	[illegible]	[illegible]	0.14
2c	acetonitrile	30	0.200	[illegible]	
2e	acetonitrile	[illegible]	0.200	[illegible]	
2e	acetonitrile	60	0.200	[illegible]	[illegible]
2e	acetonitrile	60	0.200	[illegible]	
2f	acetonitrile	60	0.200	[illegible]	[illegible]
2f	acetonitrile	60	[illegible]	0.163	
2g	acetonitrile	60	[illegible]	[illegible]	

Table 4. ρ-Values and correlation coefficients calculated from Hammett plots for the reaction of **1b**, **1c** and **1f** with **2a–h** using σ^+- and σ-substitution constants

compound	temp	ρ (σ^+)	corr. coeff.	ρ (σ)	corr. coeff.
1b	40	0.905	0.947	1.05	0.950
1c	20	1.02	0.922	1.61	0.984
1f	60	1.63	0.998	1.91	0.985

with the solvent parameters[15] E_T, $(\epsilon - 1)/(2\epsilon + 1)$ and δ we chose dioxan as the solvent with low polarity, because **2c** does not dissolve in hexane or cyclohexane. For **1f** (measured in four different solvents) a very satisfactory linear correlation between log k and E_T was found (correlation coefficient 0.994). From this plot and similar plots for **1b** and **1c** we calculated $k_{acetonitrile}/k_{dioxan}$ = ~8 (for **1b** at 40°), = ~19 (for **1c** at 20 and **1f** at 60°).

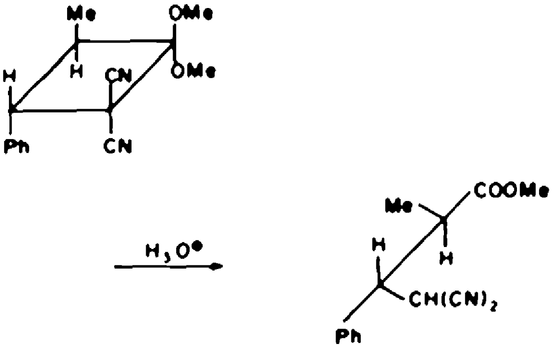
Trapping experiments. When the reaction of **1a** or **1c** with **2c** or **2f** was carried out in tetrahydrofuran (THF) at 20° in the presence of a tenfold excess of water the ester **6** was isolated (Scheme 4). In the reactions of **1c** (R^1=H, R^2=Me) the product was a mixture of diastereomers according to ^{1}H NMR.

$$\underset{\mathbf{1a,c}}{R^1R^2C{=}C(OMe)_2} + \underset{\mathbf{2c,f}}{ArCH{=}C(CN)_2} \xrightarrow{THF/H_2O} HC(CN)_2\text{–}$$

$$\underset{\mathbf{6}}{CHAr\text{–}CR^1R^2\text{–}COOMe}$$

Scheme 4

When the cyclobutane derivative **3c**, previously formed from **1c** and **2f** was converted into **6** (Ar=C_6H_5, R^1=H, R^2=Me) by mild, acid-catalysed hydrolysis, only one diastereomer (sharp melting point 90–91°, sharp doublets in the NMR-spectrum for $\underline{H}C(CN)_2$ at δ4.50 and for $HCCH_3$ at δ1.05 ppm) was formed. X-ray analysis[16] revealed that in this case only the R,S-isomer had been formed (Scheme 5) showing that cyclobutane **3c** had the *trans* configuration.



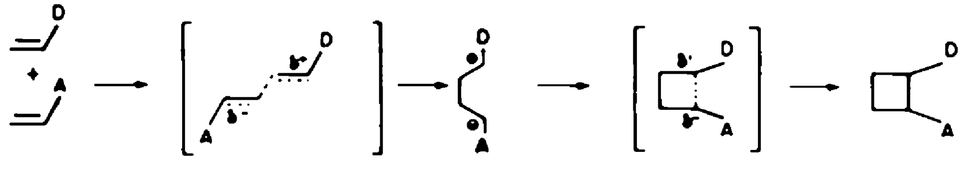
(R,S + S,R)

Scheme 5

The ketene acetals **1d**, **e** and **f** behaved quite differently; even in the presence of a hundredfold excess of water the reactions with **2f** gave only the cycloadducts **3d-f**, no esters **6**. The cyclobutane **3d** could be hydrolysed with 4N HCl at room temperature giving **6** (R^1=R^2=Me, Ar=C_6H_5) in good yield. Similar hydrolyses of **3e** and **3f** required prolonged reflux in dioxan/water in the presence of *p*-toluene sulphonic acid. In these cases the resulting ester arose together with considerable amounts of **2f**, showing that the hydrolysis is accompanied by reversal of the cycloaddition.

