01-7; **4c**, 4160-95-6; **4d**, 80721-12-6; **4e**, 4160-99-0; **5a**, 61193-04-2; **5b**, 1135-62-2; **5c**, 80721-13-7; **5d**, 64635-91-2; **5e**, 4161-05-1; **6c**, 868-04-2; **6d**, 759-54-6; **6e**, 868-00-8; **7a**, 17804-59-0; **7b**, 80721-14-8; **7c**, 51111-06-9; **7d**, 80721-15-9; **7e**, 80721-16-0; **8a**, 54851-48-8; **8b**, 72826-61-0; **8c**, 72807-62-6; **8d**, 80721-17-1; **8e**, 80721-18-2; **9a**, 68757-99-3; **9b**, 72807-70-6; **9c**, 72807-69-3; **9d**, 80721-19-3; **9e**, 80721-20-6; **10a**, 80721-21-7; **10b**, 80721-22-8; **10c**, 80721-23-9; **10d**, 80721-24-0; **10e**, 80721-25-1; cyclopentadiene, 542-92-7; 5,5-diphenylcyclopentadiene, 71516-78-4; spiro[4.3]octa-5,7-diene, 15439-15-3; spiro[4.4]nona-1,3-diene, 766-29-0.

(Carbomethoxy)maleic Anhydride, a Highly Reactive New Dienophile and Comonomer

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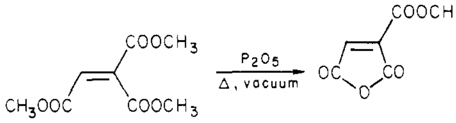
(Carbomethoxy)maleic anhydride (CMA), is an extremely reactive dienophile in [4 + 2] cycloadditions with butadiene, isoprene, and chloroprene. The second-order rate constants prove it to be more reactive than tetracyanoethylene. Diels–Alder reaction with anthracene gives the normal addition product. With cyclopentadiene, the endo adduct is obtained and with furan the exo adduct. With *p*-methoxystyrene, anethole, and diphenylethylene, the 2:1 Wagner-Jauregg-type adducts are obtained, while with styrene both the Wagner-Jauregg and the Diels–Alder ene adduct are formed. Copolymers form in certain conditions. With isobutyl and phenyl vinyl ether, an inverse-electron-demand Diels–Alder reaction with CMA yields 2-isobutoxy- or 2-phenoxy-6-methoxy-3,4-dihydro-2*H*-pyran-3,4-dicarboxylic anhydride. These labile dihydropyrans revert to copolymers.

Introduction

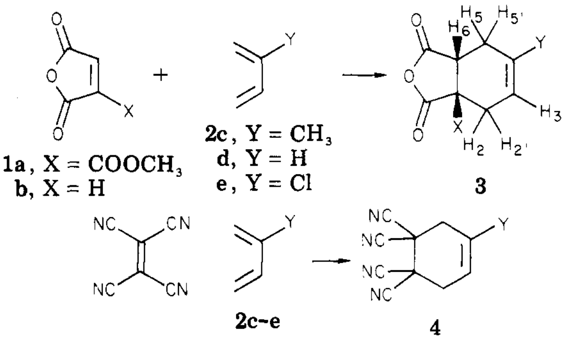
Maleic anhydride takes part in a variety of cycloaddition and copolymerization reactions not readily undergone by 1,2-disubstituted ethylenes due to the minimization of the steric effect by confining the two substituents into a ring and to the planar structure which permits effective resonance stabilization of radical or anionic intermediates. These cycloadditions have been recently reviewed by Sauer and Sustmann.[1]

Our work on electrophilic trisubstituted ethylenes such as trimethyl ethylenetricarboxylate has shown that they are also much more reactive than their 1,2-disubstituted counterparts in cycloaddition and copolymerization reactions.[2-8] Here the reason is that two α-substituents stabilize reactive intermediates much more effectively than one.

Accordingly, a maleic anhydride carrying an electrophilic carbon function should be especially reactive in these reactions. The literature did not offer such a compound. We recently[9] synthesized (carbomethoxy)maleic anhydride (CMA) by a little-used demethoxylation–cyclization reaction:[10]



Scheme I



In the present paper we report a study of the reactions of CMA with electron-rich 1,3-dienes, styrenes, and vinyl ethers.

