

satisfactory elemental analyses, and their ^1H NMR spectra are reported in Table II.

If the isolation of 2,2'-alkylidenebis(phenols) (3) was of interest, the crude reaction mixture was submitted to steam distillation, which gave almost pure 3.

Compounds 4f and 4g consisted of mixtures of *E* and *Z* isomers, as shown by analysis on a 5% DEGS GLC column.

Trapping of *o*-Quinone Methide Intermediate 8a. Phenoxymagnesium bromide (2 mmol) was reacted in refluxing benzene (15 mL) with 2-methylpropanal (2 mmol) in the presence of ethyl vinyl ether (2 mmol) for 24 h. After the usual workup, a GS/MS analysis of the reaction mixture showed the presence of a new compound [mass spectrum, *m/e* (relative intensity) 220 (M^+ , 19), 177 (100), 149 (30), 133 (29), 121 (10)] identical with the product 12 obtained from the magnesium salt of 7a and ethyl vinyl ether.

Reaction of Magnesium Salt of 7a with Ethyl Vinyl Ether. The alcohol 7a was prepared from 2-hydroxybenzaldehyde and a fourfold molar excess of *i*-PrMgBr. The product was recrystallized from petroleum ether: mp 48–49 °C; mass spectrum, *m/e* (relative intensity) 166 (M^+ , 16), 148 (11), 133 (40), 123 (100); ^1H NMR (CDCl_3) δ 0.85 and 0.95 (2 d, 6 H), 2.05 (m, 1 H), 3.23 (bs, OH), 4.42 (d, 1 H), 7.0 (m, 4 H), 8.2 (bs, OH). Anal. Calcd for $\text{C}_{10}\text{H}_{14}\text{O}_2$: C, 72.26; H, 8.49. Found: C, 72.45; H, 8.58. 7a was reacted in diethyl ether with an equimolar amount of EtMgBr. After removal of the solvent under vacuum and its replacement by benzene, an equimolar amount of ethyl vinyl ether was added, and the mixture was refluxed for 24 h. GLC analysis (OV 101 column) showed the formation of 4a (45%) and 12 (25%). Product 12 was isolated by preparative TLC (hexane/ethyl acetate, 99:1) as an oil: ^1H NMR (200 MHz, CDCl_3) δ 0.70 and 1.04 (2 d, 6 H, $\text{CH}^c(\text{CH}_3)_2$, $J = 7.2$ Hz), 1.27 (t, 3 H, $\text{OCH}_2^{\text{ab}}\text{CH}_3$, $J = 7.2$ Hz), 1.78 (m, 1 H, H-3, $J_{33'} = 13$ Hz, $J_{23} = 8.5$ Hz, $J_{34} = 11.2$ Hz), 2.01 (m, 1 H, H-3', $J_{23'} = 2.5$ Hz, $J_{3'4} = 6.5$ Hz), 2.43 (m, 1 H, H^c, $J_{4c} = 4.6$ Hz), 2.94 (m, 1 H, H-4), 3.61 and 4.08 (2 m, 2 H, H^a and H^b, $J_{\text{ab}} = 11.0$ Hz), 5.04 (dd, 1 H, H-2), 6.08 and 7.10 (2 m, 4 H, ArH). Anal. Calcd for $\text{C}_{14}\text{H}_{20}\text{O}_2$: C, 76.32; H, 9.15. Found: C, 76.51; H, 9.06.

Stability of Magnesium Salt of 2,2'-(2-Methylpropylidene)bis(phenol) (3a). Two experiments were performed: the first with the mono and the second one with the bis magnesium salts of 2,2'-(2-methylpropylidene)bis(phenol) (0.13 M), which were obtained as usual through the reaction with EtMgBr. These salts gave only starting material after 24 h of reflux in benzene.

Stability of 2,3-Dihydro-2,2-dimethylbenzofuran (5a) in

the Presence of (Aryloxy)magnesium Bromides. This product was allowed to react in benzene (0.13 M) at reflux in the presence of phenoxymagnesium bromide (1:1 molar ratio) and of the more soluble (2,4,6-trimethylphenoxy)magnesium bromide. After 24 h 5a was recovered unchanged.