DISCUSSION

The majority of previous mechanistic studies on thermal (2 + 2)-cycloadditions concern reactions of enole ethers and some other weakly electron-rich alkenes with tetracyanoethylene (TCNE).[17] The generally accepted mechanism is given in Scheme 6. An essential feature is the occurrence of a dipolar intermediate which should be separated from the reactants and products by energy barriers (transition states) of nearly equal height.[18]



Scheme 6

The occurrence of the intermediate is substantiated by trapping experiments, large solvent effects, and the sign and magnitude of activation entropies and activation volumes.

Our results do not fit into this scheme. A less serious difficulty are the small solvent effects which were measured. They may be caused by the strong polarity[19] of the dicyanostyrenes, used as the electron-poor component (**2a**: μ=3.05; **2f**: μ=5.24; **2h**: μ=6.26D), especially when the transition state should be reached relatively early and has relatively little dipolar character. Small solvent effects have been found previously in (2 + 2)-cycloadditions of strongly electron-rich alkenes.[10,20]

A more fundamental explanation is, however, required to understand, why trapping experiments in aqueous solvents were without any result in cycloadditions of **1d**, **e**, **f**, and to get insight into the stereochemical course of the reactions. Finally, there is the seemingly conflicting result that the stability of the cyclobutanes, increasing in going from **3a** to **3f**, apparently corresponds to the Π-bond stability of the ketene acetal, which decreases from **1a** to **1f**, whereas the reaction rates of the various ketene acetals do not only depend on the HOMO-energy (**1c** is more reactive than **1b**) but also on the Π-electron distribution; **3f** having the highest HOMO-energy but a symmetrical electron distribution, has the lowest reactivity. The contradictory variations in product stability and reaction rates in reactions between **2** and various ketene acetals suggests a gradual variation of the reaction mechanism in going from unsymmetrically substituted ketene acetals to ketene acetals having a symmetrical Π-electron distribution.

According to the frontier orbital theory two limiting geometries of addend approach[21] are possible in reactions of electron-rich alkenes with electron-poor alkenes, having the higher LUMO-coefficient on the β-C atom (Fig. 1). The $1S^D + 1S^A$ approach is preferred by ketene acetals, having a much larger HOMO-coefficient on C(β) than on C(α). The $2S^D + 1S^A$ approach becomes more probable as the difference between the HOMO-coefficients decreases and finally vanishes. In the latter case (reactions of **1d**, **e** and especially **1f**) the developing charges at the dipolar ends arise rather close together, mutual bond formation between them is fast, much faster than the reaction with water if present. The energy profile must have a rather broad and flat maximum, so that a dipolar intermediate, if occurring should be a very short-living species.

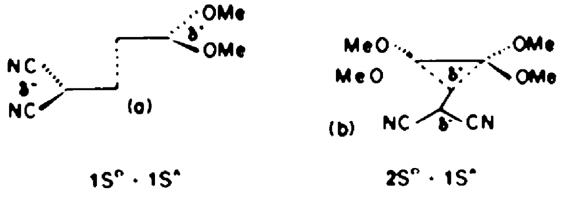


Fig. 1. Limiting geometries for approach of "unsymmetrical" electron-rich alkenes (a) and "symmetrical" electron-rich alkenes (b) in cycloadditions with electron-poor alkenes.

In the cycloaddition of **1e** two cyclobutanes (*cis* or *trans* **3e**) might be formed, but only the more stable *trans* product is isolated. This suggests that the transition state geometry is close to that of the product (e.g. like Fig. 2).