Results

Reactions with 1,3-Dienes. CMA reacted far more rapidly than maleic anhydride (MAnh) with isoprene, butadiene, and chloroprene. It was even more reactive than tetracyanoethylene (TCNE). The products were the expected Diels–Alder cycloadducts (Scheme I). The structure of adduct **3ac** obtained in the reaction of CMA with isoprene was analyzed by 250-MHz ^{1}H NMR spectroscopy. The details are listed in the Experimental Section. Second-order rate plots are shown in Figure 1. The rate constants for these reactions are reported in Table I.

In chloroform solution at room temperature, CMA reacted with anthracene within a few minutes, as did TCNE.[1,11] MAnh still showed a mixture of adduct and

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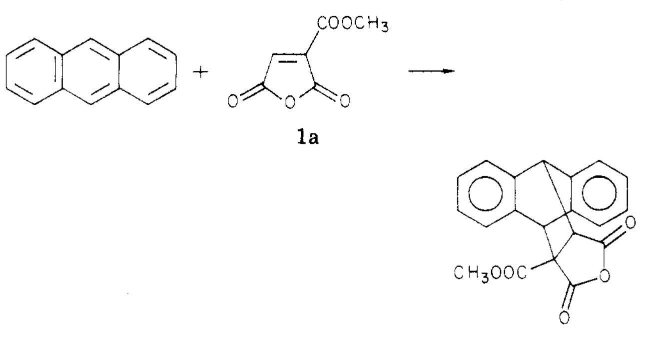
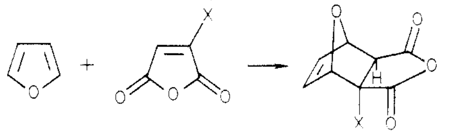
starting materials after 12 days in chloroform-d_3.



1a

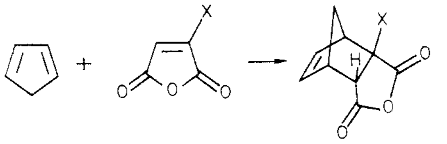
5

With furan both CMA and MAnh gave equilibrium mixtures of reactants and adducts. Again, the rate of approach to equilibrium was much faster for CMA than for maleic anhydride. This equilibrium could be shifted in favor of products by running the reaction in excess furan or in a poor solvent to precipitate the adduct as formed. The CMA–furan adduct **6a**, dissolved in chloroform, reverted immediately to the equilibrium composition, whereas the maleic anhydride–furan adduct **6b** required 2 weeks. The anhydride function is exo in this adduct as proven by NMR spectroscopy.[12]



6

CMA and MAnh reacted rapidly at room temperature with cyclopentadiene in $CDCl_3$ to form the corresponding adducts **7a** and **7b**. Here both reactions were too fast for comparison. The extensively split signals in the NMR spectrum indicate that the anhydride function is in the expected endo position.

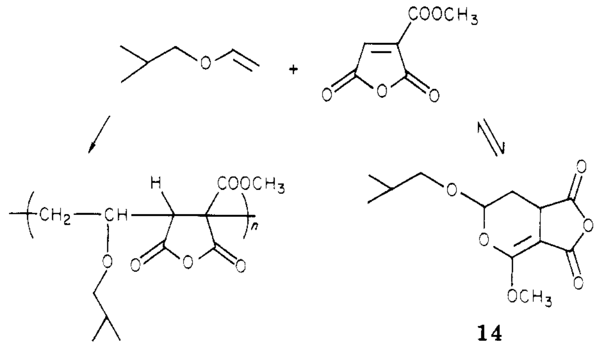


7

Reactions with Styrenes. *p*-Methoxystyrene, anethole (*p*-methoxy-β-methylstyrene), styrene, and 1,1-diphenylethylene reacted with CMA at 28 °C to give high yields of Wagner–Jauregg-type adducts[13] formed by two consecutive Diels–Alder reactions. In the case of styrene the so-called "Diels–Alder ene" adduct **9** is also formed. In certain conditions copolymer formation occurred with styrene and diphenylethylene. Scheme II outlines the possible reaction paths with styrene and CMA. Table II summarizes the results.

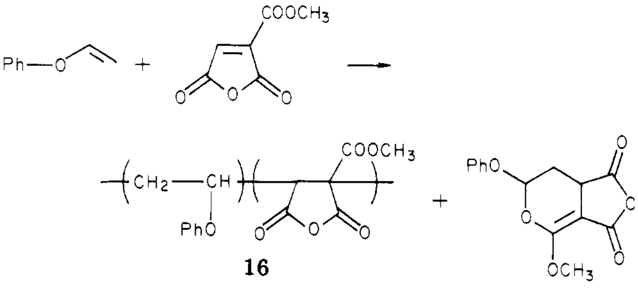
Reactions with Vinyl Ethers. The reactions of CMA with several vinyl ethers with decreasing electron richness were examined.