Reaction of Magnesium Salt of 7i with Ethyl Vinyl Ether. The alcohol 7i was prepared from 3,6-dimethyl-2-hydroxybenzaldehyde and a fourfold molar excess of *i*-PrMgBr. The product was recrystallized from petroleum ether: mp 130–131 °C; mass spectrum, *m/e* (relative intensity) 194 (M^+ , 19), 176 (21), 161 (54), 151 (100); ^1H NMR (CDCl_3) δ 0.75 and 1.10 (2 d, 6 H), 1.95 (m, 1 H), 2.21 (s, 6 H), 2.5 (bs, OH), 4.72 (d, 1 H), 6.49 (d, 1 H), 6.93 (d, 1 H), 8.5 (bs, OH). Anal. Calcd for $\text{C}_{12}\text{H}_{18}\text{O}_2$: C, 74.19; H, 9.34. Found: C, 74.05; H, 9.18. 7i was reacted in diethyl ether with an equimolar amount of EtMgBr. After removal of the solvent under vacuum and its replacement by benzene, an equimolar amount of ethyl vinyl ether was added and the mixture was refluxed for 24 h. GLC analysis (OV 101 column) showed the formation of 4i as the only reaction product.

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Registry No. 1 (R = H), 35770-74-2; 1 (R = 4- CH_3), 36359-92-9; 1 (R = 4-*t*- C_4H_9), 36359-99-6; 1 (R = 2-*t*- C_4H_9), 36359-98-5; 1 (R = 2,5-(CH_3)₂), 53863-59-5; 1 (R = 2-*t*- C_4H_9 , 5- CH_3), 53863-60-8; 2 (R¹ = R² = CH_3), 78-84-2; 2 (R¹ = R² = C_2H_5), 97-96-1; 2 (R¹ = CH_3 ; R² = *n*- C_3H_7), 123-15-9; 2 (R¹ = C_2H_5 ; R² = *n*- C_4H_9), 123-05-7; 3a, 86847-31-6; 3b, 86847-32-7; 3c, 86847-33-8; 3d, 86847-34-9; 3e, 86862-64-8; 3f, 86847-35-0; 3g, 86847-36-1; 3h, 86847-37-2; 4a, 6395-29-5; 4c, 86847-38-3; 4d, 86847-39-4; 4e, 86847-40-7; (E)-4f, 86847-41-8; (Z)-4f, 86847-42-9; (E)-4g, 86847-43-0; (Z)-4g, 86847-44-1; 4i, 86847-45-2; 4j, 86847-46-3; 5a, 6337-33-3; 5d, 86847-47-4; 5k, 86853-50-1; 7a, 86847-48-5; 7a diol, 78131-81-4; 7i, 86847-49-6; 7i diol, 86847-50-9; 12, 86847-51-0; EtMgBr, 925-90-6; *i*-PrBr, 75-26-3; phenol, 108-95-2; 4-methylphenol, 106-44-5; 4-*tert*-butylphenol, 98-54-4; 2-*tert*-butylphenol, 88-18-6; 2,5-dimethylphenol, 95-87-4; 2-*tert*-butyl-5-methylphenol, 88-60-8; 2-naphthol, 1321-67-1; (2-naphthylloxy)magnesium bromide, 36381-65-4; ethyl vinyl ether, 109-92-2; 2-hydroxybenzaldehyde, 90-02-8; 3,6-dimethyl-2-hydroxybenzaldehyde, 1666-04-2.

Transition from Concerted to Stepwise [2 + 4] Cycloaddition Reactions of α,β -Unsaturated Carboxylic Esters

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The stereospecificity of the [2 + 4] cycloaddition reaction of electrophilic α,β -unsaturated esters with *cis*- and *trans*-propenyl ethers and with *trans*-anethole, leading to 3,4-dihydro-2H-pyran derivatives, is studied. Reactions with trisubstituted electrophilic olefins are stereospecific and are considered to be concerted, except with methyl 4,4,4-trichloro-2-cyanocrotonate where accompanying cyclobutane formation indicates some stepwise behavior. With tetrasubstituted electrophilic olefins, the reaction products are not stereospecific, and simultaneous cyclobutane formation also indicates stepwise behavior. The reactivity of these olefins is determined by their electronegativity, but the transition from a concerted to a stepwise mechanism appears to be governed by steric hindrance.

The Diels–Alder 1,4-cycloaddition reaction of α,β -unsaturated carbonyl compounds provides an attractive route to 3,4-dihydro-2H-pyrans and has been reviewed by Desimoni and Tacconi.¹ The carbonyl compounds include

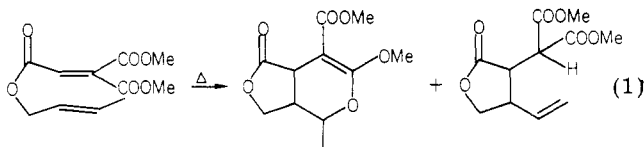
α,β -unsaturated ketones, aldehydes, *N*-acyl imines, etc. More recent reports of similar reactions include the reaction of a vinyl ether with 2-methoxymethylene 1,3-dicarbonyl compounds,² cyclic 2-alkylidene 1,3-dicarbonyl compounds,³ 2-acetyl-2-cyclohexenone,⁴ α,β -unsaturated