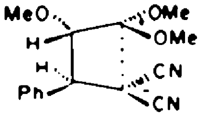
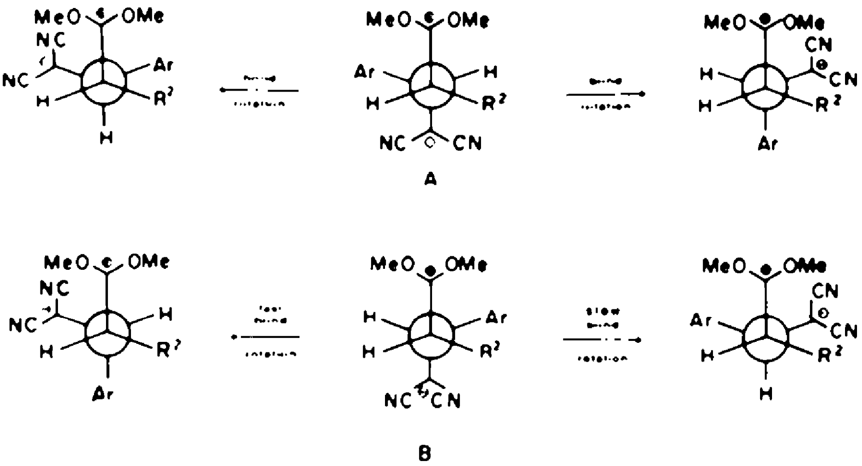


Fig. 2

It has been supposed that in the $1S^D - 1S^A$ approach unsymmetrically substituted reactants start their interaction in a *trans* arrangement (**a** in Fig. 1). The developing charges are far apart and rotation around the primary formed C–C bond into a *cisoid* gauche conformation is necessary for the completion of the cyclobutane formation.[22] In these reactions (cycloaddition of **1a-c**) a rather long-living, dipolar intermediate is formed, which can be trapped by one of the reactants (see **1a** + **2f**) or water. In Scheme 7 the main conformations (**A** and **B**) of an intermediate state, arising *via* the *transoid* approach are given for reactions in which R^1=H, R^2≠H. A



Scheme 7

is the less crowded conformation: rotation in both directions to a cisoid gauche conformation leads to an increase of crowding. The energy barrier between **A** and the product (a cyclobutane) is higher than between **A** and the reactants (**1** and **2**). Therefore **A** will mainly revert to the starting compounds. On the other hand, the more crowded intermediate, **B** will be a shorter-living intermediate, because single-bond rotation leading to a 4-membered ring compound, can proceed under release of crowding. These kinetic arguments are not necessary to explain the formation of the thermodynamically more stable *trans* cyclobutane (**3c**) from **1c** and **2f**, because the (2 + 2)-cycloaddition is reversible under the reaction conditions. They may explain, however, that the formation of a β-hydroxyester (**6**, Scheme 4) from **1c** and **2f** in the presence of water does not proceed stereoselectively, the *erythro*-isomer will arise by trapping of the dipolar intermediate having the more stable conformation **A**.

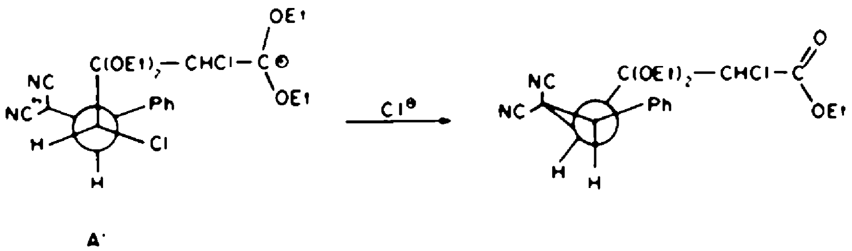
Different behaviour between the conformations **A** and **B** of the dipolar intermediate is more convincingly found in the cycloaddition between the diethoxy acetal $HCCl{=}C(OEt)_2$ and **2f**. The intramolecular substitution in the intermediate, leading to **5b** (Scheme 2), apparently occurs mainly from the less stable, but easily rotating conformation **B** ($R^2{=}Cl$), since **5b** is isolated as a *trans* compound. The occurrence of **A** ($R^2{=}Cl$) appears from the formation of the diastereomeric side-products **5c** and **5d** which are both *cis* substituted compounds.

Apparently **A** is sufficiently long-living to be intercepted by a second molecule of $HCCl{=}C(OEt)_2$, which is more reactive against electrophiles like **A** than the corresponding dimethoxy acetal (**1b**). In this way another *trans*oid intermediate (**A'**, Scheme 8) arises, which is apparently stable enough to allow rotation to a more crowded conformation from which ring-closure to the *cis*-substituted cyclopropane derivative occurs.