In the reaction of isobutyl vinyl ether and CMA, a "inverse electron demand" Diels–Alder reaction occurs at room temperature to form a pyran derivative 2-isobutoxy-6-methoxy-3,4-dihydro-2*H*-pyran-3,4-dicarboxylic anhydride **14**. This reaction is reversible and the labile pyran is slowly converted into copolymer **15** in 90% yield.



15

14



16

17

Phenyl vinyl ether reacts spontaneously with CMA at room temperature to form mostly copolymer **16** richer in CMA and 10% pyran derivative **17**.

Tribromophenyl vinyl ether is much less reactive. With CMA in chloroform at 70 °C only poly-CMA is formed (60% yield). No cycloadduct or copolymer is detected.

Discussion

As hoped for, CMA indeed proved to be very reactive in [4 + 2] cycloadditions with 1,3-dienes. In fact, it is by far the most reactive dienophile composed of only C, H, and O and is also more reactive than tetracyanoethylene.

In the cycloaddition with cyclopentadiene and furan, CMA parallels the behavior of MAnh. With cyclopentadiene the expected endo adduct is formed in agreement with the Alder endo rule. With furan the exo adduct is obtained, similar to the MAnh–furan adduct as proven by Lee and Herndon.[12] With anthracene and CMA, the normal addition across the 9- and 10-carbons leads to **5**.

The high dienophilic character of CMA extended to the styrenes studied. As described by Wagner-Jauregg in his extensive review,[13] in vinylogues of aromatic compounds, the extracyclic ethylene moiety together with an adjacent ring "double bond" can function as a diene system. The reaction will frequently lead to so-called "Wagner-Jauregg-type" 2:1 adducts. Such 2:1 adducts were obtained in the cycloaddition of CMA to *p*-methoxystyrene, anethole, diphenylethylene, and styrene. In the styrene–CMA cycloaddition the 2:1 "Diels–Alder ene" adduct **9** is also obtained. Similar reactions have also been noted for maleic anhydride but required far more severe reaction conditions.[1,14,15] Copolymers of CMA with the styrenes were obtained as side products, depending on the conditions.

CMA reacted rapidly with isobutyl and phenyl vinyl ether at room temperature. The cyclo adducts, namely, 6-methoxydihydropyrans **14** and **17**, were identified and result from an inverse-electron-demand Diels–Alder reaction in which CMA acts as an electrophilic diene. Such

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Table I. Kinetics Data for $_{\pi}2 + {}_{\pi}4$ Reactions of CMA with Acyclic 1,3-Dienes[a]

	initial	CMA			TCNE			MAnh		
diene	concn, M	adduct	10^3k_2	$t_{1/2}$	adduct	10^3k_2	$t_{1/2}$	adduct	10^5k_2	$t_{1/2}$
isoprene	0.83	**3ac**	>20	<1 min	**4c**	>4 [11.3]	<5 min	**3bc**	8.4 [15.4]	4 h
butadiene	0.83	**3ad**	>4	<5 min	**4d**	1.34	15 min	**3bd**	3.7	9 h
butadiene	0.24	**3ad**	5.8	12 min	**4d**	1.29	54 min	**3bd**	2.4	2 days
chloroprene	0.83	**3ae**	0.27	1.25 h	**4e**	equil [0.01]		**3be**	0.28 [0.69]	5 days

[a] Conditions: solvent, acetone-d_6; temperature, 35 °C; followed by NMR. Data in brackets are those of Huisgen[11] obtained in dioxane; 20 °C for TCNE, 30 °C for MAnh. k_2 in M^{-1} s^{-1}.

Table II. Summary of the Reactions between CMA and Various Styrenes

	solvent	rctn cndtns	result
p-methoxystyrene	ether	28 °C/20 min	67% adduct **11**
	none	70 °C	24% 1:1 copolymer + 24% **11**
anethole	acetone	28 °C	70% adduct **12**
	none	28 °C	72% adduct **12**
1,1-diphenylethylene	ether	28 °C	20% **13** + 1:1 copolymer
styrene	none	70 °C/3 h	60% (**8** + **9**) + 27% 1:1 copolymer
	$CHCl_3$	28 °C/2 h	20% 1:1 copolymer + 40% adduct (40% **8** + 60% **9**)
	acetone	28 °C/10 h	**8** + **9**
	ether	28 °C	mostly copolymer **10** (richer in CMA)