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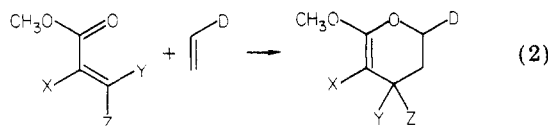
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acyl cyanides,⁵ and malonaldehyde derivatives.⁶

Azo esters, on the other hand, undergo both 1,2- and 1,4-cycloaddition, depending on the nature of the electron-rich olefin as described by Von Gustorf and co-workers.⁷ Snider and co-workers reported the first case of an α,β -unsaturated ester functioning as a diene in a [2 + 4] cycloaddition.⁸ This intramolecular reaction (eq 1) yielded a bicyclic 2-alkoxy-3,4-dihydro-2*H*-pyran (besides an ene reaction adduct).



Our previous paper discussed the intermolecular cycloaddition reactions of electrophilic tri- and tetrasubstituted α,β -unsaturated carboxylic esters with various electron-rich olefins to form 3,4-dihydro-2*H*-pyrans.⁹



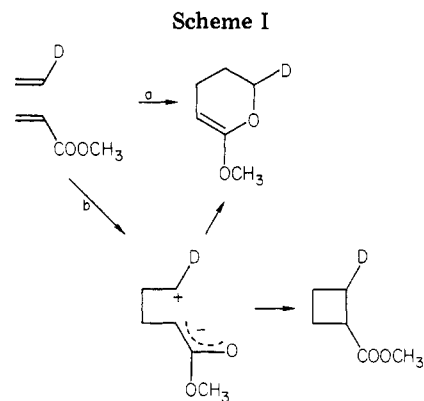
D (donor) = OiBu, C₆H₄-p-OCH₃, ...
X, Y, Z = CN, COOCH₃, H

According to the Woodward-Hoffmann rules, these six-electron reactions are symmetry allowed and may be concerted. The stereospecificity of these reactions has been studied by several investigators.^{3,6,8}

Desimoni¹ describes an exception to this rule in the cycloaddition of heterocyclic carbonyl compounds and dihydropyran; a fraction of the dihydropyran is bonded in the *trans* fashion, while the concerted reaction would yield exclusively *cis*. The authors ascribe this deviation to a two-step mechanism, most likely via zwitterionic intermediates. In numerous reactions on unsaturated ketones with enamines, dipolar intermediates have been described, which can then collapse to a 1,4-cycloadduct (in addition to a variety of different products). The high nucleophilicity of the enamines accounts for these facts.

Another exception to the rule are the azo esters cited above. A characteristic borderline case, discussed by Firl and Sommer,¹¹ is the reaction of azo esters with a vinyl aryl ether. 1,2-Cycloaddition is preferred over 1,4-addition if an electron-donating group increases the nucleophilicity of the vinyl ether. Large solvent effects support the existence of a zwitterionic intermediate. Von Gustorf in his study of the azo ester cycloadditions reactions extensively discusses the necessary criteria to distinguish stepwise and concerted reactions.⁷

Our interest in this area results from our study of the reactions of tri and tetrasubstituted olefins. We have previously reported that these olefins react with elec-

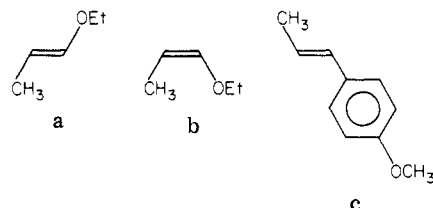


tron-rich olefins to yield cyclobutane derivatives and spontaneous polymerizations.¹²⁻¹⁴ The cyclobutanes clearly form in [2 + 2] stepwise reactions involving a zwitterionic-biradical intermediate.¹⁵ These intermediates are also thought to be the initiating species in the observed accompanying ionic or free radical polymerizations.¹⁶ The question regarding the concerted or stepwise behavior of dihydropyran formation in the reaction of these same or very similar compounds naturally arises.

Dihydropyran can be formed by two possible routes, either by a concerted (route a) or a stepwise mechanism (route b) (Scheme I). The concerted [2 + 4] reaction leads to dihydropyran with retention of configuration. In route b, the intermediate can lead to dihydropyran or to cyclobutane. In this case, at least a portion of the [2 + 4] cycloadduct must arise from the stepwise mechanism, as discussed by Bartlett.¹⁷ This can occur with partial or even total retention of configuration.