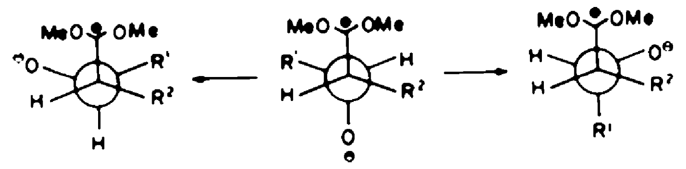
There is a remarkable difference in the interception of the dipolar intermediate by one of the reactants in the cycloadditions of **1a** and $HCCl{=}C(OEt)_2$ with **2f**. In the former case the intermediate is intercepted at the anion-site by the electron-poor olefin, although **2f** has a more hindered β-carbon than the electron-rich reactant **1a**. The formation of the new C–C bond proceeds preferentially *via* combination of the soft centers. In the cycloadditions of $HCCl{=}C(OEt)_2$, however, the interception of the intermediate occurs at the relatively hard dioxenium ion site by the ketene acetal used. This tendency has been previously observed[7,8] and may be ascribed to the strong polarization of the latter ketene acetal.

It is of interest that in the analogous cycloadditions of ketene acetals with aldehydes a *cis*-substituted oxetane is always the result of kinetically determined product formation.[21–24] In these (2 + 2)-cycloadditions the *trans*oid approach *via* the more stable intermediate conformation (Scheme 9) has a better chance to rotate to a more crowded conformation before going back to the starting compounds, because of the smaller size of oxygen in comparison with the $C(CN)_2$ residue. Stronger attraction between the positive pole and the *localized* negative charge may be another factor.

A final point of discussion concerns the results of our kinetic measurements. In a preceding paper[3b] we found very good linear relationships between log k-values and σ^*-substituent constants, yielding positive ρ-values, for Diels Alder reactions of the compounds **2a-h** with several electron-rich alkoxybutadienes. Similar results have been



Scheme 8



Scheme 9

reported for other Diels Alder reactions, in which the electron-poor double bond is linked to an aryl residue.[27] As for Diels Alder reactions, in general, good correlations are found between log k and $1/(E_{HOMO} - E_{LUMO})$ the substituent effects on log k can be ascribed to the influence of substituents on the LUMO-energy, whereas the ρ-value is a measure of the energy gap between HOMO and LUMO[25] The increase of reactivity with increase of electron-withdrawing ability of substituents in the phenyl ring of **2** can be ascribed in a similar way to the effect of the substituents on the LUMO-energy. In the cycloadditions of **2(a–h)** with the unsymmetrically substituted ketene acetal **1c** log k correlates better with σ- than σ^+-values, as a "one-bond" reaction (2 + 2)-cycloaddition is less frontier-orbital-controlled than the two-bond-forming [4 + 2]-cycloaddition.[26] In the transition state of the (2 + 2)-cycloaddition the relevant LUMO is more perturbated and the influence of the substituent is mainly an inductive effect on the generation of negative charge at the β-C atom. A similar correlation between log k and σ-values should be expected for the cycloaddition of **2** with **1b**, but in this case the experimental data are less clear because of the instability of **1b** in combination with its low reactivity towards **2**.

The symmetrically substituted ketene acetal **1f** has also a low reactitity but is very stable under the reaction conditions. The better correlation of log k with σ^+-values in this case points to a transition state in which the LUMO of **2** is less disturbed. This is in accordance with the $2S_D + 1S_A$ addend approach pictured in Fig. 1. The transition state may be close to a Π-complex.

EXPERIMENTAL

Ketene acetals, **1a-f**. Compounds, **1a**, **1b**, **1c**, **1d**, **1e** and **1f** were prepared as described in the literature.[28] They were stored at 20° in vessels pretreated with ammonia. Solns of **1b**, used in the following experiments were always freshly prepared because of the instability of **1b**.

Cyclobutanes (**3a**, **c**, **d**, **e**, **f**) see Table 5. A soln of **2f** (7.7 g, 0.05 mole) and a ketene acetal (0.07 mole) in 20 ml THF (acetonitrile for **1d** and **1f**) was kept at the temp and for the time given in Table 5. Then 75 ml of a mixture of pentane and ether (2:1) were added and the ppt removed by filtration. The NMR spectrum of **3a**, **3c** and **3d** showed the presence of small amounts of **2f**. Further purification by crystallization was not possible, however, as the cyclobutanes decomposed under these circumstances. The cyclobutanes **3e** and **3f** were isolated by evaporation of the solvent *in vacuo* and crystallization of the residue from cyclohexane and MeOH, respectively. Yields, physical constants and spectroscopic data are given in Table 5.