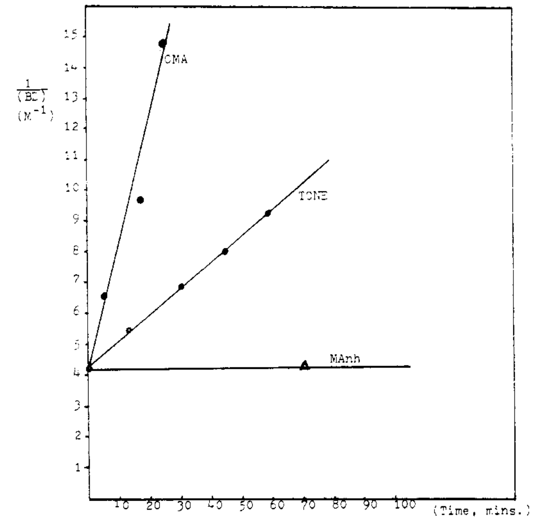
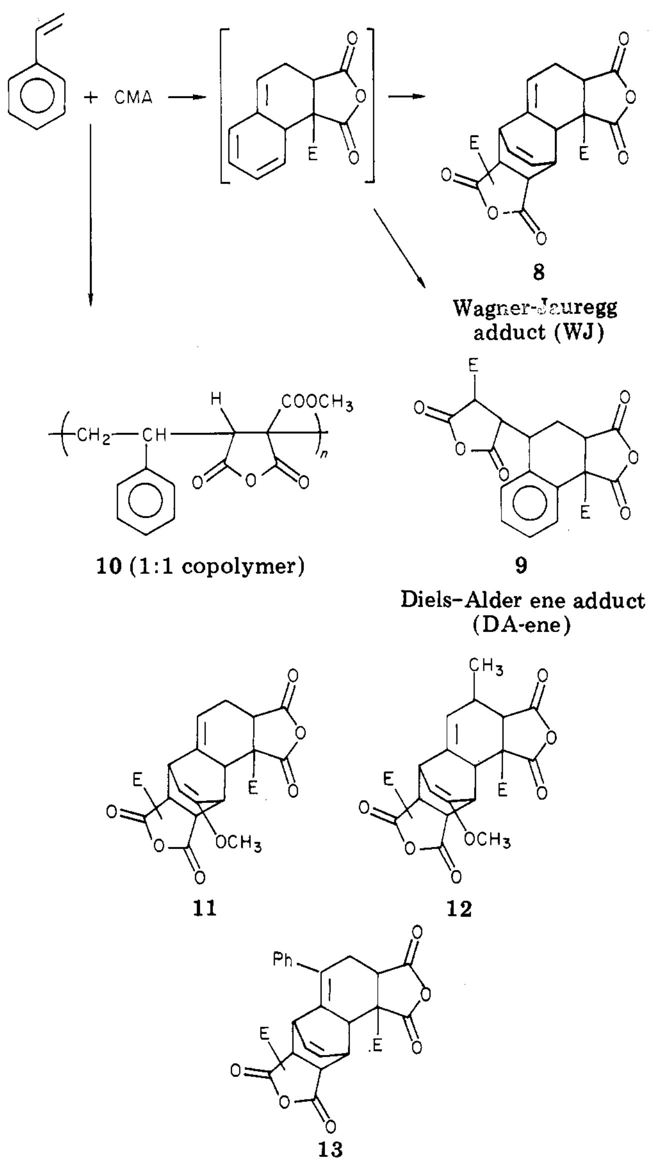


Figure 1. Second-order rate plots for reactions of butadiene with CMA, TCNE, and MAnh: initial concentrations, 0.24 M; solvent, acetone-d_6; temperature, 35 °C.

Scheme II[a]



[a] E = $COOCH_3$.

cycloadducts have recently been observed in cycloaddition reactions of electrophilic α,β-unsaturated esters with electron-rich olefins.[16] The labile dihydropyrans readily revert to copolymer.

Contrary to the behavior of tetracyanoethylene, which will preferentially form cyclobutanes with styrenes and vinyl ethers, CMA always forms the [4 + 2] adducts. MAnh has been reported to form a 2:1 cyclohexane adduct with dialkoxyethylene derivatives.[17] To our knowledge thermal reactions of MAnh with styrenes lead to copolymers or Wagner-Jauregg adducts, while with vinyl ethers only copolymers have been reported. Parallel to the CMA behavior, no [2 + 2] cycloadditions are known for MAnh.