In our continuing study of the reaction of electron-poor and electron-rich olefins, we have accumulated a series of cyano and carbomethoxy tri- and tetrasubstituted olefins. The description of the reaction of these compounds with electron-rich olefins has been presented in earlier publications.^{12,13,18-20} The reaction we are concerned with, the [2 + 4] cycloaddition reaction leading to 3,4-dihydro-2*H*-pyran, can occur when at least one acceptor group in the electron-poor olefin is an ester group.

In this study, ethyl *cis*- and *trans*-propenyl ether and *trans*-anethole (b, a, and c, respectively) were used to study the stereospecificity of these [2 + 4] cycloadditions. Methyl 4,4,4-trichloro-2-cyanocrotonate was included as a new electron-poor olefin.



Results

Reactions with Propenyl Ethers. Products. In

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Table I, the reaction conditions used in the inverse electron demand [2 + 4] cycloadditions are listed, as well as the products formed in each reaction. The disappearance of all starting materials and the appearance of all products were followed continuously by NMR. The products were isolated whenever possible.

All [2 + 4] cycloadditions are regiospecific, yielding only 2-alkoxy-3,4-dihydro-2*H*-pyrans. In most cases, only one stereoisomer of the dihydropyran is formed within the detection limits of the NMR instrument used (<5%). In the reaction of the trichloromethyl-substituted olefin **5** and of dicyanofumarate **7**, cyclobutanes are formed simultaneously with dihydropyrans.

Table II lists NMR data of the different isomers of dihydropyran obtained. The chemical shifts of the ring protons and the coupling constants of the acetal proton have been listed. Absorbing in the region δ 5.0–5.5, this acetal proton is easily analyzed and is the most distinguishing feature of the dihydropyran structure. One doublet is observed for each isomer due to splitting by a single adjacent hydrogen.

Table III lists the NMR data of the cyclobutanes.

Conformation. Dihydropyran stereochemistry was assigned on the basis of comparison of NMR coupling constants with the expected configuration and conformation. The configuration at C-4 cannot be obtained directly from $J_{3,4}$ as this coupling is difficult to determine in the NMR. In most cases, the configuration is determined by the Alder rule or the endo effect (Table I). If both endo and exo isomers are formed, we have no way of identifying them.

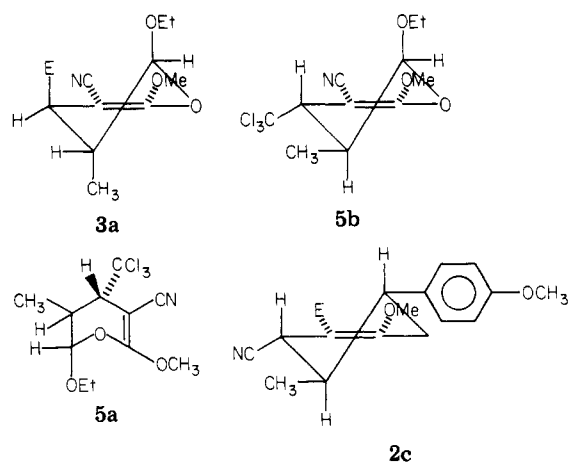
According to the Karplus equation,²¹ diaxial vicinal hydrogens are expected to give large coupling constants (10–14 Hz). The observed coupling constants between H-2 and H-3 are in the range of 2–8 Hz, thus indicating that OR is axial at C-2 in the dihydropyrans obtained from reaction of electrophilic olefins with β ester and/or nitrile substituents with vinyl ethers. The axial position of the 2-alkoxy group is in accordance with the anomeric effect.

The configuration about C-3 and the overall conformation can be deduced from the *cis* and *trans* coupling constants of H-2 and H-3. The magnitude of these coupling constants can be explained in terms of diaxial, diequatorial, and axial–equatorial orientations. In 2,3-*cis*-disubstituted dihydropyrans obtained from ethyl *cis*-propenyl ether, the coupling constant between H-2 and H-3 is very small (1.5–2.2 Hz), corresponding to the coupling between an equatorial and axial hydrogen. For the 2,3-*trans*-disubstituted dihydropyrans, the coupling constant between H-2 and H-3 is 6–8 Hz, both hydrogens being equatorial (Chart I, **3a**). These values correspond to a half-chair conformation with the 2-alkoxy substituent in the axial position.²²

In the adducts obtained from the reactions of **5**, 1,3-diaxial interactions become more important than the anomeric effect. The coupling constant $J_{2,3}$ observed in the adducts of **5** with ethyl *cis*-propenyl ether (Chart I, **5b**) corresponds to a half-chair conformation in which the bulky trichloromethyl group is equatorial. In the dihydropyran obtained from **5** with ethyl *trans*-propenyl ether, a half-boat (or boat) is sterically most favorable due to added 2,3 steric interactions (Chart I, **5a**).