1,1,3,3-Tetracyano-4,4-dimethoxy-2,6-diphenylcyclohexane **4a, b**. A soln of **2f** (3.1 g, 0.02 mole) and **1a** (1.8 g, 0.02 mol) in 10 ml acetonitrile was kept for 5 hr at room temp. Evaporation of the solvent *in vacuo* yielded a mixture of two stereoisomers **4a** and **4b**. One isomer (**4a**) was obtained as a pure compound by crystallization from MeOH, m.p. 250° (dec). H¹NMR ($CDCl_3$), 2.35–3.00 (m, AB part of ABX, 2H), 3.30–3.36 (m, X part of ABX, 1H), 3.47 (s, 3H), 3.67 (3, H), 3.77 (s, 1H), 7.30–8.00 (m, 5H) probably the *trans*-isomer.

From the H¹NMR spectrum of the reaction mixture δ-values of protons in **4b** could be determined: 2.35–3.00 (m, AB part of ABX, 2H), 3.47 (s, 3H), 3.60 (s, 3H), 3.88 (s, 1H), 3.80–4.24 (d of d, X part of ABX, 1H) (probably the *cis*-isomer).

2,2-dicyano-3-phenylcyclopropane carboxylic acid methyl ester (**5a**). A soln of **1b** (1.45 g; 0.015 mole) and **2f** (1.5 g, 0.01 mole) in 10 ml acetonitrile was kept for 3 hr at room temp. The solvent was evaporated *in vacuo*. After extraction of the residue with pentane it crystallized from MeOH. Yield, physical constants and NMR data are given in Table 5. The mother liquid after evaporation of MeOH appeared to be a mixture of several compounds which could not be separated. According to NMR a considerable amount of **5a** was still present in the mixture. The presence of a doublet at 4.63 ppm in the NMR spectrum, indicated a product with a H-C(CN)₂-CH-group, probably the open ester HC(CN)₂–CHPh–CHCl–COOMe.

Preparation of the esters **6** *by hydrolysis of 1,1-dimethoxycylobutanes* **3**. A soln of **3a** or **3c** in THF was treated with 2 equivs of water and two drops 1N HCl for 15 min. The cyclobutane **3d** was hydrolyzed with 2 equivs of 4N HCl for 2 hr. After removal of the solvent and the excess of water *in vacuo* the residue was purified by bulb to bulb distillation with a Buchi Kugelrohr oven and subsequently crystallized from cyclohexane. All compounds gave satisfactory microanalysis (C ± 0.5%, H ± 0.2%).

Compound **6a** ($R^1=R^2=H$, Ar=phenyl), yield 85%, b.p. 180°/10 mm (Kugelrohr). H¹NMR ($CDCl_3$) δ2.90 – 3.15 (AB part of ABX with $\Delta\delta(AB) \gg J_{AB}$, 2H), 3.55–3.95 (d of d, X part of ABX, 1H), 3.65 (s, 3H), 4.45 (d, J=6 Hz, 1H), 7.35 (s, 5H).

Compound **6b** ($R^1=H$, $R^2=Me$, Ar=phenyl), yield 85%, m.p. 90–91°. H¹NMR ($CDCl_3$) δ1.05 (d, J=7 Hz, 3H), 2.90–3.60 (m, 2H), 3.75 (s, 3H), 4.50 (d, J=6 Hz, 1H), 7.35 (s, 5H), RS + SR mixture according to X-ray analysis.

Compound **6c** ($R^1=H$, $R^2=Me$, Ar=m-Cl-phenyl, prepared *via* the cyclobutane from **1c** and **2c**), yield 85%, m.p. 84–84.5°. H¹NMR ($CDCl_3$) δ1.00 (d, J=7 Hz, 3H), 2.90–3.60 (m, 2H), 3.85 (s, 3H), 4.55 (d, J=6 Hz, 1H), 7.25–7.50 (m, 4H), RS + SR mixture according to X-ray analysis.

Compound **6d** ($R^1=R^2=Me$, Ar=phenyl), yield 70%, m.p. 112–113°. H¹NMR ($CDCl_3$) δ1.20 (s, 3H), 1.30 (s, 3H), 3.65 (d, J=7 Hz, 1H), 3.75 (s, 3H), 4.50 (d, J=7 Hz, 1H).

Trapping of dipolar intermediates

A ketene acetal (**1a**, **c**, **d**, **e** or **f**, 0.02 mole) was added to a soln of **2f** (0.02 mole, 3.1 g) in 20 ml THF containing 0.2 mole water (3.6 g). Evaporation of the solvent yielded an open ester **6a** or **6b** (from **1a** or **1c** and **2f**) or the cylobutane **3d**, **3e** or **3f** (from **1d**, **e**, **f** and **2f**).