As described in previous work,[7,8] the spontaneous polymerizations are believed to be initiated by a tetramethylene intermediate formed by reaction of the electron-poor and the electron-rich olefin. This tetramethylene is a hybrid of a zwitterion and a biradical.[18] In the reactions of CMA described in this work, the biradical tetramethylene is the predominant resonance form as wit-

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Table III. NMR Assignments of Diels-Alder Adducts from CMA, MAnh, and TCNE with Isoprene, Chloroprene, and Butadiene

structure	NMR, δ
3ad	2.7 (m, 4 H), 3.8 (s, 3 H), 4.0 (m, 1 H), 6.1 (m, 2 H)
3ae	2.9 (d, 4 H), 3.8 (s, 3 H), 4.2 (t, 1 H), 6.0 (m, 1 H)
3bc	1.8 (m, 3 H), 2.4 (m, 4 H), 3.5 (m, 2 H), 5.6 (m, 1 H)
3bd	2.4 (m, 4 H), 3.6 (m, 2 H), 5.9 (m, 2 H)
3be	2.7 (m, 4 H), 3.7 (m, 2 H), 6.0 (m, 1 H)
4c	2.0 (m, 3 H), 3.4 (m, 4 H), 5.8 (m, 1 H)
4d	3.4 (d, 4 H), 6.0 (m, 2 H)
4e	3.6 (m, 2 H), 3.8 (m, 2 H), 6.2 (m, 1 H)

nessed by the formation of copolymers.

Experimental Section

Instrumentation. All melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected. Nuclear magnetic resonance spectra were determined on a Varian Model T-60 spectrometer at 60 MHz and a Brucker spectrometer at 250 MHz. Infrared spectra were obtained with a Perkin-Elmer 337 grating infrared spectrophotometer. Mass spectra were determined on a Hewlett-Packard 5930A quadrupole mass spectrometer. Elemental analyses were performed by Chemalytics, Inc., Tempe, AZ and the University of Arizona Analytical Center in Tucson.

(Carbomethoxy)maleic Anhydride (CMA) 1a was synthesized by using the method described by Hall and co-workers.[9] Tricarbomethoxyethylene (10.1 g, 0.05 mol) was mixed with 14.2 g (0.1 mol) of P_2O_5 and heated at 160 °C for 5 h. The product was then distilled from the black mass [120 °C (0.2 mm)] as a liquid which solidified upon cooling. Redistillation from diethyl ether gave pure anhydride: mp 37–38 °C; yield 60%; NMR ($CDCl_3$) δ 3.85 (s, 3 H), 7.35 (s, 1 H); IR (NaCl) 1840, 1770 (anhydride), 1725 (ester), 1640 (C=C); mass spectrum (70 eV), 156 (M^+). Anal. Calcd for $C_6H_4O_5$: C, 46.16; H, 2.59. Found: C, 46.09; H, 2.81.

Cycloaddition Reactions of CMA and MAnh with 1,3-Dienes. All reactions were carried out at 28 °C with 0.25 mmol of each reagent dissolved in acetone-d_6 to give a 0.83 M solution. Progress of the reaction was followed by NMR spectroscopy. TCNE reactions were bright yellow; CMA and MAnh reactions were colorless. All of these reactions went to completion except for chloroprene–TCNE, where an equilibrium existed between the adduct and the starting materials. Diene disappearance and adduct formation presented complementary curves vs. time in these reactions.

The NMR spectrum of the CMA–isoprene adduct **3ac** was completely analyzed at 250 MHz to determine the position of the methyl group: NMR ($CDCl_3$) δ 1.785 (d, Me, $J = 0.7$ Hz, 3 H), 2.347 (dd, H-5, $J_{5-5'} = 15.6$ Hz, $J_{5-6} = 7.1$ Hz, 1 H), 2.56 (m, H-2′, H-5′, $J_{2-2'} = 15.6$ Hz, $J_{5'-6} = 2.5$ Hz, 2 H), 2.760 (dd, H-2, $J_{2-3} = 6.3$ Hz, 1 H), 3.743 (dd, H-6, 1 H), 3.830 (s, $COOCH_3$, 3 H), 5.63 (m, H-3, 1 H). The 250-MHz ^{1}H NMR spectrum of **3ad** could not be analyzed due to extensive overlap of the peaks.