Mechanism. A concerted reaction requires preservation of the vinyl ether stereochemistry at the 2,3-positions of the dihydropyran. Loss of this stereochemistry indicates

Chart I



a stepwise reaction mechanism.

The reactions of the trisubstituted olefins **1–4** with ethyl *cis*- and *trans*-propenyl ether yield one isomer of dihydropyran each, with only one exception. In the reaction of **2** with the *cis*-propenyl ether, isomers resulting from both endo and exo attack of the vinyl ether are obtained due to unfavorable steric interactions in the transition state leading to the endo isomer. These reactions may be concerted as shown by their stereospecificity.

Reaction of **5** with ethyl *cis*-propenyl ether gives one isomer of dihydropyran (resulting from exo attack of the ethyl ether), which slowly isomerizes to give an isomer of dihydropyran which is identical with that obtained upon reaction of **5** with the *trans*-propenyl ether (resulting from endo attack of the ethyl ether). The dihydropyran formation could still be mostly concerted, but simultaneously formed cyclobutane indicates the occurrence of a competing stepwise reaction.

Reaction of tetrasubstituted olefin **6** with the *cis*-propenyl ether yields only one isomer of dihydropyran, and so the reaction may be concerted. Reaction of **6** with the *trans*-propenyl ether yields both the 2,3-*cis*- and 2,3-*trans*-substituted dihydropyrans and is nonstereospecific.

Reaction of the tetrasubstituted olefin **7** with the *trans*-propenyl ether gives two isomers of dihydropyran in which the *trans* configuration of the vinyl ether is retained as shown by the magnitude of $J_{2,3'}$ (7.0 and 5.9 Hz). A cyclobutane is also observed. The stepwise and concerted reactions may be occurring simultaneously. Reaction of **7** with the *cis*-propenyl ether gives the four possible isomers of dihydropyran and a mixture of cyclobutane isomers. This reaction is definitely stepwise.

Reactions with Anethole. Table IV summarizes the results of the reactions of the electrophilic olefins with *trans*-anethole. Two conclusions can be made from these results. First, *trans*-anethole is much less reactive than the propenyl ethers; the cycloadditions are much slower and in some cases do not occur at all. Second, all cycloadditions yield only one isomer of the dihydropyran. The NMR data are included in Table II.








We again postulate that the Alder rule is observed, and structural assignments at C-4 of the dihydropyran isomers are based on endo attack. The bulky *p*-methoxyphenyl group at C-2 prefers the equatorial position in a half-chair conformation.²³ The observed $J_{2,3}$ values are larger (greater than 10 Hz) due to the large dihedral angle between the two axial protons (Chart I, **2c**). The reaction

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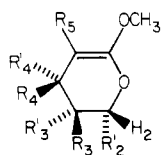
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Table I. Products from Electron-Poor Olefins with Propenyl Ethers^{a, b}

electron-poor olefin	propenyl ether	reaction conditions	product (% yield) ^c	2-alkoxy substituent	3-Me substituent	can be concerted?	β substituent	endo or exo approach
	trans a cis b	65 °C, 48 h 65 °C, 48 h	1a (100) 1b (100)	axial axial	axial equat	yes yes	equat equat	endo endo
	trans a cis b	25 °C, 20 h 25 °C, 20 h	2a (100) 2b ^d 2b'	axial axial axial	axial equat equat	yes yes	equat equat axial	endo endo endo
	trans a cis b	25 °C, 5 h 25 °C, 5 h	3a (100) 3b (100)	axial axial	axial equat	yes yes	axial axial	endo endo
	trans a cis b	25 °C, 1 h 25 °C, 1 h	4a (100) 4b (100)	axial axial	axial equat	yes yes	axial axial	endo endo
	trans a cis b	25 °C, 3 h 25 °C, 12 h	5a (100) 5b' (10) + 5a (25) + cyclobutane 5d (65)	^e axial	equat	yes no	equat	endo exo
	trans a cis b	25 °C, 2 h 25 °C, 1.5 h	6a (70) + 6b (30) 6b (100)	axial axial	axial equat	no yes	axial/ equat axial/ equat	"endo and/or exo" "endo and/or exo"
	trans a cis b	25 °C, 1.5 h 25 °C, 1.5 h	7a ^f 7a' + cyclobutane 7d (40) 7b ^g 7b' + 7a + 7a' + cyclobutanes 7d' (30)	axial axial axial axial	axial axial equat equat	no no	CN equat, E axial CN axial, E equat CN equat, E axial CN axial, E equat	"endo" "exo" "endo" "exo"