The ester **6b** was obtained as a mixture of diastereomers. The racemate of the RS and SR compounds described above, was the main product (60%). The diastereomers were not further purified. H¹NMR data for the other diastereomer (RR + SS) were obtained from the mixture. $\delta(CDCl_3)$ 1.25 (d, J=7 Hz, 3H), 3.50 (s, 3H), 4.55 (d, J=7 Hz, 1H), 7.30 (s, 5H).

Kinetic measurements

Reactions of 1,1-dimethoxy-2-chloroethene **1b** *and 1,1-dimethoxypropene* **1c** *with dicyanostyrenes* **2a–h** (Tables 1 and 2). Equal amounts (2 ml) of solns of **1b** (0.2–0.8 mole/l) or **1c** ($4 \cdot 10^{-3}$–$2 \cdot 10^{-2}$ mole/l) and of **2a–h** ($5 \cdot 10^{-5}$ mole/l) were pipetted into a thermostated photometric cuvet. The extinction (E) was measured at λ_{max} of the dicyanostyrene where the adduct and ketene acetals had "zero" absorbance. The addition reactions were followed within the range of 20–90% conversion. The rate

Table 5. Products from the reaction of keteneacetals 1a-f with dicyanostyrene 2f

Product	reaction conditions	m.p. (°C)	yield (%)	mass spectra m/e	¹H NMR δ (CDCl₃)
3a	20°/5 min THF	dec.	75		[illegible] (m, AA' part of AA'BB'), 3.32 (s, 3H), 3.55 (s, 3H), 3.23-4 [illegible] (m, 1H, BB' part of AA'BB'), 7.28 (b.s., 5H)
3c	25°/20 min THF	dec. >75	90		1.27 (d, J 7 Hz, 3H), 3.07-3.65 (m, 2H), 3.40 (s, 3H), 3.66 (s, 3H), 7.36 (b.s., 5H)
3d	80°/2 hrs CH_3CN	dec. 25	75		1.20 (s, 3H), 1.26 (s, 3H), 3.44 (s, 3H), 3.51 (s, 3H), 3.57 (s, 3H), 7.35 (b.s., 5H)
3e*	25°/2 hrs	131-134	95	273 (M⁺), 257 (M-CH₃), 241 (M-[illegible]), 156, [illegible], 116, [illegible]	1.43 (s, 3H), 1.57 (s, 3H), 3.6? (s, 3H), [illegible] (d, J 10 Hz, 1H), 4.37 (d, J 10 Hz, 1H), 7.37 (b.s., 5H)
3f*	90°/2 hrs CH_3CN		95	287 (M-CH₃), 2?? (M-[illegible]), 175 (M-[illegible]), 174 (M-1f), 114 (M-2f)	1.16 (s, 3H), 3.43 (s, 3H), 3.5? (s, 3H), 3.63 (s, 3H), 3.69 (s, 3H), 7.22-7.?1 (m, 5H)
4(a,b)	25°/5 hrs CH_3CN	dec. >250	85	376 (M⁺), 361 (M-CH₃), 365 (M-[illegible]), 24? (M-[illegible])	see experimental part
5*	25°/3 hrs	101-104	50	226 (M⁺), 195 (M-OCH₃), 142 (M-[illegible]), 161 (M-[illegible])	1.14 (d, J 7 Hz, 3H), 3.66 (q, J 7 Hz, 1H), 3.75 (s, 3H), 7.37 (b.s., 5H)

*Satisfactory micro analyses were obtained for these compounds (C ± 0.5%, H ± 0.2%)

constants were determined graphically by fitting the experimental results into the appropriate pseudo-first order rate equation. $\ln(E_\infty - E_0)/(E_\infty - E_t) = k[1b.c] \cdot t$ using a least square fit program The reaction led to an equilibrium from which the equilibrium constant K_c could be determined according $K_c = (E_0 - E_e)/([1b.c[E_e])$ in which E_e is the extinction of the equilibrium mixture

Reactions of tetramethoxyethene **1f** *with dicyanostyrenes* **2a–g** (Table 3) Solns of **1f** (0.2–0.6 mole/l) and **2a–g** ($6 \cdot 10^{-3}$ mole/l) in the appropriate solvents (50 ml) were brought to the desired temp in a thermostated bath The reaction was started by mixing 10 ml of both solns in a reaction vessel placed in the thermostated bath At appropriate time intervals a sample (1 ml) was taken from the mixture and diluted to 100 ml with diethyl ether at room temp

The measuring of the extinction and determination of the rate constants were carried out as described above

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