11-(Methoxycarbonyl)-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic Anhydride (5). CMA (1 g, 6.41 mmol) in 20 mL of chloroform and 1.14 g (6.41 mmol) of anthracene in 20 mL of chloroform were mixed, and the solution turned orange. This color gradually faded in a few hours. Partial evaporation of the solvent causes adduct **5** to crystallize: yield 1.2 g (55%); mp 178–180 °C; NMR ($CDCl_3$) δ 3.6 (s, 3 H), 3.8 (m, 1 H), 4.8 (d, 1 H), 5.1 (s, 1 H), 7.2 (m, 8 H).

5-(Methoxycarbonyl)-7-oxabicyclo[2.2.1]hept-2-ene-5,6-*exo*-dicarboxylic Anhydride (6). CMA (160 mg, 1 mmol) was mixed with 6.8 mg (1 mmol) of furan in 1 mL of deuterated chloroform. After 15 min, the NMR spectrum showed an equilibrium mixture: NMR ($CDCl_3$) δ 3.35 (s, 1 H), 3.9 (s, 3 H), 5.5 (m, 2 H), 6.65 (m, 2 H).

5-(Methoxycarbonyl)bicyclo[2.2.1]hept-2-ene-5,6-*endo*-dicarboxylic Anhydride (7). CMA (160 mg, 1 mmol) was dissolved in 2 mL of ether; 70 mg (1 mmol) of cyclopentadiene was added. Twelve hours later, the ether was pumped off, leaving **7b** as a colorless oil: NMR ($CDCl_3$) δ 1.8 (m, 2 H), 3.5–3.8 (m, 3 H), 3.9 (s, 3 H), 6.3 (s, 2 H).

Reaction of Styrene and CMA. CMA (0.78 g, 5 mmol) was dissolved in 5 mL of acetone-d_6; to this solution was added 0.52 g (5 mmol) of styrene previously diluted in 5 mL of acetone-d_6. The solution was allowed to stand 24 h. CMA was completely reacted; half of the initial styrene remained unreacted. After removal of the styrene, the NMR spectrum indicated the presence of 40% of the Wagner-Jauregg adduct **8** and 60% of the Diels–Alder ene adduct **9**. All attempts to crystallize the adducts failed: mass spectrum, *m/e* 416 (M^+); IR (KBr) 1850, 1780 (anhydride), 1735 (ester), 1640 cm^{-1} (unsaturation).

Copolymerization of (Carbomethoxy)maleic Anhydride with Styrene. (Carbomethoxy)maleic anhydride (156 mg, 1.0 mmol) was placed in a vial, swept with nitrogen, and covered with a rubber septum. The CMA was warmed to melt and 114 μL (104 mg, 1.0 mmol) of styrene was injected. The solution turned yellow, became hot, and set up to a viscous oil as the color faded. The reaction was complete within 5 min. After 24 h, the polymer **10** was dissolved in acetone and precipitated in ether. The solid was washed 3 time with ether and dried under vacuum: yield 89.6 mg (34%); η_{inh} (0.25% in acetone) 0.35 dL g^{-1} at 22.5 °C; NMR spectrum ($CDCl_3$) presents two broad absorption at 7.3 (5 H) and 1.5–4.0 (7 H).

1,12-Bis(methoxycarbonyl)-7-methoxy-1,2,3,5,8,9-hexahydro-5,8-ethanonaphthalene-1,2,11,12-tetracarboxylic Dianhydride (11). CMA (47 mg, 0.30 mmol) was dissolved in ether and 46% (0.34 mmol) of *p*-methoxystyrene was added. The solution turned yellow, but the yellow color gradually faded and a white precipitate was formed. The ether was decanted and the precipitate dried under vacuum: yield 48 mg (72%); mp 207–212 °C dec; NMR (acetone-d_6) δ 2.3–3.0 (m, 3 H), 3.5 (s, 3 H), 3.7 (s, 3 H), 3.9 (s, 3 H), 4.1 (m, 4 H), 5.2 (dd, 1 H), 6.0 (m, 1 H); mass spectrum, *m/e* 446 (M^+); IR (KBr) 1885, 1785 (anhydride), 1735 (ester), 1635 cm^{-1} (sh, unsaturation). Anal. Calcd for $C_{21}H_{18}O_{11}$: C, 56.50; H, 4.06. Found: C, 56.47; H, 4.19.