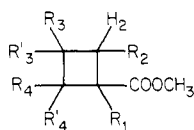
^a E = COOCH₃. ^b All reactions run in 1 mL of CDCl₃; 1 mmol of electron-poor olefin and 2 mmol of electron-rich olefin (except for 5, only 1 mmol). ^c All yields are determined by NMR. ^d Total yield is 100%; ratio of isomers = 2/1. ^e See Figure 1c: half-boat conformation. ^f Total yield of pyrans is 60%; ratio of isomers = 2/1. ^g Total yield of pyrans is 70%.

Table II. 3,4-Dihydro-2H-pyran Properties^{a, b}

isomer	substituents						mp, °C	¹ H NMR, δ			coupling constant, Hz	
	R ₂ '	R ₃	R ₃ '	R ₄	R ₄ '	R ₅		H ₂	H ₃ /H ₃ '	H ₄ /H ₄ '	J _{2,3} '	J _{2,3}
1a	OEt	CH ₃	H	E	H	E	*	5.15 (d)			7.5	
1b	OEt	H	CH ₃	E	H	E	*	5.15 (d)	2.1 (m)	3.3 (d)		2.0
2a	OEt	CH ₃	H	CN	H	E	70-74*	5.1 (d)	2.1 (m)		8.1	
2b (2b')	OEt	H	CH ₃	CN(H)	H(CN)	E	*	5.3 (d)	2.3 (m)	3.4		2.0
								5.2 (d)	2.2 (m)	3.4		2.1
2c	Ar	CH ₃	H	CN	H	E	92-94	4.8 (d)			10.1	
3a	OEt	CH ₃	H	H	E	CN	*	5.0 (d)	2.6 (m)		3.5	
3b	OEt	H	CH ₃	H	E	CN	*	5.05 (d)	2.4 (m)			1.5
3c	Ar	CH ₃	H	H	E	CN	*	4.5 (d)	2.3 (m)	3.1 (d)	10.4	
4a	OEt	CH ₃	H	H	CN	CN	119-121	5.1 (d)	2.4 (m)	3.2 (d)	3.8	
4b	OEt	H	CH ₃	H	CN	CN	83-86	5.2 (d)	2.2 (m)	3.5 (d)		1.8
4c	Ar	CH ₃	H	H	CN	CN	113-115	4.6 (d)	2.4 (m)	3.5 (d)	10.4	
5a	OEt	CH ₃	H	H	CCl ₃	CN	95-106*	5.15 (d)	2.7 (m)	3.7 (d)	2.1	
5b'	OEt	H	CH ₃	CCl ₃	H	CN	*	5.22 (d)	3.1 (m)	3.8 (d)		1.3
6a	OEt	CH ₃	H	E	E	CN	99-112	5.2 (d)	2.7 (m)		5.6	
6b	OEt	H	CH ₃	E	E	CN	102-107	5.3 (d)	2.6 (m)			1.8
6c	Ar	CH ₃	H	E	E	CN	141-143	5.1 (d)	2.6 (m)		11.0	
7a (7a')	OEt	CH ₃	H	CN(E)	E(CN)	CN	90-98	5.45 (d)	2.7 (m)		7.0	
								5.25 (d)	2.7 (m)		5.9	
7b (7b')	OEt	H	CH ₃	CN(E)	E(CN)	CN	*	5.41 (d)	2.6 (m)			1.8
								5.35 (d)	2.6 (m)			2.2
7c	Ar	CH ₃	H	CN	E	CN	125-128	5.02 (d)	2.7 (m)		10.7	
8	OEt	H	H	H	CCl ₃	CN	112-114	5.23 (dd)	2.2-2.8 (m)	3.7	10.0	2.4

^a E = COOCH₃, Ar = C₆H₄OCH₃, and an asterisk * = unstable. ^b Infrared spectral data (cm⁻¹, KBr) are as follows. 2c: 2960, (2250), 1750, 1610, 1520, 1460, 1260. 4a: 2950, 2205, 1620, 1470, 1380, 1320, 1250. 4b: 2980, 220, 1630, 1470, 1385, 1330, 1260. 4c: 2210, 1620, 1510, 1460, 1380, 1250, 1170. 5a: 2960, 2205, 1600, 1465, 1375, 1320, 1290, 1160. 6a: 2970, 2225, 1750, 1630, 1460, 1390, 1320, 1280. 6b: 2960, 2230, 1760, 1740, 1615, 1470, 1440, 1390, 1260. 6c: 2950, 2210, 1750, 1720, 1615, 1510, 1465, 1250. 7a: 2980, 2225, 1750, 1620, 1750, 1380, 1260. 7c: 2970, 2220, 1750, 1615, 1520, 1475, 1440, 1380, 1260. 8: 2975, 2200, 1600, 1455, 1370.

Table III. NMR Data of Cyclobutanes



isomer	substituents ^a						¹ H NMR, δ			J _{2,3} , Hz
	R ₂	R ₃	R ₃ '	R ₄	R ₄ '	R ₁	H ₂	H ₃	H ₄	
5d ^b	OEt	CH ₃	H	H	CCl ₃	CN	4.53	3.0-3.4	4.1	8.8
7d	OEt	H	CH ₃	E	CN	CN	4.52	2.3-2.5	3.5	9.1
7d'	OEt	CH ₃	H	E	CN	CN	4.5-4.8	2.4-2.7	3.6	
8d	OEt	H	H	H	CCl ₃	CN	4.67	2.5-2.8	4.2	8.4

^a E = COOCH₃. ^b Infrared spectral data (KBr) for 5d: 2990, 2250, 1740, 1605, 1440 cm⁻¹.

Table IV. Products from Electron-Poor Olefins with *trans*-Anethole (c)

electron-poor olefin ^a	reaction conditions ^b	product (% yield)	2- <i>p</i> -MeOPh substituent	3-Me substituent	can be concerted?	β substituent	endo or exo approach
1	65 °C	no reaction					
2	25 °C, 7 weeks	2c (50)	equat	equat	yes	axial	endo
3	25 °C, 2 weeks	3c (75)	equat	equat	yes	equat	endo
4	25 °C, 20 h	4c (100)	equat	equat	yes	equat	endo
5	65 °C	no reaction					
6	65 °C, 1 week	6c (30)	equat	equat	yes	equat and axial	endo
7	65 °C, 20 h	7c (100)	equat	equat	yes	CN axial E equat	endo endo

^a E = COOCH₃. ^b All reactions run in 1 mL of CDCl₃: 1 mmol of electron-poor olefin and 2 mmol of electron-rich olefine (except for 5, only 1 mmol).

is stereospecific and retains the *trans* configuration of the *trans*-anethole moiety.

Reactivity of Electrophilic Olefins. The relative reactivities of the electron-poor olefins can be deduced from the reaction conditions necessary to obtain complete conversion. The following order is established: methyl (*E*)-2,3-dicyanoacrylate (4) > dimethyl dicyanofumarate (7) ≥ trimethyl cyanoethylenetricarboxylate (6) > dimethyl cyanofumarate (3) > methyl 4,4,4-trichloro-2-cyanocrotonate (5) > dimethyl 2-cyanoethylene-1,1-dicarboxylate (2) > trimethyl ethylenetricarboxylate (1). More polar or more electronegative olefins such as dimethyl 2,2-dicyanoethylene-1,1-dicarboxylate lead mostly to cyclobutanes.²⁰ Tetramethyl ethylenetetracarboxylate is very unreactive and yields only cyclobutane at high temperature.¹⁹

Discussion

As mentioned at the beginning of this paper, previous investigators of [2 + 4] cycloadditions yielding dihydropyrans have generally accepted a concerted mechanism. Although the criteria of stereospecificity are not fully sufficient in differentiating concerted from stepwise behavior, it should be considered a good indicator, particularly in indicating that a reaction is *not* concerted. Furthermore, accompanying formation of cyclobutane adducts does occur via a stepwise mechanism.

Reactions of the trisubstituted olefins 1–4 with electron-donating olefins yield stereospecific products. Accordingly, these [2 + 4] cycloaddition reactions are considered to be concerted.

The tetrasubstituted olefins 6 and 7 show evidence of some stepwise behavior. Steric factors are very important in these cases and force the reaction to proceed partially or totally stepwise with loss of vinyl ether stereochemistry in the dihydropyrans formed. In the reactions of the trichloromethyl-substituted olefin 5, the additional steric bulk of the trichloromethyl group allows a simultaneous stepwise mechanism to compete with the concerted mechanism; cyclobutanes are formed along with dihydropyrans.

On the electron-rich side, a transition from concerted to stepwise reaction is observed with the propenyl ethers. With *trans*-anethole all reactions are considered to be concerted. The alkoxy group of the vinyl ether has a greater ability to stabilize a cation in a zwitterionic tetramethylene intermediate, and this could account for the greater tendency toward stepwise reactions with the vinyl ethers. This behavior mimics the cases described by previous investigators, in which the nucleophilicity of the dienophile determined the mechanism.