1,12-Bis(methoxycarbonyl)-3-methyl-7-methoxy-1,2,3,5,8,9-hexahydro-5,8-ethanonaphthalene-1,2,11,12-tetracarboxylic Dianhydride (12). To CMA (156 mg, 1 mmol) in 5 mL of ether in a vial was added 149 μL (148 mg, 1 mmol) of anethole. Immediately, the solution turned yellow. Within a few minutes, a white precipitate was formed and the color of the solution faded. After 5 h, the color was gone, but the vial was allowed to stand overnight. The ether was decanted off and the solid washed 3 times with ether and dried under vacuum: mp 178–182 °C dec; yield 155 mg (67%); NMR (acetone-d_6) δ 1.5 (d, 3 H), 2.5 (m, 1 H), 3.0 (br s, 1 H), 3.5 (s, 3 H), 3.8 (s, 3 H), 3.9 (s, 3 H), 4.0 (m, 4 H), 5.0 (dd, 1 H), 5.7 (t, 1 H); mass spectrum (relative intensity), *m/e* 460 (M^+, 2), 304 (22), 232 (9), 148 (100); IR (KBr) 1850, 1780 (anhydride), 1740 (ester), 1635 cm^{-1} (sh, unsaturation). Anal. Calcd for $C_{22}H_{20}O_{11}$: C, 57.39; H, 4.30. Found: C, 57.21; H, 4.50.

1,12-Bis(methoxycarbonyl)-4-phenyl-1,2,3,5,8,9-hexahydro-5,8-ethanonaphthalene-1,2,11,12-tetracarboxylic Dianhydride (13). To CMA (78 mg, 0.5 mmol) in 2 mL of ether was added 90 mg (0.5 mmol) of 1,1-diphenylethylene. Immediately, the solution turned yellow. Within a few hours a white precipitate was formed; this powder was the 1:1 alternating copolymer of MCA and 1,1-diphenylethylene. From ether the Wagner-Jauregg adduct was recrystallized. The crystals were washed with ether and dried under vacuum: yield 20%; NMR (acetone-d_6) δ 2.9 (m, 2 H), 3.3 (s, 1 H), 3.65 (s, 3 H), 4.0 (s, 3 H), 4.1–4.4 (m, 4 H), 6.5 (m, 2 H), 7.4 (m, 5 H). IR (KBr) 1855, 1780 (anhydride), 1750, 1730 (ester), 1730 cm^{-1} (br, unsaturation). Anal. Calcd for $C_{26}H_{20}O_{10}$: C, 63.4; H, 4.1. Found: C, 63.4; H, 4.1.

Phenyl Vinyl Ether. Phenyl vinyl ether is prepared following the procedure of Fueno[19] in which phenol and 1,2-dibromoethane were condensed with a strong base in water. In a second step, β-phenoxyethyl bromide was treated with potassium hydroxide in bulk to give phenyl vinyl ether.

Tribromophenyl Vinyl Ether. By the same route as above, tribromophenyl vinyl ether was prepared from tribromophenol:

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J. Org. Chem. **1982**, *47*, 1455-1459 **1455**

NMR ($CDCl_3$) δ 4.1-4.4 (m, 2 H), 6.5 (dd, 1 H), 7.7 (s, 2 H). Anal. Calcd for $C_8H_5OBr_3$: C, 26.9; H, 1.4. Found: C, 26.7; H, 1.4.

Reactions of CMA with Vinyl Ethers. Equimolar amounts of CMA and a vinyl ether (isobutyl, phenyl, and tribromophenyl) were mixed in chloroform and kept at room temperature or at 70 °C for the latter. The occurrence of pyran **14** and **17** was proven by NMR spectroscopy. As shown in our previous paper,[16] the proton in the α-position of the ether function was responsible for a doublet of doublets peak pattern in the 5-6-ppm region. Adduct**10**: NMR δ 5.4 (dd). Adduct **11**: NMR δ 6.1 (dd). The yields of pyran and copolymer were determined by NMR spectroscopy.

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Registry No. 1a, 69327-00-0; **1b**, 108-31-6; **2c**, 78-79-5; **2d**, 106-99-0; **2e**, 126-99-8; **3ac**, 80698-25-5; **3ad**, 80698-26-6; **3ae**, 80698-27-7; **3bc**, 1694-82-2; **3bd**, 935-79-5; **3be**, 14180-91-7; **4c**, 74503-42-7; **4d**, 13358-22-0; **4e**, 80698-28-8; **5**, 80698-29-9; **6**, 80698-30-2; **7b**, 80698-31-3; **8**, 80698-32-4; **9**, 80698-33-5; **10**, 80698-21-1; **11**, 80698-34-6; **12**, 80698-35-7; **13**, 80698-36-8; **14**, 80698-37-9; **15**, 80698-22-2; **16**, 80698-23-3; **17**, 80698-38-0; TCNE, 670-54-2; anthracene, 120-12-7; furan, 110-00-9; cyclopentadiene, 542-92-7; styrene, 100-42-5; *p*-methoxystyrene, 637-69-4; anethole, 104-46-1; 1,1-diphenylethylene, 530-48-3; MCA 1,1-diphenylethylene copolymer, 80698-24-4; phenyl vinyl ether, 766-94-9; tribromophenyl vinyl ether, 3748-03-6; isobutyl vinyl ether, 109-53-5.