In predicting whether a reaction will proceed in a stepwise or concerted fashion, it is not possible to correlate the electronegativity of the electrophilic olefin with the mechanism. The electronic factors do correspond to the reactivity, meaning that the more electron-poor olefin will react faster. Stepwise behavior, though, is only observed in the highly sterically hindered systems. As mentioned

earlier, the highly polar and very electrophilic olefins, such as the ones with two terminal cyano groups, also react in a stepwise fashion, leading predominantly to cyclobutanes.

In conclusion, we can state that in these systems a transition from concerted to stepwise behavior has been observed.

Experimental Section

Instrumentation. The NMR spectra have been recorded on a Varian T-60 NMR spectrometer. In a few cases a 250-MHz NMR spectrum was run on a Bruker WM-250 FT spectrometer for verification purposes only. The melting points were measured on a Thomas-Hoover melting apparatus and are uncorrected. The infrared spectra were recorded on a Perkin-Elmer 710A spectrophotometer. The chemical analyses were performed by Micanal, Tucson, AZ.

Chemicals. The known electron-poor olefins were prepared as described in the literature.^{12,13,18–20} Ethyl *cis*- and *trans*-propenyl ether were purchased from Fluka as a 60/40 mixture and separated by spinning-band column distillation as described;²⁴ bp 63 °C (*cis*), 69 °C (*trans*) (lit. *cis*, 69.7 °C; *trans*, 75.7 °C). *trans*-Anethole was obtained from Aldrich and used without purification. The chloroform-*d* was also obtained from Aldrich and used as such. Methyl 4,4,4-trichloro-2-cyanocrotonate (5) was obtained as follows. Freshly distilled chloral (40.2 g, 0.27 mol), 22.3 g (0.23 mol) of methyl cyanoacetate, 4.5 g of glacial acetic acid, 0.68 g of β-alanine, and 60 mL of benzene were refluxed with a Dean-Stark trap for 24 h. The benzene was removed under aspirator vacuum and the remaining solution vacuum distilled. Olefin 5 was collected at 73–75 °C (.07 torr). The crystalline solid (mp 39 °C) was redistilled to give pure product: 0.12 mol (51%); ¹H NMR (CDCl₃) δ 3.95 (s), 7.9 (s); IR (KBr) 3050, 2245, 1710, 1610, 1440, 1340 cm⁻¹. Anal. Calcd for C₅H₄Cl₃NO₂: C, 31.54; H, 1.76; N, 6.13. Found: C, 31.49; H, 1.63; N, 6.13.

Typical Procedure. Trimethyl ethylenetricarboxylate (2; 1 mmol, 202 mg) is dissolved in 1 mL of chloroform-*d* and mixed with 2 mmol of ethyl *cis*-propenyl ether (170 mg, 221 μL). The mixture is placed in a capped NMR tube and kept at the desired temperature (room temperature or 65 °C). The NMR spectrum is periodically checked. After total consumption of the electron-poor olefin, the excess propenyl ether and the solvent are evaporated, and the dihydropyran is dissolved in a minimum amount of diethyl ether. The solution is placed at –50 °C to recrystallize. Several dihydropyrans are not stable and will decompose on standing or attempted isolation. The infrared spectral data are summarized in the footnote of Table II. The chemical analyses are satisfactory (within 0.3%).

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Registry No. 1, 51175-48-5; 1a, 87040-07-1; 1b, 87040-08-2; 2, 62693-70-3; 2a, 87040-09-3; 2b, 87040-10-6; 2b', 87040-11-7; 2c, 87040-12-8; (*E*)-3, 54797-29-4; 3a, 87040-13-9; 3b, 87040-14-0; 3c, 87050-09-7; (*E*)-4, 84591-89-9; 4a, 87040-15-1; 4b, 87040-16-2; 4c, 87040-17-3; (*E*)-5, 87040-05-9; 5a, 87040-18-4; 5b', 87040-19-5; 5d, 87040-29-7; 6, 87040-06-0; 6a, 87040-20-8; 6b, 87040-21-9; 6c, 87040-21-9; (*E*)-7, 35234-87-8; 7a, 87040-23-1; 7a', 87040-24-2; 7b, 87040-25-3; 7b', 87040-26-4; 7c, 87040-27-5; 7d, 87040-30-0; 8, 87040-28-6; 8d, 87040-31-1; a, 4696-26-8; b, 4696-25-7; c, 4180-23-8.

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