Absolute Rate Constants for the Reactions of *tert*-Butoxyl with Ethers: Importance of the Stereoelectronic Effect†

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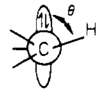
Absolute rates of hydrogen atom abstraction by *tert*-butoxyl from a variety of cyclic and acyclic ethers, orthoformates, and acetals have been measured at 27 °C by laser flash photolysis techniques. High rates of abstraction from the C-H bond adjacent to oxygen and forming small dihedral angle (ca. 30°) with the π-type orbital(s) on the oxygen(s) have been observed. For larger dihedral angles (ca. 90°) the rate of C-H abstraction is much lower. Arrhenius parameters have also been measured for a few representative cyclic ethers.

It now seems well established that stereoelectronic effects are important in heterolytic[1-5] and homolytic[6-13] chemistry. According to the principle enunciated by Deslongchamps,[1] the molecular reactivities of certain classes of compounds are determined by the relative orientation of the bond being broken or formed and the lone pair(s) on the heteroatom(s) adjacent to the reaction center.

The theoretical rationalization of such an effect is based on the concept of conjugative delocalization[14] between the electron pair(s) and the nonbonded carbon orbital ψ of the reaction center. The extent of the delocalization is a function of the dihedral angle, θ, between the C-H bond and the orbital(s) on the heteroatom(s).

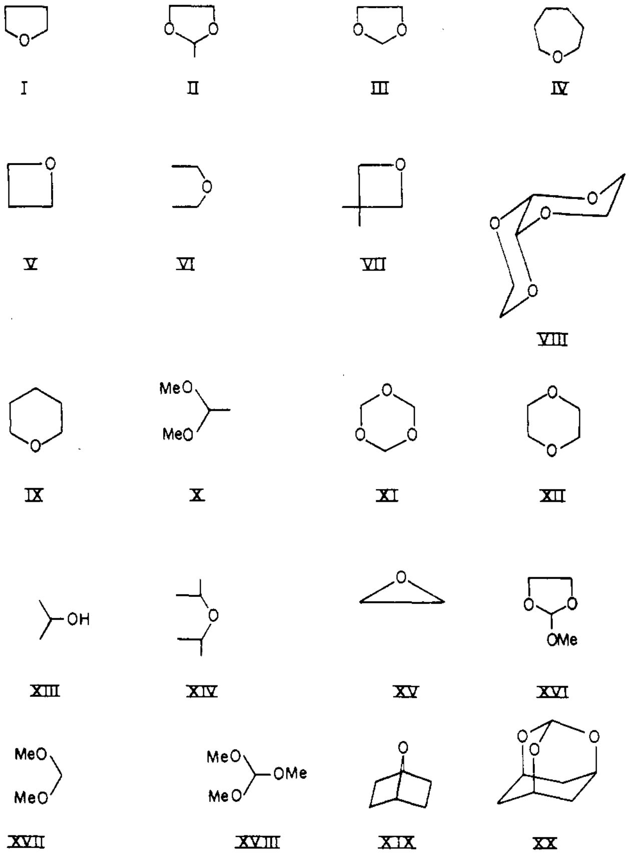


The posit of such a rationalization is an energetic and orientational nonequivalence of the heteroatom lone pairs,[15] and there is ample experimental support for this assumption.

For instance, photoelectron spectroscopy studies[16] have shown that one of the two lone pairs of electrons on oxygen is essentially a pure p type of higher energy (lower IP), with the second being approximately an s-type orbital characterized by a lower energy (higher IP).

A series of recent papers[11,13] has pointed out the importance of the stereoelectronic effects in H atom abstraction reactions from cyclic and acyclic ethers and amines. We have now extended this study to include substrates for which it is difficult or impossible to determine rate constants by an EPR technique, frequently because of difficulties in observing the EPR spectra of

Chart I



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